# Suhaib A. Bandh Fayaz A. Malla *Editors*

# Biofuels in Circular Economy



## Contents

<b>Biofuels: Potential Alternatives to Fossil Fuels</b> Fayaz A. Malla, Suhaib A. Bandh, Shahid A. Wani, Anh Tuan Hoang, and Nazir Ahmad Sofi	1
<b>Biofuel Economy, Development, and Food Security</b> Rowena P. Varela, Raquel M. Balanay, Rey Y. Capangpangan, and Anthony B. Halog	17
<b>Biofuels in Low Carbon Economies and Societies</b> César Ruiz Palomar, Alfonso García-Alvaro, Vanessa de Almeida Guimarães, Eva Blasco Hedo, Raúl Muñoz, and Ignacio de Godos Crespo	31
Role of Biofuels in Building Circular Bioeconomy Hamna Bashir, Irshad Bibi, Aqsa Jafar, Nabeel Khan Niazi, Fahad Rasheed, Naila Ghafoor, Ahmer Saleem, Muhammad Mahroz Hussain, and Zia-Ur-Rehman Farooqi	59
<b>Biofuel Projects and Current Environmental Policies: Vietnam's</b> <b>Case and Neighboring Asian Countries</b> Tuan-Dung Hoang, Pham Thi Ha, Anthony B. Halog, Fayaz A. Malla, and Suhaib A. Bandh	73
<b>Biofuels an Option for Reducing Ecological Footprint</b> Jinnath Rehana Ritu, Saleha Khan, Ranga Rao Ambati, and Ravishankar Gokare Aswathanarayana	89
<b>Biofuel in Constructing Green Circular Societies: Circular</b> <b>Biorefinery of TPOMW</b> Consolación Sánchez Sánchez, Francisco Cuadros Blázquez, Almudena González González, and Francisco Cuadros Salcedo	103
<b>Transitional Framework from Conventional Fuels to Biofuels</b> Ananya Roy Chowdhury and Achintya Das	123

Contents

<b>Developmental Perspectives of the Biofuel-Based Economy</b> Alfonso García Álvaro, César Ruiz Palomar, Vanessa de Almeida Guimarães, Eva Blasco Hedo, Raúl Muñoz Torre, and Ignacio de Godos Crespo	133
Biofuel and Bio-economy Nexus Sunzida Sultana, Saleha Khan, Ranga Rao Ambati, and Ravishankar Gokare Aswathanarayana	157
Adopting a Circular Bio-economy: The Biorefinery Concept Anita V. Handore, Sharad R. Khandelwal, Mrunal S. Ghayal, and Dilip V. Handore	183
<b>Biofuels as Economic Security for the Poor</b>	201
Circular Economy Potential of Microalgal Refinery G. Saranya and T. V. Ramachandra	219
<b>Biodiesel in Circular Economy</b> Violeta Y. Mena-Cervantes, Raúl Hernández-Altamirano, S. Montserrat García-Solares, and E. Arreola-Valerio	251
Circular Economy Involving Microbial Consortia in Consolidated Bioprocesses to Produce Biofuels	279
The Biofuel Industry and Global Trade Nexus Deepayan Debnath and Jarrett Whistance	303

### **Circular Economy Potential** of Microalgal Refinery



G. Saranya and T. V. Ramachandra

#### **1** Introduction

Renewable energy resources are intrinsically linked to social, economic, and environmental dimensions and need to be economically viable, technically feasible. socially acceptable, and environmentally sound to achieve sustainability (Chatterjee & Rayudu, 2018). Industrialization and subsequent globalization witnessed an escalation in energy utilization, evident from the increase in the average per capita electricity consumption from 2.5 MJ d<sup>-1</sup> to more than 200 MJ d<sup>-1</sup> (Ramachandra & Hegde, 2015). Next to electricity, the major energy required is the conventional nonrenewable fuels such as refined petroleum products and natural gas for mobility in the transportation sector. The global primary energy consumption is about 25,912 quadrillion Btu in petroleum (in 2019). The biomass and natural gas contribution was about 1411 and 978 quadrillion Btu. However, the fast-perishing stock of fossil resources with the escalating greenhouse gas (GHG) footprint necessitates the investigation of sustainable alternatives to meet the ever-increasing demand for energy in the transportation sector. The transition to biofuels gives the additional benefits of decarbonization, decentralized employment generation (and remediation, in the case of feedstock cultivation in wastewater), and the scope for economic viability through a circular economy in the algal refinery. Decarbonization aids in mitigating global warming and changes in the climate (Jaccard, 2006). Currently, there are numerous biofuel initiatives across the globe to reduce the reliance on petroleum

G. Saranya · T. V. Ramachandra (🖂)

Energy and Wetlands Research Group, Centre for Ecological Sciences [CES], Bangalore, India e-mail: tvr@iisc.ac.in; energy.ces@iisc.ac.in URL: http://ces.iisc.ernet.in/energy

Centre for Sustainable Technologies (Astra), Bangalore, India

T. V. Ramachandra

Centre for Infrastructure, Sustainable Transportation and Urban Planning [CiSTUP], Indian Institute of Science, Bangalore, Karnataka 560012, India

<sup>©</sup> The Author(s), under exclusive license to Springer Nature Singapore Pte Ltd. 2022 219 S. A. Bandh and F. A. Malla (eds.), *Biofuels in Circular Economy*, https://doi.org/10.1007/978-981-19-5837-3\_13

fuel (Vlysidis et al., 2011) through decentralized local resources such as microalgae, etc. Biodiesel is one of the most promising biofuels shown to give engine performance with reduced particulate, carbon monoxide, and hydrocarbon emissions compared to conventional diesel (Graboski & McCormick, 1998). Biodiesel has been produced from triglycerides derived from terrestrial oil seeds, animal fats, or algae. Biodiesel production from vegetable oils has been increasing during the past decade. However, the amount of oil produced in a hectare area from terrestrial oil seeds is limited. In this context, microalgae-derived oil has received significant attention due to its non-conflicting nature of fuel in terms of arable land availability or food (Ribeiro et al., 2015).

Microalgae rich in carbohydrates, phycobilin, vitamins, proteins, pigments, antioxidants, bioactive compounds, and essential fatty acids offer vast potential for commercial exploitation. The biochemical composition of microalgae and biodiesel feedstock widens the scope for other bioenergy and value-added product production (Guldhe et al., 2017). There has been renewed interest in utilizing algae in various sectors, including pharmaceuticals, food, and animal feed. The main advantages of using microalgae are: (i) the most promising non-food feedstock for biofuel production; (ii) does not require arable lands with the ability to grow in degraded lands including saline waters/wastewaters; (iii) ability for an efficient fixation of CO<sub>2</sub>; (iv) remediation of wastewater with the uptake of nutrients for growth; (v) algae possess the capacity to produce lipids that are 300-400 times higher than terrestrial feedstocks; (vi) carbon sequestration potential of biomass; (vii) diverse mix of energy and value-added bioproducts; (viii) livestock feed as a source of protein etc.; (ix) algal biofuel is non-toxic with no sulphur content and is exceptionally biodegradable. Remediation of wastewater through microalgal growth is gaining momentum as an economical and environmentally friendly option for wastewater treatment with biofuel production (Clarens et al., 2010). Hence, microalgae-based biofuel is emerging as an essential alternate resource to fossil fuels. However, significant challenges in microalgal biofuels are higher energy demand during (i) cultivation (upstream) and harvesting, (ii) drying, and (iii) biofuel production (downstream). Thus, employing efficient microalgae cultivation considering appropriate substrate (with biofilm inoculum) would render both cultivation and harvesting less expensive to accomplish the economic viability of microalgal biofuel. The exploitation of different microalgal components as a whole or in parts as co-exploitable products and minimizing waste production would enhance the economic viability with the potential of a circular economy. Optimal growth conditions would enhance hyperaccumulation of different bioproducts as a function of nitrogen concentration during different growth stages (Gifuni et al., 2019), as during exponential growth phase, proteins, chlorophylls and phycobiliproteins are accumulated, followed by accumulation of starch (during late exponential phase), PUFAs, TAGs, and UV protective pigments like carotenoids/astaxanthin are secreted during the stationary growth phase (triggered with nitrogen depletion). Thus, microalgae produce a plethora of products that find application in diverse industrial sectors (Chew et al., 2017).

#### 2 Circular Economy Through the Microalgal Refinery

The raw material (e.g., crude petroleum) undergoes a series of production processes with a potential output of diverse energy sources (gasoline, diesel, LPG, and ethanol) and an array of complex and valuable chemicals (volatile acids, fine chemicals, detergents, pharmaceuticals, waxes, and asphalt) in the conventional refinery. Similarly, biorefineries permit renewable raw materials utilization widely at low costs to produce high-value products with inherent energy potential (Laurens et al., 2017). The biorefinery concept integrates the production of various products, and cumulative benefits prove microalgal biofuel generation sustainable by providing economic viability. Figure 1 depicts the biorefinery using aquaculture wastewater for diverse bioproduct production with an added advantage of wastewater remediation.

The biorefinery process involves valorizing microalgal biomass into a broad spectrum of value-added products and diverse energy forms (Linares et al., 2017). Microalgal biorefineries through efficient biomass processing would provide energy, polymers, food additives, nutraceuticals, bioactive compounds, co-products, etc. Processing biomass at multiple stages by targeting both primary and secondary products of commercial interest would enhance the environmental and economic benefits (Hemalatha et al., 2019) compared to product valorization.



Fig. 1 Integrated microalgal cultivation system for biodiesel with bioproducts

#### 2.1 Primary Products from Microalgae

The macromolecular composition of microalgae includes (i) ash (5–17%); (ii) carbohydrates (18-46%); (iii) crude protein (18-46%); (iv) lipids (12-48%); and (v) energy (19-27 MJ/kg) (Tibbetts et al., 2015). Microalgae accumulate carbohydrates in complex forms (such as cellulose, and starch.) apart from other exocellular polysaccharides (EPS). EPS is gaining considerable attention as hygroscopic agents (in cosmetic industries), topical agents, and antioxidants (Dragone et al., 2011). EPS is useful as natural auto-flocculating agents (Marella et al., 2020), surfactants, emulsifiers, anti-tumour, anti-viral, anti-coagulant, and anti-inflammatory agents (Venkata Mohan et al., 2020). Other primary products exploitable from microalgae are pigments (chlorophyll and carotenoids such as fucoxanthin and astaxanthin), amino acids (such as alanine linoleic acid and nucleic acid), etc. Phycobiliproteins are rich sources of vitamin B1 (Mobin & Alam, 2017). Microalgae possess different carotenoids such as beta carotene, lutein, lycopene, astaxanthin, zeaxanthin, fucoxanthin, and neoxanthin diadinoxanthin, canthaxanthin, violaxanthin (Mulders et al., 2014). Carotenoid finds its application in diverse domains of human health care, pharmaceuticals, nutraceuticals, and food processing (Sathasivam et al., 2019). Microalgae also aid as substitutes for fish oil, especially omega-3, Docosahexaenoic acid (DHA), Eicosapentaenoic acid (EPA), omega-6, and arachidonic acid (ARA) (Marella & Tiwari, 2020). A range of primary products that are possible from model pennate diatom Phaeodactylum tricornutum as reported in (Butler et al., 2020) are: EPA, DHA, ARA, Triacylglycerol (TAG), and Brassicosterol that forms the major components of lipids, and Chrysolaminarin forms the major portion of carbohydrates. Fucoxanthin, Lupeol, and betulin from the major terpenoids class in the model diatom P. tricornutum. A marine microalga, Nannochloropsis oceanica, is targeted as a source of EPA and violaxanthin. Synechocystis sp. and Arthrospira sp. belong to cyanobacteria used to extract phycocyanin, terpenoids, and polyhydroxy butyrate (PHB) (Mobin & Alam, 2017). Microalgae are valuable sources of vitamins like A, B1, E, C, B6, B12, riboflavin, nicotinic acid, biotin, folic acid, and pantothenate (Chittora et al., 2020).

#### 2.2 Microalgae as Biofertilizers and Functional Foods

Ensuring food security to the burgeoning population in developing economies has been a significant challenge. Green practices are gaining attention with the adoption of eco-friendly technologies to sustain food production while reducing the risk of chemical-based fertilizers (Andrade, 2018). Cyanobacteria are emerging as low-cost and eco-friendly biofertilizers. They help control the nitrogen deficiency in plants and are known to improve water holding capacity, enhance aeration of the soil, and act as reservoirs of vitamin B12 (Hall et al., 1995). The efficient nitrogen-fixing bacteria are Anabaena variabilis, Nostoc linkia, Calothrix sp., Tolypothrix sp., Spirulina platensis (Chittora et al., 2020), which are useful as N, P, and K supplements for biofortification of soil (Anitha et al., 2016). Earlier studies show Spirulina, Chlorella sp., and Palmaria palmata helps in bio-augmentation NO<sub>3</sub><sup>-</sup>N and NH<sub>4</sub><sup>+</sup>N during its field application (Alobwede et al., 2019). Microalgae, primarily diatoms, are being used widely as feeds and high-quality nutritional supplements for bivalves, juvenile fishes and shrimp larvae, and post-larvae (Marella et al., 2020; Shah et al., 2018). Diatoms also produce vitamins and proteins beneficial for aquaculture growth with proven antibacterial and anti-viral properties against pathogens proliferating in aquaculture ponds. Table 1 lists the research institutions across the globe that are working on industrially relevant products from microalgae (diatoms) with details of targeted biomolecules.

#### 2.3 Valorization of Secondary Products from Microalgal Biomass

Cell walls of many microalgae are made of complex microfibrillar structures placed within a glutinous protein cell matrix (Yap et al., 2016). However, some microalgae that belong to Bacillariophyceae and Charophyceae family are protected by a rigid inorganic wall of silica or calcium carbonate (Bolton et al., 2016), and the growth environment significantly influences the thickness and microalgal cell wall composition (Praveenkumar et al., 2015). The cell wall is disrupted to extract lipid, which is done either by physical or chemical pretreatment methods to improve amenability of cell constituents by organic solvents. Various physicochemical cell disruption methods experimented with bead milling, osmotic shock, pulsed electric field, microwave, ultrasound, and freezing/thawing. Various pretreatment and bioenergy conversion processes used for bioenergy production from microalgal biomass are illustrated in Fig. 2.

Among diverse cell disruption methods, ultrasound treatment (sonication) is reported to improve the cell disruption efficiency of microalgae (Ramachandra et al., 2011, 2013). Microwave treatment was a rapid process that enabled 80% of the cell lysis (Abbassi et al., 2014). After cell disruption, either thermochemical or biological processes are carried out to derive secondary products like bioethanol, bio-oil, biogas, biobutanol, volatile fatty acids, biohydrogen, and biopolymers (Venkata Mohan et al., 2020). Gasification, pyrolysis, hydrogenation, liquefaction, and combustion are thermochemical conversion processes that involve applying heat energy to obtain end products. The energy obtained from such thermochemical processes is mainly gaseous forms or energy-rich biocrude that is upgraded to bioenergy products. Biological treatments such as anaerobic digestion, fermentation, and heterotrophic fermentation would result in biogas, bioethanol, alcohols, and liquid hydrocarbons, whereas physicochemical conversion using extraction and transesterification would lead to biodiesel (Jankowska et al., 2017). Possible bioenergy components from microalgal biomass from an energy perspective are methane, biodiesel, biocrude possible refinement into gasoline and green diesel, biobutanol and ethanol, biohydrogen, and bioelectricity from microalgal carbohydrates. Figure 3 illustrates the valorization of microalgal biomass into various forms of bioenergy as secondary products.

Species	Research institution	Targeted biomolecules	References
Navicula cincta, Nitzschia punctata, Amphiprora sp., Chaetoceros spp., Cyclotella sp.	Indian Institute of Science, Bangalore	Biodiesel and EPA	Saranya and Ramachandra (2020)
Amphora coffeaeformis	Centre for advanced studies in botany, University of Madras, Chennai	Biofuel and essential fatty acids	Rajaram et al. (2018)
Nitzschia paea, Gomphonema parvulum, Nitzschia inconspicua, Diadesmis confervaceae, Sellaphora sp., Placoneis elginensis	Harish Singh Gour University, Madhya Pradesh	Diatom lipids and diatom solar panels	
Pinnularia sp.	School of Chemical, Biological and Environmental Engineering, Oregon State University, USA	Solar cells, batteries and electroluminescent devices, and diatom solar panels	Jeffryes et al. (2011)
Coscinodiscus walesii	National Council of Research Institute for Microelectronics and Microsystems-Department of Naples	Diatom solar panels	De Stefano et al. (2007)
Synedra sp., Diatom consortium	Noida International University, Uttar Pradesh	Fatty acids and triglycerides	Li et al. (2017)
Achnanthes sp.	Scripps Institution of Oceanography	Biofuel	Hildebrand et al. (2012)
Halamphora coffeaformis, Navicula cincta	Bahia Blanca, Argentina	Biodiesel and essential fatty acids	Martín et al. (2018)
Diatom	The University of Colorado, Boulder, USA	Diatom-based taxonomy and limnological studies	Andrejić et al. (2018)
Diatom	Rutgers University, New Brunswick, USA	Physiological and molecular aspects of diatoms	Kranzler et al. (2019)

 Table 1
 Research institutions across the globe working on microalgae (diatom)

(continued)

Species	Research institution	Targeted biomolecules	References
Phaeodatylum tricornutum	Shandong University, China	Seasonal dynamics studies	Zhang et al. (2019)
P. tricornutum, Skeletonema costatum	University of Iceland, Reykjavik, Iceland	Anti-cancer compounds	Hussein and Abdullah (2020)
Thalassiosira weisflogii, Cyclotella cryptica	Istituto di Chimica Biomolecolare (ICB)—CNR, Via Campi Flegrei 34, 80,078 Pozzuoli, NA, Italy	Biofuel	D'Ippolito et al. (2015)
Phaeodatylum tricornutum	Swansea University, UK	Diatom biorefinery	Butler et al. (2020)
Thalassiosira pseudonana	University of Sheffield, UK	Bioactive compounds	Sethi et al. (2020)
Thalassiosira weissflogi	International Crop Research Institute for Semi-arid Tropics (ICRISAT), Patancheru 502 324, Telangana State, India	Diatom biorefinery	Marella and Tiwari (2020)

Table 1 (continued)



Fig. 2 Different conversion processes for various energy products production from microalgae



Fig. 3 Valorization of microalgal biomass into an array of bioenergy (secondary) products

#### 2.4 Biogas from Microalgal Biomass

Anaerobic digestion (AD) of microalgal biomass has emerged as a promising technology through the decomposition of organic matter by anaerobic bacteria into biogas. AD is a four-step process involving hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Ward et al., 2008). The main components of biogas are methane and carbon dioxide. The biogas quality is usually determined by the relative amount of methane, which depends on the substrate and operating conditions for anaerobic fermentation (Sialve et al., 2009). Several studies have shown the possibility of using spent. The microalgal biomass constitutes appropriate feedstock for biogas production as it contains a high quantity of proteins (51-64%), followed by carbohydrates (6-21%) and lipids (7-16%) (Jankowska et al., 2017) with a yield of 0.09-0.54 L CH<sub>4</sub>  $g^{-1}$  (Sialve et al., 2009). However, the efficiency of biogas production is speciesspecific as complex recalcitrant cell wall structure and composition of some algae hinder the anaerobic digestion due to the inability to penetrate cell walls by bacteria (termed as anaerobic biodegradability). Hence, various pretreatment methods for disrupting cell walls include thermal, microwave, ultrasonic, chemical, and mechanical processes (Kwietniewska & Tys, 2014). A comparison of methane yields with and without pretreatment techniques is given in Table 2.

Techno-economic feasibility studies have demonstrated a 35% cost reduction in production (Harun et al., 2011), energy recovery, and improvement in the energy balance by integrating methane production with biodiesel production (Alzate et al., 2014; Francisco et al., 2010; Zhao et al., 2014). Energy recovery of 80% was recorded in a study that used *Isochrysis galbana* for integrated biodiesel and biogas production biorefinery approach.

Microalgae	Pretreatment	Operating conditions (Temp °C, days)	$\begin{array}{c} CH_4 \text{ production} \\ (mL \text{ g}^{-1} \text{ VS}) \end{array}$	Reference
Chlorella vulgaris	Lipid extraction	35, 25	$314 \pm 18$	Zhao et al. (2014)
Nannochloropsis salina	Without lipid extraction	35, 25	557 ± 5	Zhao et al. (2014)
Phaeodactylum tricornutum	Without lipid extraction	35, 25	337 ± 15	Zhao et al. (2014)
Phaeodactylum tricornutum	After lipid extraction		339 ± 13	Zhao et al. (2014)
Nannochloropsis gaditana	Lipid extraction with ethanol	35, 53	$327 \pm 2$	Alzate et al. (2014)
Nannochloropsis gaditana	Without lipid extraction	35, 53	$303 \pm 5$	Alzate et al. (2014)
Tetraselmis sp.	Without lipid extraction	38, 65	160	Hernández et al. (2014)
Tetraselmis sp.	Supercritical CO <sub>2</sub> extraction	38, 65	236	Hernández et al. (2014)
Scenedesmus sp.	Without oil extraction	ND, 32–40	$212.3 \pm 5.6$	Ramos-Suárez and Carreras (2014)
Isochrysis galbana	After lipid extraction	38, 30	310	Sánchez-Bayo et al. (2020)

Table 2 Pretreatment methods and methane production from different microalgae

ND data unavailable

#### 2.5 Fermentation into Bioethanol

Microalgae have been receiving attention as a carbohydrate feedstock for their effective fermentation into bioethanol. After lipid extraction, the deoiled biomass containing starch and cellulose can be used for bioethanol production (Shokrkar et al., 2018). Simultaneous saccharification and fermentation of microalgal biomass using enzymes have shown higher yields of reducing sugars with prospects in cost-effective fermentation into bioethanol (Shokrkar & Ebrahimi, 2018). A study on enzymatic hydrolysis of microalga *Chlorella vulgaris* as feedstock for bioethanol production (Ho et al., 2013). A microalgal biorefinery of microalga *Dunaliella tertiolecta* biomass after lipid extraction subjected to chemoenzymatic saccharification yielded 0.14 g/g residual biomass (Lee et al., 2013).

#### 2.6 ABE Fermentation to Biobutanol

The microalgal residue with readily digestible polysaccharides like starch is being used as feedstocks for selective fermentation into higher alcohols such as biobutanol. For instance, green microalgae C. vulgaris is reported to accumulate starch in the range of 12-37% (Hirano et al., 1997; Spolaore et al., 2006). Microalgae can be cultivated throughout the year with a possibility of continuous harvesting (John et al., 2011), and less readily fermentable sugars such as galactose, xylose, and mannose are present only in minimal quantities, unlike lignocellulosic biomasses (Foley et al., 2011). Microalgae cultivation does not require arable lands and does not constitute a major food resource (Foley et al., 2011). Butanol has been sought after fuel in recent times owing to its superior alternative to ethanol considering (i) heating value, (ii) less volatile, and (iii) less corrosive, thus favourable for easy distribution and storage infrastructure. Biological production of biobutanol is achieved by acetone-butanol-ethanol (ABE) fermentation of microalgal biomass using a solventogenic anaerobic bacterium belonging to the genus Clostridium. This bacterium is known for its capability to convert a wide range of organic carbon sources, including glucose, cellobiose, arabinose, galactose, xylose, and mannose by secreting numerous polymer degrading enzymes such as alpha-amylase, beta-amylase and beta glucosidase, glucoamylase, amylopullulanase, and pullulanase (Ezeji et al., 2007a, 2007b). Incorporating these bacterial strains into carbohydrate-rich feedstocks under anaerobic conditions, the bacterium breaks down complex polysaccharides into butyric and acetic acid through an acidogenic process solventogenesis with the synthesis of acetone, ethanol, and butanol (Lee et al., 2008). Microalgal carbohydrates serve as feedstocks for fermentative bioethanol or biobutanol. Thus, the species-specific carbohydrate composition of microalgae determines the efficiency of ABE fermentation. The starch or carbohydrate contents of different microalgae are given in Table 3.

The carbohydrate content of microalgae varies significantly across species is divided into two functional components as (i) energy reserves (e.g., starch, glycogen) and (ii) structural polysaccharides (such as cellulose). The cell wall and storage components of cyanophycean members are lipopolysaccharides, peptidoglycan, and

Microalgae	Total carbohydrates (% dry weight)	Reference
Nostoc sp.	52.3	Efremenko et al. (2012)
Dunalliella tertiolecta	50.6	Efremenko et al. (2012)
Arthrospira platensis	40.8	Efremenko et al. (2012)
Tetraselmis sp. CS-362	26.0	Brown et al. (1998)
Nannochloropsis sp.	56.8	Efremenko et al. (2012)
Arthrospira platensis	40.8	Efremenko et al. (2012)
Scenedesmus obliquus	51.8	Ho et al. (2012)

 Table 3
 Carbohydrate content of different microalgae

Microalgae	Biomass treatment	Fermentative bacteria	Butanol production (g L <sup>-1</sup> )	Reference
Arthrospira platensis	Sulfuric acid	Clostridium acetobutylicum B1787	9.13	Efremenko et al. (2012)
Nannochloropsis sp.	Sulfuric acid	C. acetobutylicum B1787	10.9	Efremenko et al. (2012)
Chlorella vulgaris JSC-6	NaOH (1%), H <sub>2</sub> SO <sub>4</sub> 3%	C. acetobutylicum ATCC 824	13.1	Wang et al. (2016)
<i>Chlorella</i> <i>sorokiniana</i> (lipid extracted biomass)	H <sub>2</sub> SO <sub>4</sub> (2%) + NaOH (2%)	C. acetobutylicum ATCC 824	3.86	Cheng et al. (2015)
Wastewater algae	H <sub>2</sub> SO <sub>4</sub> and enzyme treatment	C. Saccharoperbutylacetonicum N1-4	7.79	Ellis et al. (2012)

Table 4 Microalgae feedstock for biobutanol production

cyanophycean starch, respectively. Cellulose and hemicellulose are from the structural polysaccharides, while starch/lipids include the storage polysaccharides in species of Chlorophyta division. The cell wall component is absent in the division Euglenophyta, and the storage product comprises Paramylum/Lipid. Cellulose, agar, carrageenan, and calcium carbonate form the significant components of the cell wall, and Floridian starch is the primary storage component in Rhodophyta, owing to the variations in the cell wall, biological treatment of microalgae requires pretreatment methods based on cell wall compositions. The pretreatment methods aid in cell wall disruptions and make the internal storage components available for the microbial consortium. Different physical, mechanical, and thermo-chemical pretreatments have been experimented with to improve the bioavailability of microalgal cell components to increase fermentation efficiency for biobutanol production are given in Table 4.

Despite having numerous advantages, biobutanol production technology is still in its nascent stage, which warrants further investigations. The biorefinery approach of utilizing biofilm cultivated biomass after lipid extraction for ABE fermentation would have the potential of attaining economic feasibility with sustainable biofuel production.

#### 2.7 Biocrude From HTL

Hydrothermal liquefaction (HTL) entails converting wet microalgal biomass into liquid biocrude by subjecting the biomass to a high temperature (280-370 °C) and pressure (10-25 MPa), circumventing higher energy costs in biomass drying.

Algal concentration ranging between 5 and 20%, HTL treatment can be carried out with just < 5% of the energy costs required for drying (Xu et al., 2011), and synthesized biocrude possess an energy value close to fossil petroleum (Jena & Das, 2011), which can be fractionated into different energy products. Hydrothermal degradation of microalgal biochemical constituents (carbohydrates, lipids, proteins) provides biocrude, a dark, viscous, energy-rich liquid (López Barreiro et al., 2013). Research on HTL has considerably increased, which is evident from publications related to HTL of S. platensis, Botryococcus barunii, Desmodesmus sp., C. vulgaris, and Nannochloropsis sp. (Biller & Ross, 2011; Brown et al., 2010). Typical elemental composition analysis of biocrude produced from Desmodesmus sp. with operating conditions of 375 °C for 5 min reaction time yielded 74.5% C, 8.6% H, 10.5% O, and 6.3% N with a higher heating value (HHV) of 35.4 MJ/kg. In comparison with other thermo-chemical conversion technologies of pyrolysis and gasification, HTL possess prominent characteristics such as (i) higher oil vield with the complete conversion of whole algal biomass into biocrude and other chemicals, (ii) elimination of drying process, (iii) higher lipid content (not an important criterion in HTL), (iv) enhanced HTL efficiency due to the enthalpy of phase change of water at higher pressure, (v) additional rectification or extraction is not required, and (vi) principal product is selfregulated (Tian et al., 2014). The current approach of biofuel conversion of algae to biodiesel needs to be economically viable. However, integration of HTL technology with current algae conversion technology would lead to sustainable utilization of algae residue after extracting lipids for biocrude production. Various experimental conditions of the microalgae-based HTL process, and its corresponding biocrude vields are given in Table 5.

Microalgae	Temp (°C), holding time (min)	Catalyst used	Biocrude yield (%)	Reference
Botryococcus braunii	300, 60	Na <sub>2</sub> CO <sub>3</sub> (5%)	64	Dote et al. (1994)
Desmodesmus sp.	375, 5	No catalyst	49	Garcia Alba et al. (2012)
Chlorella vulgaris	350, 60	$Pt/Al_2O_3 (1 \text{ mol } L^{-1})$	38.9	Biller and Ross (2011)
Nannochloropsis sp.	350, 60	Pd/C	~ 57	Brown et al. (2010)
Spirulina platensis	350, 60	No catalyst	39.9	Jena and Das (2011)
Nannochloropsis occulata	350, 60	No catalyst	34.3	Biller and Ross (2011)
Chlorella pyrenoidosa	280, 120	No catalyst	39.4	Cheng et al. $(2017)$

Table 5 HTL experimental conditions and biocrude yield reported on different microalgae

#### 2.8 Algae as Feedstock for Biopolymers

Bio-based polymers are gaining significant attention over petroleum-based polymers due to their biodegradability and benign environmental characteristics (Garrison et al., 2016). A variety of bio-based raw materials such as resins and lignin derivatives, polysaccharides sourced from various feedstocks, proteins, and vegetable oils have been investigated for their suitability in bio-polymer production (Gandini, 2008). The current primary production of bioplastics is from terrestrial plant-based starch, and poly-lactic acid (PLA) polymers derived from corn and sugar beets (Sreedevi et al., 2014) competes with arable lands. Several bacterial strains capable of producing a range of exopolysaccharides and polyhydroxyalkanoates (PHA) have been commercially used as precursors for bioplastics (Rehm, 2010). However, with the enhanced plastic demand, and conventional plastics are posing significant threats to the environment, especially to marine ecosystems (Rahman & Miller, 2017). Microalgae secrete extracellular polymeric substances (EPS) comprising polysaccharides, proteins, lipids, and uronic and nucleic acids (Venkata Mohan et al., 2020). These EPS are being converted into bioplastics (polyhydroxyalkanoates (PHA), Polylactic acid (PLA), or thermoplastic starch (TPS) through the thermochemical conversion process by using glycerol as a co-substrate (Jerez et al., 2007). Biological routes of bioplastic production from microalgae are realized either through direct utilization and conversion of microalgal biomass or by utilizing the aqueous phase (hydrolysate) spent biomass as a source of nutrient for growing recombinant Escherichia coli which produces the bioplastic polyhydroxy butyrate (PHB) (Rahman et al., 2015).

#### 2.9 Bioelectricity Through Microbial Fuel Cells

Microalgae-microbial fuel cells (mMFC) convert solar energy into electricity through a bioelectrochemical process through a combination of live and dead microalgae in respective cathodic and anodic chambers (Lee et al., 2015). In microbial fuel cell (MFC) technology, live microalgae are placed in a cathode chamber (photoreactor) that acts as a biocathode. This biocathode produces O2 due to photosynthesis and acts as an electron acceptor from the external circuit (Wang et al., 2010). The anode chamber consisting of organics undergo digestion by releasing CO<sub>2</sub> and excess protons to the cathode chamber and also acts as an electron donor resulting in the generation of electricity (Juang et al., 2012). Live green algae growing in cathode chamber and used dead microalgal biomass as the substrate for anodic biofilm have been utilized to understand its feasibility for bioelectricity production. For example, microalga C. vulgaris grown in a cathodic chamber was found to photosynthesize increase the dissolved oxygen levels of the chamber. This increase in DO had a positive correlation with voltage output (Juang et al., 2012). The influence of light intensity on the cathodic resistance was investigated (Wu et al., 2014) and found that the light intensity was found to increase the rate of photosynthesis of Desmodesmus sp.,

resulting in higher  $O_2$  levels, which enhanced the mMFC's cathodic resistance to induce bioelectricity. Though mMFC is at the nascent stages of research, substantial improvements have been made on microalgae coupled microbial fuel cell processes in recent years. However, further research is required to integrate this technology in a biorefinery approach to attain a circular bioeconomy.

#### 2.10 Commercial Applications of Microalgal Biomass

Microalgae possess characteristics that are favourable for diverse commercial applications. The most important commercial application is in food nutrition as a protein source such as Chlorella, Spirulina, and Dunaliella (Javed et al., 2019). Studies have shown that microalgal biomass pellets have shown curing effects of gastrointestinal ailments through enhancement of intestinal Lactobacillus and treatment of renal failure (Yamaguchi, 1996). Green microalgae have potential applications in cosmetic industries, especially as sun and hair care products. For instance, Chlorella and Arthrospira sp. are being used as skincare essentials in the cosmetic industry as anti-irritants, anti-wrinkle agents, and anti-ageing creams. Algae like Chlorella, Scenedesmus, and Spirulina have been explored for their use as animal feed, especially as shrimp and aquaculture feed (Chuntapa et al., 2003). Microalgae are used as nutraceutical raw material for extraction of polyunsaturated fatty acid (PUFA), which is being used as an additive in infant milk and as feed to rear farm chicken enriches the amount of Omega-3 fatty acids in eggs (Pulz & Gross, 2004). Figure 4 illustrates the industrially relevant bioproducts possible from microalgae. Table 6 lists the price/ton for different microalgal species and estimated production per year.



Fig. 4 Different industrially relevant bioproducts extractable from microalgae

Table 6Estimated price perton of microalgal biomass(Brennan & Owende, 2010;Tredici et al. 2016)	Microalgae species	Estimated production in kilo tons per year	Price (millions)/ton INR
110alei et uli, 2010)	Spirulina	3	2.99
	Chlorella	2	2.99
	Dunaliella	1.2	98.3
	Crypthecodinium cohnii	0.24	3.5 (billion)
	Tetraselmis suceica	0.036	

#### **3** Algal Refinery with Microalgal Bioreactor

The microalgal bioreactor was implemented using granite stones as substrates for microalgal cultivation in an abandoned *gazani* (flood plain where earlier salt tolerant paddy was cultivated) land present in the coastal regions of Karnataka. The various processes involved in the installation of the microalgal bioreactor are illustrated in Fig. 5.

The land preparation techniques required for setting up a microalgal bioreactor include: (i) liming, (ii) pitching, (iii) mud bank formation, and (iv) watergate installation. Land preparation is done using lime (in the form of crushed dolomite  $(CaMg(CO_3)_2)$  or crushed limestone  $(CaCO_3)$ . Pitching is a process of levelling the land, which requires five persons working on the activity for 3-human days (7 h a day) in one-hectare land. A workforce of 2 persons for the 1-human day (7 h) is required for the liming activity. The granite stones are to be placed at an elevated position to avoid sediment interferences during microalgal biofilm formation. A combination of manual labour and machinery (JCB) is used for bioreactor installation.

Microalgae cultivated using substrate-based bioreactor has most diatoms in its species composition in the study region. Natural self-seeding of microalgae on the substrate was assumed with no addition of any external inoculum. A hybrid system involving harvesting manually and scrubbing using mechanized scrubbers at the end of a 5-7 days growth period was considered for the study. The drying of harvested algal biomass was carried out through direct solar drying in the first scenario while drying using a filter press, followed by solar drying in the second scenario. Transesterification of microalgal oil was carried out through direct transesterification of dried biomass using acid (dilute mineral acid (2% H<sub>2</sub>SO<sub>4</sub>) and biocatalyst (lipase). FAME conversion efficiencies of 83% for acid catalyst and 87% for biocatalyst was considered (based on conversion efficiencies obtained in prototype lab-scale experiments). Bioproducts from algal refineries include biodiesel, glycerol, biogas, algal meal, and fertilizer. Acid/biocatalyst-based transesterification of algal biomass results in biodiesel as the primary energy product and crude glycerol as the reaction byproduct. The crude glycerol after refining has diverse applications in the pharmaceutical and cosmetic industries. The spent algal biomass, when subjected to anaerobic digestion,



Fig. 5 Processes in biodiesel production with material inputs

results in biogas. The solid residue left over after biogas production was considered a biofertilizer source with scope for direct application as a source of nitrogen in agricultural fields.

#### 3.1 Techno-Economic Analysis

Techno-economic analyses were carried out for a bioreactor in a one-hectare plot in the flood plains. Considering (i) different nutrients input, (ii) acid and biocatalysts (lipase), and (iii) varied FAME conversion efficiencies. Discounted cash flow model was used to assess the financial feasibility of the proposed microalgal cultivation system. The model considered 60% of the capital investments as project financing

loans from the National Bank for Agriculture and Rural Development (NABARD) with an annual loan repayment determined by a 4.5% interest rate for a loan tenure of 5 years and the remaining 40% of farmer's investment share. The capital and operating (fixed and variable) costs were determined by considering the material and energy inputs at each stage (Table 7). The capital costs were estimated to evaluate the different processes considered with details of equipment, transportation costs, and raw material requirement incurred under each unit operation. Under capital costs, inventory of materials used for constructing bioreactor (granite stones for substrates, etc.) in a land area of 9000 m<sup>2</sup> (0.9 ha). The capital cost was fixed based on the actual market prices of the bioreactor materials and workforce requirements at the installation time. The cost of fermenters for biocatalyst production was included as an additional capital cost (in the biocatalyst scenario).

Operating costs include the following contributions: energy, materials, land lease, maintenance, and loan repayments. For operating cost estimation, the processes involved in algal biodiesel production were categorized into five different phases: (i) feedstock growth, (ii) biomass harvest, (iii) pretreatment, (iv) transesterification,

Methods	used for calculating techno-economic analysis		
S. No.	Parameter	Calculation methods	
Facility l	ifetime	30 years	
Capital c	cost		
1.a	Bioreactor material/fermenter procurement	Actual prices from manufacturers	
1.b	Pitching, mud bank, and watergate installation cost	Through personal interviews and interaction with landowners and shrimp farmers	
1.c	Labour cost for land preparation	Fixed as per the minimum wages act after confirming the same with the current scenario in the study region	
Operating cost			
	Fixed operating cost		
2.a	Gazani land lease value	Fixed as per current lease trend in the study region	
2.b	Labour cost for harvesting	Same as 1.c	
2.c	Loan repayment cost	Calculated by considering 4.5% interest rates on principal for a loan tenure of 5 years	
Variable	costs		
2.d	Cost of lime fertilizer and solvents	Actual prices of chemicals, fertilizers, and solvents	
2.e	Biodiesel production and other downstream processing costs	Fixed as per Karnataka electricity regulation commission's standard power tariffs for industrial uses	

 Table 7 Methods used for techno-economic analysis

and (v) refining biodiesel. The system boundaries were based on land preparation (pitching, liming, making mud banks, and watergate installation) until biodiesel refining. Both the energy expended and the material inputs were considered with associated costs for TE analysis. Under fixed operating cost, gazani land lease value  $(C_{\rm LV})$ , loan repayment  $(C_{\rm LR})$ , and workforce requirement for manual harvesting  $(C_{\rm ML})$  at the end of every cycle (considering 5–7 days cycling time) for a total of 32 cycles (excluding monsoon and initial colonization period). In variable costs, the costs of chemicals (lime, fertilizers) and solvents required on an annual basis to run the production facility were estimated, and the charges were fixed based on the market prices of the respective chemicals. The costs incurred due to the energy spent in each of the downstream processes were calculated by estimating the energy required to perform each unit operation and converting the energy into costs ( $C_{\rm EC}$ ) by multiplying the energy spent (kWh) with its standard power tariffs fixed as per the Karnataka electricity regulatory commission. Biodiesel production cost (INR/kg), payback period (years), return on investment, and annual profit (INR/ha/yr.) was calculated using Eqs. 1-4, respectively, assuming a facility lifespan of 30 years.

$$Biodiesel \cos t = \frac{Total operating \cos(C_{TOC})(INR)}{Biodiesel production volume(L)}$$
(1)

where

$$C_{\text{TOC}} = C_{\text{FOC}} + C_{\text{VOC}}; \quad C_{\text{FOC}} = C_{\text{LV}} + C_{\text{LR}} + C_{\text{ML}} \text{ and } C_{\text{VOC}} = C_{\text{EC}}$$

Payback period = 
$$1 + n_y - \frac{n}{p}$$
 (2)

where

 $n_y$  = The year at which the last negative cumulative cash flow occurs n = The value of cash flow at the year  $n_y$ 

p =Cumulative value at first positive cash flow

$$ROI(\%) = \frac{\text{Total profit}}{\text{Total operating cost}} \times 100$$
(3)

$$Profit = Revenue - cost \tag{4}$$

The detailed cost breakup on fixed capital investments and operating costs required for setting up a substrate-based microalgal cultivation setup is summarized in Tables 8 and 9, respectively. Capital investment for all three scenarios was the same (₹ 67,500 INR/ha) for bioreactor (substrate–granite stone: procurement and installation and ₹ 18,500 INR/ha for land preparation). Earlier studies considered land costs as a capital investment as land is purchased for setting up bioreactor facilities. For instance, a land cost of \$7800/ha (Davis et al., 2011), \$138,000/ha (Norsker et al., 2011), \$1200/ha (Xin et al., 2016) was considered as capital cost. However, the land lease value (₹ 20,000/ha/yr.) of the abandoned flood plains was considered under operating costs in this study.

Other operating costs considered in the present study include manpower labour charges (₹ 28,800 INR/ha/yr.), transesterification (chemicals + energy) costs, and yearly loan repayment costs. The loan repayment cost was estimated as ₹ 22,368 INR/yr. for scenarios 1 and 2, considering 4% interest. In contrast, for scenario 3, the loan repayment cost was higher (₹ 50,040 INR/yr.), which was influenced by the fertilizer costs in the acid catalyst sub-scenario. In contrast, in the case of the biocatalyst sub-scenario, ₹ 67,116 INR/yr was estimated due to the additional costs required for fermenter procurement. The material input for acid and biocatalyst sub-scenarios was different among the three varying nutrient input scenarios as the nature and amount of chemicals, solvents, and reaction conditions were different for transesterification using acid and biocatalysts were also different (based on the FAME productivity). Thus, the significant scenarios (Scenario 1–3) were explained with two different sub-scenarios of acid and enzyme (lipase) as catalysts for transesterification.

The material and energy outputs considered for analysis were (i) algal biomass (AFDW) (kg/ha/yr), (ii) Biodiesel from the harvested biomass (kg/ha/yr), (iii) the quantity of crude glycerol obtained as a byproduct during the biodiesel process, and (iv) biogas production from spent biomass (m<sup>3</sup>). Conventionally, biodiesel production produces 10% crude glycerol (v/v) as the main byproduct (Yang et al., 2012). Hence, 10% of the total biodiesel yield possible per ha area for a period of one year was taken as the crude glycerol yield. After lipid extraction, the biogas production potential of the spent algal residue was about  $0.272 \text{ m}^3$  of biogas per kg of spent algal biomass used (Harun et al., 2011). Revenue estimation from microalgal cultivation setup includes byproducts from transesterification (crude glycerol) and other value-added products (biogas and spent biogas leachate as algal meal fertilizer) be generated out of the spent microalgal biomass rich in protein and polysaccharides. Estimates revealed that for assumed biomass productivity of 6.7, 15.3, and 28.8 tons/ha/yr under different nutrient input scenarios, acid catalyst-based transesterification could yield a biodiesel quantity of 1499.2, 3407.2, and 6388.6 kg (assuming 83% FAME conversion efficiency).

In contrast, for the biocatalyst scenario, a higher biodiesel yield of 1571.4, 3571.5, and 6696.6 kg is possible with an assumed 87% effective conversion of microalgal oil into FAME (biodiesel). FAME conversion efficiencies were based on the experimental results of using a different catalyst (Saranya & Ramachandra, 2020). To estimate the revenue possible from spent algal fertilizer, one-fourth of the spent microalgal biomass remained after biodiesel extraction and biogas production. Profit evaluation indicates that ~5 times more profit in scenario three than scenario one while using an acid catalyst and ~6 times more profit in biocatalyst scenario, which could be attributed to the higher FAME conversion efficiencies possible from biocatalyst. In addition, biocatalyst reduces the problem of environmental pollution otherwise posed by the acid catalyst. Return on investment is the percentage of initial investment that can be recovered annually as profit, and the payback period is the time required to retrieve investments. The return on investment (ROI) varied between 18.4

Input costs	Different scenarios		
	Scenario 1	Scenario 2	Scenario 3
Fixed capital costs	Value (INR)	Value (INR)	Value (INR)
Gravel stones procurement	₹ 67,500	₹ 67,500	₹ 67,500
Pitching, mud bank formation, laterite stone purchase, liming, and water gate installation	₹ 18,500	₹ 18,500	₹ 18,500
Operational costs			
Gazani land lease value (per ha)	₹ 20,000	₹ 20,000	₹ 20,000
Fertilizer input cost (kg/ha/yr.)	-	-	₹ 167,530
Harvesting (manual) yearly manpower requirement (INR/yr.)	₹ 28,800	₹ 28,800	₹ 28,800
Biomass drying (shade drying)	NA	NA	NA
Transesterification (material + energy) costs	₹ 9953	₹ 28,601	₹ 51,234
Biodiesel purification cost	₹ 1224	₹2734	₹ 5126
Loan repayment	₹ 22,368	₹ 22,368	₹ 50,040
Material and Energy Output			
Biomass obtained per cycle (kg)	211	480	900
No. of cycles harvesting can be made (excluding monsoon)	32 cycles	32 cycles	32 cycles
Biomass yield per year (kg/ha/yr.)	6758.4	15,360	28,800
Biodiesel production possible (kg) from harvested biomass	1499.2	3407.2	6388.6
Quantity of crude glycerol (byproduct) (L/ha/yr.)	150.3	341.7	640.8
Biogas production (m <sup>3</sup> )	1768	4019	7536
Revenue estimation			
Revenue from biodiesel production (INR)	₹ 89,863	₹ 204,233	₹ 382,937
Revenue from crude glycerol	₹ 3757.5	₹ 8543	₹ 16,020
Revenue from biogas production using spent biomass	₹ 16,230	₹ 36,896	₹ 69,180
Revenue from spent algal residue as fertilizer (INR/ha/yr.)	₹ 14,643	₹ 33,280	₹ 62,400
Total revenue (INR/ha/yr.)	₹ 124,493	₹ 282,951	₹ 530,537
Payback period	6.97	0.98	2.98
Return on investment (%)	25.0	95.7	50.8
Biodiesel production cost (INR/kg of biodiesel)	₹ 54.93	₹ 30.08	₹ 50.52
Profit (INR/ha/yr.)	₹ 42,148	₹ 180,449	₹ 207,807

 Table 8
 Detailed cost budgeting for different biomass productivity scenarios using acid catalyst

Input costs	Different scenarios		
	Scenario 1	Scenario 2	Scenario 3
Fixed capital costs	Value (INR)	Value (INR)	Value (INR)
Fermenter for biocatalyst production	₹ 45,000	₹45,000	₹ 45,000
Gravel stones procurement	₹ 67,500	₹ 67,500	₹ 67,500
Pitching, mud bank formation, laterite stone purchase, liming, and water gate installation	₹ 18,500	₹ 18,500	₹ 18,500
Operational costs			
Gazani land lease value (per ha)	₹ 20,000	₹ 20,000	₹ 20,000
Fertilizer input cost (kg/ha/yr.)	_	-	₹ 167,530
Harvesting (manual) yearly manpower requirement (INR/yr.)	₹ 28,800	₹ 28,800	₹ 28,800
Biomass drying (shade drying)	NA	NA	NA
Transesterification (material + energy) costs	₹ 9953	₹ 28,601	₹ 51,234
Biodiesel purification cost	₹ 1224	₹2734	₹ 5126
Loan repayment	₹ 33,552	₹ 33,552	₹67,116
Material and energy output			
Biomass obtained per cycle (kg)	211	480	900
No. of cycles harvesting can be made (excluding monsoon)	32 cycles	32 cycles	32 cycles
Biomass yield per year (kg/ha/yr.)	6758	15,360	28,800
Biodiesel production possible (kg) from harvested biomass	1571.4	3571.5	6696.6
Quantity of crude glycerol (byproduct) (L/ha/yr.)	150.3	341.7	640.8
Biogas production (m <sup>3</sup> )	1768	4019	7536
Revenue estimation		,	
Revenue from biodiesel production (INR)	₹ 94,195	₹214,078	₹ 401,397
Revenue from crude glycerol	₹ 3757.5	₹ 8543	₹ 16,020
Revenue from biogas production using spent biomass (INR)	₹ 16,230	₹ 36,896	₹ 69,180
Revenue from spent algal residue as fertilizer (INR)	₹ 14,643	₹ 33,280	₹ 62,400
Total revenue (INR/ha/yr.)	₹ 128,825	₹ 292,797	₹ 548,996
Payback period (years)	17.67	1.27	2.96
Return on investment (%)	18.4	84.8	51.8
Biodiesel production cost (INR/kg of biodiesel)	₹ 59.52	₹ 31.83	₹ 50.74
Profit (INR/ha/yr.)	₹ 35,296	₹ 179,110.48	₹ 209,190

 Table 9
 Detailed cost budgeting for different biomass productivity scenarios using biocatalyst

and 95.7% for the scenarios considered, with higher ROI (95.7%) was estimated for scenario 2 (wastewater input–acid catalyst), representing a possible favourable higher return on the investments made. The payback period for scenario 1 was the highest for biocatalyst (17 years) due to the projected less annual biomass productivity with estimated higher capital investment. However, the payback period for scenario 2 and scenario 3 was 1.27 and 2.96 years, respectively, showing the financial viability of the proposed algal reactor with biodiesel production. An earlier study that assessed the techno-economic viability of biodiesel biorefinery had demonstrated an ROI that varied between 18.21 and 23.12% and a payback period of 4.3–5.5 years for different process scenarios considered (Vlysidis et al., 2011). The most favourable and profitable among the three considered scenarios was found to be microalgae cultivation using aquaculture wastewater, especially because of its zero associated input value as a nutrient with the wastewater remediation benefits.

The unit production cost of biodiesel for scenarios 1–3 while using acid catalyst varied between ₹ 30.08 and 54.93 INR/kg of biodiesel. The cost of production for biocatalyst-based biodiesel production ranged between ₹ 31.83 and 59.52 INR/kg. The biodiesel production cost per kg of biodiesel for scenario 2 (wastewater input) was found to be the lowest (30.1-31.8 INR/kg biodiesel) while using both acid and biocatalyst of all the scenarios (Tables 8 and 9), thus showing scope for optimal biomass productivity while incurring lesser material/energy costs with remediation benefits and lower GHG emissions and maximum profit. A mass balance of algal refinery byproducts of microalgal biomass was carried out by assuming a 100 kg dry algal biomass (Fig. 6). Considering a lipid content ranging between 18 and 26%, a biodiesel yield of 14.94–22.62 kg is possible when the biomass is subjected to direct transesterification. Crude glycerol of 1.49-2.26 kg is also produced as a byproduct during transesterification, which is estimated as 10% of the biodiesel (Rodrigues et al., 2017). The raw biogas obtained can be purified/upgraded by passing on to a CO<sub>2</sub> stripper absorption column or directly used for domestic cooking/heating applications. A 10% loss in biomass was assumed during the direct transesterification of microalgal biomass into biodiesel. The slurry left out after biogas production (~55–70 kg) can be used as an organic biofertilizer in agricultural fields.

Thus, a biorefinery-based microalgal bioreactor is proposed, which utilizes microalgal biomass to produce two different forms of bioenergy, such as biodiesel and biogas, in addition to the value-added products such as glycerol and biofertilizer. Deployment of such substrate-based microalgal bioreactor in the brackish water flood plains (that are left abandoned) along the coastal regions of Karnataka would provide a livelihood for the coastal population at a decentralized level through bioenergy production for their localized usage along with potential scope for GHG emission reduction through  $CO_2$  sequestration.



Fig. 6 Schematics of mass balance of microalgal bioreactor from a biorefinery perspective

#### 3.2 Circular Economy in Biorefinery

One of the challenges in the advancement of the economic viability of microalgal biofuel is reducing the cost incurred in harvesting, drying, and lipid extraction processes. Biofilm-based algal cultivation helps in addressing the issues relating to harvesting, apart from addressing light limitation issues, while enhancing  $CO_2$ mass transfer (Gross et al., 2015). Thus, integrating biofilm-based algal cultivation into a biorefinery would bring in multiple benefits (products) useful for diverse industrial applications apart from providing economic feasibility. As microalgae are rich in carbohydrates, they could be converted into a range of bioenergy components like biogas, biohydrogen, and liquid biofuels through different biological processes. Algal biomass, when subjected to anaerobic digestion, will result in biogas. The carbohydrates from algal biomass subjected to fermentation give butanol and ethanol. Acetone-Butanol-Ethanol (ABE) fermentation is an anaerobic fermentation process carried out using a gram-negative bacterium called *Clostridium beijer*inckii. Butanol is gaining considerable attention due to its superior fuel value and better storage characteristics. Another way of converting wet algal biomass produced is by hydrothermal liquefaction (HTL). HTL enables direct conversion of wet algal biomass into biocrude with medium temperature and pressure conditions varying between 350–550 °C and 20–25 MPa (Elliott et al., 2013). At specified operating conditions, the liquid water present in the algal biomass maintained at sub-critical levels act as a catalyst for biocrude production. HTL pathway to produce biocrude research is now in progress across the globe (Dote et al., 1994; Stephens et al., 2010; Wiley et al., 2013). This HTL process greatly reduces the energy spent on biomass harvesting and drying. Microalgal biomass rich in pigments like carotenoids is valuable as feedstock for bioactive/value-added product synthesis. The harvested



Fig. 7 Sustainable biorefinery for utilizing microalgal biomass

biomass subjected to oil extraction and subsequent transesterification would result in biodiesel. A detailed illustration of various ways of utilizing algal biomass grown using a low-cost sustainable algal production system is shown in Fig. 7.

The current research focus is towards zero-waste biorefinery based on reducing, reuse, and recycling waste. Zero waste biorefineries eliminate the use of external energy or material inputs by understanding the material's use-value, efficient use of materials, and a planned framework on technologies for establishing a sustainable zero-waste biorefinery (Venkata Mohan et al., 2020). Microalgal cultivation in wastewater helps in the cost-effective treatment of wastewater with resource recovery. Thus, the biorefinery framework by using microalgae as feedstock provides a promising sustainable path with the circular bioeconomy.

#### 4 Conclusion

Algal biofuel has emerged as a viable, sustainable solution to meet the growing demand for energy while addressing the environmental issues associated with the GHG footprint. Integrated bioprocessing through biorefinery approach by utilizing spent biomass after oil extraction can be used as a raw material for various energy products like bioethanol, methane, and biocrude and biofertilizers. The techno-economic analysis of microalgal biorefinery has demonstrated positive aspects such as (i) using appropriate substrates for microalgal attachment that considerably reduces the costs involved in harvesting; (ii) use of wastewater for optimal biomass production with reduced biodiesel production costs and less payback period; (iii) use of biocatalyst, though it increases the capital investment, environmental implications of mineral acids could be avoided which leads to significant environmental

benefits. The utilization of microalgae grown using nutrient-rich wastewaters in an integrated biorefinery shows potential prospects in considerable energy and cost reduction. Establishing algal refineries at decentralized levels, especially along the Indian coasts, would empower local women of fisherfolk communities with secured livelihood opportunities with assured job opportunities.

Acknowledgements Authors are grateful to (i) the NRDMS division, Ministry of Science and Technology, Government of India [CES/TVR/DST1045], and (ii) the Indian Institute of Science for the infrastructure support for ecological research. The authors thank Sreekanth Naik, Vishnu D Mukri, and Gayatri Naik for their assistance during the field data collection. The official languages section scrutinized this MS at IISc (language editing).

Competing Interests There are no competing interests, either financial or non-financial.

**Research Ethics** The publication is based on the original research and has not been submitted elsewhere for publication or web hosting.

Animal Ethics The research does not involve either humans, animals, or tissues.

**Funding** The research was financially supported—(i) ISRO—IISc space technology cell [ISTC/BES/TVR/389] and Gajanana and Madhavi Hegde [CES/TVR/GJH001] endowment for biofuel research.

#### References

- Abbassi, A., Ali, M., & Watson, I. A. (2014). Temperature dependency of cell wall destruction of microalgae with liquid nitrogen pretreatment and hydraulic pressing. *Algal Research*, 5, 190–194. https://doi.org/10.1016/J.ALGAL.2013.12.008
- Alobwede, E., Leake, J. R., & Pandhal, J. (2019). Circular economy fertilization: Testing micro and macro algal species as soil improvers and nutrient sources for crop production in greenhouse and field conditions. *Geoderma*, 334, 113–123. https://doi.org/10.1016/j.geoderma.2018.07.049
- Alzate, M. E., Muñoz, R., Rogalla, F., Fdz-Polanco, F., & Pérez-Elvira, S. I. (2014). Biochemical methane potential of microalgae biomass after lipid extraction. *Chemical Engineering Journal*, 243, 405–410. https://doi.org/10.1016/j.cej.2013.07.076
- Andrade, L. M. (2018). Chlorella and Spirulina microalgae as sources of functional foods, nutraceuticals, and food supplements; an overview. MOJ Food Processing and Technology, 6(1). https:// doi.org/10.15406/mojfpt.2018.06.00144
- Andrejić, J. Z., Spaulding, S. A., Manoylov, K. M., & Edlund, M. B. (2018). Phenotypic plasticity in diatoms: Janus cells in four *Gomphonema taxa*. *Diatom Research*, 33(4), 453–470. https://doi. org/10.1080/0269249X.2019.1572652
- Anitha, L., Sai Bramari, G., & Kalpana, P. (2016). Effect of supplementation of *Spirulina platensis* to enhance the zinc status in plants of *Amaranthus gangeticus*, *Phaseolus aureus* and Tomato. *Advances in Bioscience and Biotechnology*, 07(6), 289–299. https://doi.org/10.4236/abb.2016. 76027
- Biller, P., & Ross, A. B. (2011). Potential yields and properties of oil from the hydrothermal liquefaction of microalgae with different biochemical content. *Bioresource Technology*, 102(1), 215–225. https://doi.org/10.1016/j.biortech.2010.06.028

- Bolton, C. T., Hernández-Sánchez, M. T., Fuertes, M. Á., González-Lemos, S., Abrevaya, L., Mendez-Vicente, A., Flores, J. A., Probert, I., Giosan, L., Johnson, J., & Stoll, H. M. (2016). Decrease in coccolithophore calcification and CO<sub>2</sub> since the middle miocene. *Nature Communications*, 7, 10284. https://doi.org/10.1038/ncomms10284
- Brennan, L., & Owende, P. (2010). Biofuels from microalgae—A review of technologies for production, processing, and extractions of biofuels and co-products. *Renewable and Sustainable Energy Reviews*, 14(2), 557–577. https://doi.org/10.1016/j.rser.2009.10.009
- Brown, T. M., Duan, P., & Savage, P. E. (2010). Hydrothermal liquefaction and gasification of Nannochloropsis sp. Energy and Fuels, 24(6), 3639–3646. https://doi.org/10.1021/ef100203u
- Brown, M. R., McCausland, M. A., & Kowalski, K. (1998). The nutritional value of four Australian microalgal strains fed to Pacific oyster *Crassostrea gigas* spat. *Aquaculture*, 165(3–4), 281–293. https://doi.org/10.1016/S0044-8486(98)00256-7
- Butler, T., Kapoore, R. V., & Vaidyanathan, S. (2020). Phaeodactylum tricornutum: A diatom cell factory. Trends in Biotechnology, 38(6), 606–622. https://doi.org/10.1016/j.tibtech.2019.12.023
- Chatterjee, A., & Rayudu, R. (2018). Techno-economic analysis of hybrid renewable energy system for rural electrification in India. In 2017 IEEE innovative smart grid technologies—Asia: Smart grid for smart community, ISGT-Asia 2017 (pp. 1–5). https://doi.org/10.1109/ISGT-Asia.2017. 8378470.
- Cheng, F., Cui, Z., Chen, L., Jarvis, J., Paz, N., Schaub, T., Nirmalakhandan, N., & Brewer, C. E. (2017). Hydrothermal liquefaction of high- and low-lipid algae: Bio-crude oil chemistry. *Applied Energy*, 206, 278–292. https://doi.org/10.1016/j.apenergy.2017.08.105
- Cheng, H. H., Whang, L. M., Chan, K. C., Chung, M. C., Wu, S. H., Liu, C. P., Tien, S. Y., Chen, S. Y., Chang, J. S., & Lee, W. J. (2015). Biological butanol production from microalgae-based biodiesel residues by *Clostridium acetobutylicum*. *Bioresource Technology*, 184, 379–385. https:// doi.org/10.1016/j.biortech.2014.11.017
- Chew, K. W., Yap, J. Y., Show, P. L., Suan, N. H., Juan, J. C., Ling, T. C., Lee, D. J., & Chang, J. S. (2017). Microalgae biorefinery: High value products perspectives. *Bioresource Technology*, 229, 53–62. https://doi.org/10.1016/j.biortech.2017.01.006
- Chittora, D., Meena, M., Barupal, T., & Swapnil, P. (2020). Cyanobacteria as a source of biofertilizers for sustainable agriculture. *Biochemistry and Biophysics Reports*, 22, 100737. https://doi. org/10.1016/j.bbrep.2020.100737
- Chuntapa, B., Powtongsook, S., & Menasveta, P. (2003). Water quality control using *Spirulina* platensis in shrimp culture tanks. *Aquaculture*, 220(1–4), 355–366. https://doi.org/10.1016/S0044-8486(02)00428-3
- Clarens, A. F., Resurreccion, E. P., White, M. A., & Colosi, L. M. (2010). Environmental life cycle comparison of algae to other bioenergy feedstocks. *Environmental Science and Technology*, 44(5), 1813–1819. https://doi.org/10.1021/es902838n
- d'Ippolito, G., Sardo, A., Paris, D., Vella, F. M., Adelfi, M. G., Botte, P., Gallo, C., & Fontana, A. (2015). Potential of lipid metabolism in marine diatoms for biofuel production. *Biotechnology* for Biofuels, 8, 28. https://doi.org/10.1186/s13068-015-0212-4
- Davis, R., Aden, A., & Pienkos, P. T. (2011). Techno-economic analysis of autotrophic microalgae for fuel production. *Applied Energy*, 88(10), 3524–3531. https://doi.org/10.1016/J.APENERGY. 2011.04.018
- De Stefano, L., Rea, I., Rendina, I., De Stefano, M., & Moretti, L. (2007). Lensless light focusing with the centric marine diatom *Coscinodiscus walesii*. *Optics Express*, 15(26), 18082–18088. https://doi.org/10.1364/OE.15.018082
- Dote, Y., Sawayama, S., Inoue, S., Minowa, T., & Yokoyama, S. (1994). Recovery of liquid fuel from hydrocarbon-rich microalgae by thermochemical liquefaction. *Fuel*, 73(12), 1855–1857. https://doi.org/10.1016/0016-2361(94)90211-9
- Dragone, G., Fernandes, B. D., Abreu, A. P., Vicente, A. A., & Teixeira, J. A. (2011). Nutrient limitation as a strategy for increasing starch accumulation in microalgae. *Applied Energy*, 88(10), 3331–3335. https://doi.org/10.1016/j.apenergy.2011.03.012

- Efremenko, E. N., Nikolskaya, A. B., Lyagin, I. V., Senko, O. V., Makhlis, T. A., Stepanov, N. A., Maslova, O. V., Mamedova, F., & Varfolomeev, S. D. (2012). Production of biofuels from pretreated microalgae biomass by anaerobic fermentation with immobilized *Clostridium aceto-butylicum* cells. *Bioresource Technology*, 114, 342–348. https://doi.org/10.1016/j.biortech.2012. 03.049
- Elliott, D. C., Hart, T. R., Schmidt, A. J., Neuenschwander, G. G., Rotness, L. J., Olarte, M. V., Zacher, A. H., Albrecht, K. O., Hallen, R. T., & Holladay, J. E. (2013). Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor. *Algal Research*, 2(4), 445–454. https://doi.org/10.1016/J.ALGAL.2013.08.005
- Ellis, J. T., Hengge, N. N., Sims, R. C., & Miller, C. D. (2012). Acetone, butanol, and ethanol production from wastewater algae. *Bioresource Technology*, 111, 491–495. https://doi.org/10. 1016/j.biortech.2012.02.002
- Ezeji, T. C., Qureshi, N., & Blaschek, H. P. (2007a). Bioproduction of butanol from biomass: From genes to bioreactors. *Current Opinion in Biotechnology*, 18(3), 220–227. https://doi.org/10.1016/ j.copbio.2007.04.002
- Ezeji, T., Qureshi, N., & Blaschek, H. P. (2007b). Butanol production from agricultural residues: Impact of degradation products on Clostridium beijerinckii growth and butanol fermentation. *Biotechnology and Bioengineering*, 97(6), 1460–1469. https://doi.org/10.1002/bit.21373
- Foley, P. M., Beach, E. S., & Zimmerman, J. B. (2011). Algae as a source of renewable chemicals: Opportunities and challenges. *Green Chemistry*, 13(6), 1399–1405. https://doi.org/10.1039/c1g c00015b
- Francisco, É. C., Neves, D. B., Jacob-Lopes, E., & Franco, T. T. (2010). Microalgae as feedstock for biodiesel production: Carbon dioxide sequestration, lipid production and biofuel quality. *Journal* of Chemical Technology and Biotechnology, 85(3), 395–403. https://doi.org/10.1002/jctb.2338
- Gandini, A. (2008). Polymers from renewable resources: A challenge for the future of macromolecular materials. *Macromolecules*, *41*(24), 9491–9504. https://doi.org/10.1021/ma801735u
- Garcia Alba, L., Torri, C., Samorì, C., Van Der Spek, J., Fabbri, D., Kersten, S. R. A., & Brilman, D. W. F. (2012). Hydrothermal treatment (HTT) of microalgae: Evaluation of the process as conversion method in an algae biorefinery concept. *Energy and Fuels*, 26(1), 642–657. https:// doi.org/10.1021/ef201415s
- Garrison, T. F., Murawski, A., & Quirino, R. L. (2016). Bio-based polymers with potential for biodegradability. *Polymers*, 8(7), 1–22. https://doi.org/10.3390/polym8070262
- Gifuni, I., Pollio, A., Safi, C., Marzocchella, A., & Olivieri, G. (2019). Current bottlenecks and challenges of the microalgal biorefinery. *Trends in Biotechnology*, 37(3), 242–252. https://doi. org/10.1016/j.tibtech.2018.09.006
- Graboski, M. S., & McCormick, R. L. (1998). Combustion of fat and vegetable oil derived fuels in diesel engines. *Progress in Energy and Combustion Science*, 24(2), 125–164. https://doi.org/10. 1016/S0360-1285(97)00034-8
- Gross, M., Jarboe, D., & Wen, Z. (2015). Biofilm-based algal cultivation systems. Applied Microbiology and Biotechnology, 99(14), 5781–5789. https://doi.org/10.1007/s00253-015-6736-5
- Guldhe, A., Ansari, F. A., Singh, P., & Bux, F. (2017). Heterotrophic cultivation of microalgae using aquaculture wastewater: A biorefinery concept for biomass production and nutrient remediation. *Ecological Engineering*, 99, 47–53. https://doi.org/10.1016/j.ecoleng.2016.11.013
- Hall, D. O., Markov, S. A., Watanabe, Y., & Krishna Rao, K. (1995). The potential applications of cyanobacterial photosynthesis for clean technologies. *Photosynthesis Research*, 46(1–2), 159– 167. https://doi.org/10.1007/BF00020426
- Harun, R., Davidson, M., Doyle, M., Gopiraj, R., Danquah, M., & Forde, G. (2011). Technoeconomic analysis of an integrated microalgae photobioreactor, biodiesel and biogas production facility. *Biomass and Bioenergy*, 35(1), 741–747. https://doi.org/10.1016/j.biombioe.2010.10.007
- Hemalatha, M., Sravan, J. S., Min, B., & Venkata Mohan, S. (2019). Microalgae-biorefinery with cascading resource recovery design associated to dairy wastewater treatment. *Bioresource Technology*, 284, 424–429. https://doi.org/10.1016/j.biortech.2019.03.106

- Hernández, D., Solana, M., Riaño, B., García-González, M. C., & Bertucco, A. (2014). Biofuels from microalgae: Lipid extraction and methane production from the residual biomass in a biorefinery approach. *Bioresource Technology*, 170, 370–378. https://doi.org/10.1016/j.biortech.2014.07.109
- Hildebrand, M., Davis, A. K., Smith, S. R., Traller, J. C., & Abbriano, R. (2012). The place of diatoms in the biofuels industry. *Biofuels*, 3(2), 221–240. https://doi.org/10.4155/bfs.11.157
- Hirano, A., Ueda, R., Hirayama, S., & Ogushi, Y. (1997). CO<sub>2</sub> fixation and ethanol production with microalgal photosynthesis and intracellular anaerobic fermentation. *Energy*, 22(2–3), 137–142. https://doi.org/10.1016/S0360-5442(96)00123-5
- Ho, S. H., Chen, C. Y., & Chang, J. S. (2012). Effect of light intensity and nitrogen starvation on CO<sub>2</sub> fixation and lipid/carbohydrate production of an indigenous microalga *Scenedesmus obliquus* CNW-N. *Bioresource Technology*, 113, 244–252. https://doi.org/10.1016/j.biortech.2011.11.133
- Ho, S. H., Huang, S. W., Chen, C. Y., Hasunuma, T., Kondo, A., & Chang, J. S. (2013). Bioethanol production using carbohydrate-rich microalgae biomass as feedstock. *Bioresource Technology*, 135, 191–198. https://doi.org/10.1016/j.biortech.2012.10.015
- Hussein, H. A., & Abdullah, M. A. (2020). Anticancer compounds derived from Marine diatoms. *Marine Drugs*, 18(7). https://doi.org/10.3390/md18070356
- Jaccard, M. (2006). Sustainable fossil fuels: The unusual suspect in the quest for clean and enduring energy. Cambridge University Press.
- Jankowska, E., Sahu, A. K., & Oleskowicz-Popiel, P. (2017). Biogas from microalgae: Review on microalgae's cultivation, harvesting and pretreatment for anaerobic digestion. *Renewable and Sustainable Energy Reviews*, 75, 692–709. https://doi.org/10.1016/J.RSER.2016.11.045
- Javed, F., Aslam, M., Rashid, N., Shamair, Z., Khan, A. L., Yasin, M., Fazal, T., Hafeez, A., Rehman, F., Rehman, M. S. U., Khan, Z., Iqbal, J., & Bazmi, A. A. (2019) Microalgae-based biofuels, resource recovery and wastewater treatment: A pathway towards sustainable biorefinery. *Fuel*, 255. https://doi.org/10.1016/j.fuel.2019.115826, PubMed: 115826.
- Jeffryes, C., Campbell, J., Li, H., Jiao, J., & Rorrer, G. (2011). The potential of diatom nanobiotechnology for applications in solar cells, batteries, and electroluminescent devices. *Energy and Environmental Science*, 4(10), 3930. https://doi.org/10.1039/c0ee00306a
- Jena, U., & Das, K. C. (2011). Comparative evaluation of thermochemical liquefaction and pyrolysis for bio-oil production from microalgae. *Energy and Fuels*, 25(11), 5472–5482. https://doi.org/ 10.1021/ef201373m
- Jerez, A., Partal, P., Martínez, I., Gallegos, C., & Guerrero, A. (2007). Protein-based bioplastics: Effect of thermo-mechanical processing. *Rheologica Acta*, 46(5), 711–720. https://doi.org/10. 1007/s00397-007-0165-z
- John, R. P., Anisha, G. S., Nampoothiri, K. M., & Pandey, A. (2011). Micro and macroalgal biomass: A renewable source for bioethanol. *Bioresource Technology*, 102(1), 186–193. https://doi.org/10. 1016/j.biortech.2010.06.139
- Juang, D. F., Lee, C. H., & Hsueh, S. C. (2012). Comparison of electrogenic capabilities of microbial fuel cell with different light power on algae grown cathode. *Bioresource Technology*, 123, 23–29. https://doi.org/10.1016/j.biortech.2012.07.041
- Kranzler, C. F., Krause, J. W., Brzezinski, M. A., Edwards, B. R., Biggs, W. P., Maniscalco, M., McCrow, J. P., Van Mooy, B. A. S., Bidle, K. D., Allen, A. E., & Thamatrakoln, K. (2019). Silicon limitation facilitates virus infection and mortality of marine diatoms. *Nature Microbiology*, 4(11), 1790–1797. https://doi.org/10.1038/s41564-019-0502-x
- Kwietniewska, E., & Tys, J. (2014). Process characteristics, inhibition factors and methane yields of anaerobic digestion process, with particular focus on microalgal biomass fermentation. *Renewable and Sustainable Energy Reviews*, 34, 491–500. https://doi.org/10.1016/j.rser.2014. 03.041
- Laurens, L. M. L., Markham, J., Templeton, D. W., Christensen, E. D., Van Wychen, S., Vadelius, E. W., Chen-Glasser, M., Dong, T., Davis, R., & Pienkos, P. T. (2017). Development of algae biorefinery concepts for biofuels and bioproducts; a perspective on process-compatible products and their impact on cost-reduction. *Energy and Environmental Science*, 10(8), 1716–1738. https:// doi.org/10.1039/C7EE01306J

- Lee, D. J., Chang, J. S., & Lai, J. Y. (2015). Microalgae-microbial fuel cell: A mini review. Bioresource Technology, 198, 891–895. https://doi.org/10.1016/j.biortech.2015.09.061
- Lee, O. K., Kim, A. L., Seong, D. H., Lee, C. G., Jung, Y. T., Lee, J. W., & Lee, E. Y. (2013). Chemoenzymatic saccharification and bioethanol fermentation of lipid-extracted residual biomass of the microalga, *Dunaliella tertiolecta*. *Bioresource Technology*, 132, 197–201. https:// doi.org/10.1016/j.biortech.2013.01.007
- Lee, S. Y., Park, J. H., Jang, S. H., Nielsen, L. K., Kim, J., & Jung, K. S. (2008). Fermentative butanol production by clostridia. *Biotechnology and Bioengineering*, 101(2), 209–228. https:// doi.org/10.1002/bit.22003
- Li, X. L., Marella, T. K., Tao, L., Peng, L., Song, C. F., Dai, L. L., Tiwari, A., & Li, G. (2017). A novel growth method for diatom algae in aquaculture waste water for natural food development and nutrient removal. *Water Science and Technology*, 75(12), 2777–2783. https://doi.org/10.2166/ wst.2017.156
- Linares, L. C. F., Falfán, K. Á. G., & Ramírez-López, C. (2017). Microalgal biomass: A biorefinery approach. In *Biomass volume estimation and valorization for energy* (vol. 293).
- López Barreiro, D., Prins, W., Ronsse, F., & Brilman, W. (2013). Hydrothermal liquefaction (HTL) of microalgae for biofuel production: State of the art review and future prospects. *Biomass and Bioenergy*, 53, 113–127. https://doi.org/10.1016/j.biombioe.2012.12.029
- Marella, T. K., López-Pacheco, I. Y., Parra-Saldívar, R., Dixit, S., & Tiwari, A. (2020). Wealth from waste: Diatoms as tools for phycoremediation of wastewater and for obtaining value from the biomass. *Science of the Total Environment*, 724, 137960. https://doi.org/10.1016/j.scitotenv. 2020.137960
- Marella, T. K., & Tiwari, A. (2020). Marine diatom *Thalassiosira weissflogii* based biorefinery for co-production of eicosapentaenoic acid and fucoxanthin. *Bioresource Technology*, 307, 123245. https://doi.org/10.1016/j.biortech.2020.123245
- Martín, L. A., Popovich, C. A., Martínez, A. M., Scodelaro Bilbao, P. G., Damiani, M. C., & Leonardi, P. I. (2018). Hybrid two-stage culture of Halamphora coffeaeformis for biodiesel production: Growth phases, nutritional stages and biorefinery approach. *Renewable Energy*, 118, 984–992. https://doi.org/10.1016/j.renene.2017.10.086
- Mobin, S., & Alam, F. (2017). Some promising microalgal species for commercial applications: A review. *Energy Procedia*, 110, 510–517. https://doi.org/10.1016/j.egypro.2017.03.177
- Mulders, K. J. M., Lamers, P. P., Martens, D. E., & Wijffels, R. H. (2014). Phototrophic pigment production with microalgae: Biological constraints and opportunities. *Journal of Phycology*, 50(2), 229–242. https://doi.org/10.1111/jpy.12173
- Norsker, N. H., Barbosa, M. J., Vermuë, M. H., & Wijffels, R. H. (2011). Microalgal production—A close look at the economics. *Biotechnology Advances*, 29(1), 24–27. https://doi.org/10.1016/j. biotechady.2010.08.005
- Praveenkumar, R., Lee, K., Lee, J., & Oh, Y. K. (2015). Breaking dormancy: An energy-efficient means of recovering astaxanthin from microalgae. *Green Chemistry*, 17(2), 1226–1234. https:// doi.org/10.1039/C4GC01413H
- Pulz, O., & Gross, W. (2004). Valuable products from biotechnology of microalgae. Applied Microbiology and Biotechnology, 65(6), 635–648. https://doi.org/10.1007/s00253-004-1647-x
- Rahman, A., & Miller, C. D. (2017). Microalgae as a source of bioplastics. In Algal green chemistry: Recent progress in biotechnology (pp. 121–138). https://doi.org/10.1016/B978-0-444-63784-0. 00006-0
- Rahman, A., Putman, R. J., Inan, K., Sal, F. A., Sathish, A., Smith, T., Nielsen, C., Sims, R. C., & Miller, C. D. (2015). Polyhydroxybutyrate production using a wastewater microalgae based media. *Algal Research*, 8, 95–98. https://doi.org/10.1016/j.algal.2015.01.009
- Rajaram, M. G., Nagaraj, S., Manjunath, M., Boopathy, A. B., Kurinjimalar, C., Rengasamy, R., Jayakumar, T., Sheu, J. R., & Li, J. Y. (2018). Biofuel and biochemical analysis of amphora coffeaeformis RR03, a novel marine diatom, cultivated in an open raceway pond. *Energies*, *11*(6), 1–12. https://doi.org/10.3390/en11061341

- Ramachandra, T. V., Alakananda, B., & Supriya, G. (2011). Biofuel prospects of microalgal community in Urban Wetlands. World, 1, 54–61.
- Ramachandra, T. V., Durga Madhab, M., Shilpi, S., & Joshi, N. V. (2013). Algal biofuel from urban wastewater in India: Scope and challenges. *Renewable and Sustainable Energy Reviews*, 21, 767–777. https://doi.org/10.1016/j.rser.2012.12.029
- Ramachandra, T. V., & Hegde, G. (2015). Energy trajectory in India: Challenges and opportunities for innovation. *Journal of Resources, Energy and Development*, 12(1–2), 1–24. https://doi.org/ 10.3233/RED-120115
- Ramos-Suárez, J. L., & Carreras, N. (2014). Use of microalgae residues for biogas production. *Chemical Engineering Journal*, 242, 86–95. https://doi.org/10.1016/j.cej.2013.12.053
- Rehm, B. H. A. (2010). Bacterial polymers: Biosynthesis, modifications and applications. *Nature Reviews. Microbiology*, 8(8), 578–592. https://doi.org/10.1038/nrmicro2354
- Ribeiro, L. A., da Silva, P. P., Mata, T. M., & Martins, A. A. (2015). Prospects of using microalgae for biofuels production: Results of a Delphi study. *Renewable Energy*, 75, 799–804. https://doi. org/10.1016/J.RENENE.2014.10.065
- Rodrigues, A., Bordado, J. C., & Dos Santos, R. Gd. (2017). Upgrading the glycerol from biodiesel production as a source of energy carriers and chemicals—A technological review for three chemical pathways. *Energies*, 10(11). https://doi.org/10.3390/en10111817
- Sánchez-Bayo, A., López-Chicharro, D., Morales, V., Espada, J. J., Puyol, D., Martínez, F., Astals, S., Vicente, G., Bautista, L. F., & Rodríguez, R. (2020). Biodiesel and biogas production from Isochrysis galbana using dry and wet lipid extraction: A biorefinery approach. *Renewable Energy*, 146, 188–195. https://doi.org/10.1016/j.renene.2019.06.148
- Saranya, G., & Ramachandra, T. V. (2020). Novel biocatalyst for optimal biodiesel production from diatoms. *Renewable Energy*, 153, 919–934. https://doi.org/10.1016/j.renene.2020.02.053
- Sathasivam, R., Radhakrishnan, R., Hashem, A., & Abd Allah, E. F. (2019). Microalgae metabolites: A rich source for food and medicine. *Saudi Journal of Biological Sciences*, 26(4), 709–722. https:// doi.org/10.1016/j.sjbs.2017.11.003
- Sethi, D., Butler, T. O., Shuhaili, F., & Vaidyanathan, S. (2020). Diatoms for carbon sequestration and bio-based manufacturing. *Biology*, 9(8), 1–29. https://doi.org/10.3390/biology9080217
- Shah, M. R., Lutzu, G. A., Alam, A., Sarker, P., Kabir Chowdhury, M. A., Parsaeimehr, A., Liang, Y., & Daroch, M. (2018). Microalgae in aquafeeds for a sustainable aquaculture industry. *Journal* of Applied Phycology, 30(1), 197–213. https://doi.org/10.1007/s10811-017-1234-z
- Shokrkar, H., & Ebrahimi, S. (2018). Evaluation of different enzymatic treatment procedures on sugar extraction from microalgal biomass, experimental and kinetic study. *Energy*, 148, 258–268. https://doi.org/10.1016/j.energy.2018.01.124
- Shokrkar, H., Ebrahimi, S., & Zamani, M. (2018). Enzymatic hydrolysis of microalgal cellulose for bioethanol production, modeling and sensitivity analysis. *Fuel*, 228, 30–38. https://doi.org/ 10.1016/j.fuel.2018.04.143
- Sialve, B., Bernet, N., & Bernard, O. (2009). Anaerobic digestion of microalgae as a necessary step to make microalgal biodiesel sustainable. *Biotechnology Advances*, 27(4), 409–416. https://doi. org/10.1016/j.biotechadv.2009.03.001
- Spolaore, P., Joannis-Cassan, C., Duran, E., & Isambert, A. (2006). Commercial applications of microalgae. *Journal of Bioscience and Bioengineering*, 101(2), 87–96. https://doi.org/10.1263/ jbb.101.87
- Sreedevi, S., Unni, K. N., Sajith, S., Priji, P., Josh, M. S., & Benjamin, S. (2014). Bioplastics: Advances in polyhydroxybutyrate research. In *Advances in polymer science* (pp. 1–30). Springer. https://doi.org/10.1007/12\_2014\_297
- Stephens, E., Ross, I. L., Mussgnug, J. H., Wagner, L. D., Borowitzka, M. A., Posten, C., Kruse, O., & Hankamer, B. (2010). Future prospects of microalgal biofuel production systems. *Trends* in *Plant Science*, 15(10), 554–564. https://doi.org/10.1016/J.TPLANTS.2010.06.003

- Tian, C., Li, B., Liu, Z., Zhang, Y., & Lu, H. (2014). Hydrothermal liquefaction for algal biorefinery: A critical review. *Renewable and Sustainable Energy Reviews*, 38, 933–950. https://doi.org/10. 1016/j.rser.2014.07.030
- Tibbetts, S. M., Milley, J. E., & Lall, S. P. (2015). Chemical composition and nutritional properties of freshwater and marine microalgal biomass cultured in photobioreactors. *Journal of Applied Phycology*, 27(3), 1109–1119. https://doi.org/10.1007/s10811-014-0428-x
- Tredici, M. R., Rodolfi, L., Biondi, N., Bassi, N., & Sampietro, G. (2016). Techno-economic analysis of microalgal biomass production in a 1-ha green wall panel (GWP®) plant. *Algal Research*, 19, 253–263. https://doi.org/10.1016/J.ALGAL.2016.09.005
- Venkata Mohan, S., Hemalatha, M., Chakraborty, D., Chatterjee, S., Ranadheer, P., & Kona, R. (2020). Algal biorefinery models with self-sustainable closed loop approach: Trends and prospective for blue-bioeconomy. *Bioresource Technology*, 295, 122128. https://doi.org/10.1016/j.bio rtech.2019.122128
- Vlysidis, A., Binns, M., Webb, C., & Theodoropoulos, C. (2011). A techno-economic analysis of biodiesel biorefineries: Assessment of integrated designs for the co-production of fuels and chemicals. *Energy*, 36(8), 4671–4683. https://doi.org/10.1016/j.energy.2011.04.046
- Wang, X., Feng, Y., Liu, J., Lee, H., Li, C., Li, N., & Ren, N. (2010). Sequestration of CO<sub>2</sub> discharged from anode by algal cathode in microbial carbon capture cells (MCCs). *Biosensors* and *Bioelectronics*, 25(12), 2639–2643. https://doi.org/10.1016/j.bios.2010.04.036
- Wang, Y., Guo, W., Cheng, C. L., Ho, S. H., Chang, J. S., & Ren, N. (2016). Enhancing bio-butanol production from biomass of *Chlorella vulgaris* JSC-6 with sequential alkali pretreatment and acid hydrolysis. *Bioresource Technology*, 200, 557–564. https://doi.org/10.1016/j.biortech.2015. 10.056
- Ward, A. J., Hobbs, P. J., Holliman, P. J., & Jones, D. L. (2008). Optimization of the anaerobic digestion of agricultural resources. *Bioresource Technology*, 99(17), 7928–7940. https://doi.org/ 10.1016/j.biortech.2008.02.044
- Wiley, P., Harris, L., Reinsch, S., Tozzi, S., Embaye, T., Clark, K., McKuin, B., Kolber, Z., Adams, R., Kagawa, H., Richardson, T.-M.J., Malinowski, J., Beal, C., Claxton, M. A., Geiger, E., Rask, J., Campbell, J. E., & Trent, J. D. (2013). Microalgae cultivation using offshore membrane enclosures for growing algae (OMEGA). *Journal of Sustainable Bioenergy Systems*, 03(1), 18–32. https:// doi.org/10.4236/jsbs.2013.31003
- Wu, Y., Wang, Z., Zheng, Y., Xiao, Y., Yang, Z., & Zhao, F. (2014). Light intensity affects the performance of photo microbial fuel cells with *Desmodesmus* sp. A8 as cathodic microorganism. *Applied Energy*, 116, 86–90. https://doi.org/10.1016/j.apenergy.2013.11.066
- Xin, C., Addy, M. M., Zhao, J., Cheng, Y., Cheng, S., Mu, D., Liu, Y., Ding, R., Chen, P., & Ruan, R. (2016). Comprehensive techno-economic analysis of wastewater-based algal biofuel production: A case study. *Bioresource Technology*, 211, 584–593. https://doi.org/10.1016/j.bio rtech.2016.03.102
- Xu, L., Wim Brilman, D. W. F., Withag, J. A. M., Brem, G., & Kersten, S. (2011). Assessment of a dry and a wet route for the production of biofuels from microalgae: Energy balance analysis. *Bioresource Technology*, 102(8), 5113–5122. https://doi.org/10.1016/j.biortech.2011.01.066
- Yamaguchi, K. (1996). Recent advances in microalgal bioscience in Japan, with special reference to utilization of biomass and metabolites: A review. *Journal of Applied Phycology*, 8(6), 487–502. https://doi.org/10.1007/BF02186327
- Yang, F., Hanna, M. A., & Sun, R. (2012). Value-added uses for crude glycerol—A byproduct of biodiesel production. *Biotechnology for Biofuels*, 5, 13. https://doi.org/10.1186/1754-6834-5-13
- Yap, B. H. J., Crawford, S. A., Dagastine, R. R., Scales, P. J., & Martin, G. J. O. (2016). Nitrogen deprivation of microalgae: Effect on cell size, cell wall thickness, cell strength, and resistance to mechanical disruption. *Journal of Industrial Microbiology and Biotechnology*, 43(12), 1671– 1680. https://doi.org/10.1007/s10295-016-1848-1

- Zhang, S., Pei, H., Wei, J., Zhu, Y., Wang, Y., & Yang, Z. (2019). The seasonal and spatial variations in diatom communities and the influence of environmental factors on three temperate reservoirs in Shandong Province, China. *Environmental Science and Pollution Research International*, 26(24), 24503–24515. https://doi.org/10.1007/s11356-019-05480-9
- Zhao, B., Ma, J., Zhao, Q., Laurens, L., Jarvis, E., Chen, S., & Frear, C. (2014). Efficient anaerobic digestion of whole microalgae and lipid-extracted microalgae residues for methane energy production. *Bioresource Technology*, *161*, 423–430. https://doi.org/10.1016/j.biortech. 2014.03.079