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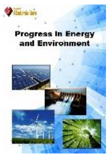

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Review Article

Review - New prospect of algae for sustainable production of lactic acid: Opportunities and challenges

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Abstract

Heavily dependent on fossil fuels has resulted in severe environmental impacts such as exhaustion of natural resources, contamination of the environment, and excessive greenhouse emission. Therefore, intensive research works to explore alternative and sustainable energy sources has been escalated in recent years. In this regard, algae have been exploited as the third-generation of biomass to produce biofuels and biochemicals. Nevertheless, research to produce lactic acid from algae is still limited in the literature. Hence, this review is aimed to provide an extensive mechanism of deriving lactic acid from algae biomass, started with the discussion of the types of algae, the involvement of other microorganisms, fermentation technology, as well as the bottleneck of the technology. The evolution of different biomass feedstocks for lactic acid production is addressed in the initial section of this paper, followed by a discussion on the perspective of novel cascading algae biorefinery systems to truly reveal the potential of algae-based lactic acid production in a sustainable manner.

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1 Introduction

Extensive use of petroleum-based plastics has significantly increased the global volume of plastics in the environment and contribution to plastic pollution. A total of 8 million metric tonnes of plastic waste have been disposed into the sea annually, and 100-250 million metric tonnes of plastic wastes were estimated to be discarded into the ocean in 2025 [1]. Therefore, the growing concerns on environmental contamination with plastic wastes lead to the shift towards the use of bioplastics as an alternative to petroleum-based plastics. In recent years, polylactic acid (PLA) was the most commonly used biodegradable and biocompatible plastics [2]. It is a sustainable product that can be produced in industrial scale via microbial fermentation of sugar-rich feedstock [3]. As reported, 50% of total lactic acid in the global market will be utilized for PLA production by 2025 [2]. Therefore, a promising feedstock for commercial production of lactic acid should be developed to avoid insufficient supply of lactic acid globally. As depicted in Fig. 1, algae as the third-generation of biomass feedstock has immense potential as substrates to produce the lactic acid as an essential building block for PLA production due to its outstanding nature and characteristics while comparing to food-crop based and

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lignocellulosic biomass. Fast growth and high photosynthetic efficiency of algae ensure the continuous supply of the feedstock to produce lactic acid with a lower cost of raw materials [4]. Besides, algae cultivation also able to mitigate agricultural land-use competition and offers better benefits in term of food security.

Additionally, low or absence of lignin content in algae eliminates the complex process of delignification [5]. Although algae have received high attention as an emerging feedstock in biorefineries, the use of algae biomass as substrates for the synthesis of lactic acid still requires further advanced research. Hence, this comprehensive review focused on the exploration of algae biomass to produce a value-added product such as lactic acid by implementing zero waste concept towards an environmental and energy sustainability process.

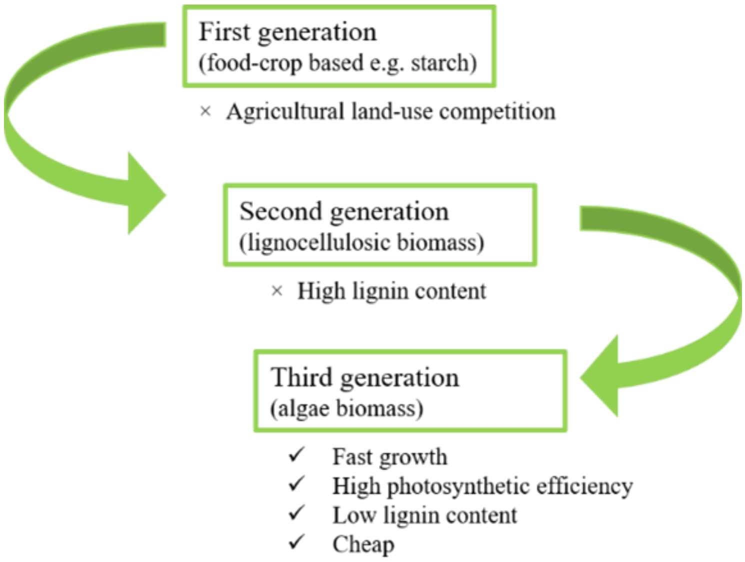

Fig. 1 The transformation of first to second and third-generation of feedstock for biochemical production [6].

2 Algae

Algae generally divided into two groups, microalgae and macroalgae based on their morphology and size. As indicated by the name, microalgae are microscopic photosynthesis organisms, where most of them are small cells with a size of about 2-200 µm and can be grown in a fresh and wastewater system. On the contrary, macroalgae are large visible algae or known as the multicellular plant that grown in the ocean with approximately 60 m length [7]. These algae are recognized as the third-generation biomass to produce valuable bio-product and bio-energy due to their high carbohydrates concentration, low or absence of lignin content, which provides facile hydrolysis of biomass to form valuable products [8]. Fig. 2 shows a list of bioproducts that can be derived by using algae biomass as feedstock [9-11].

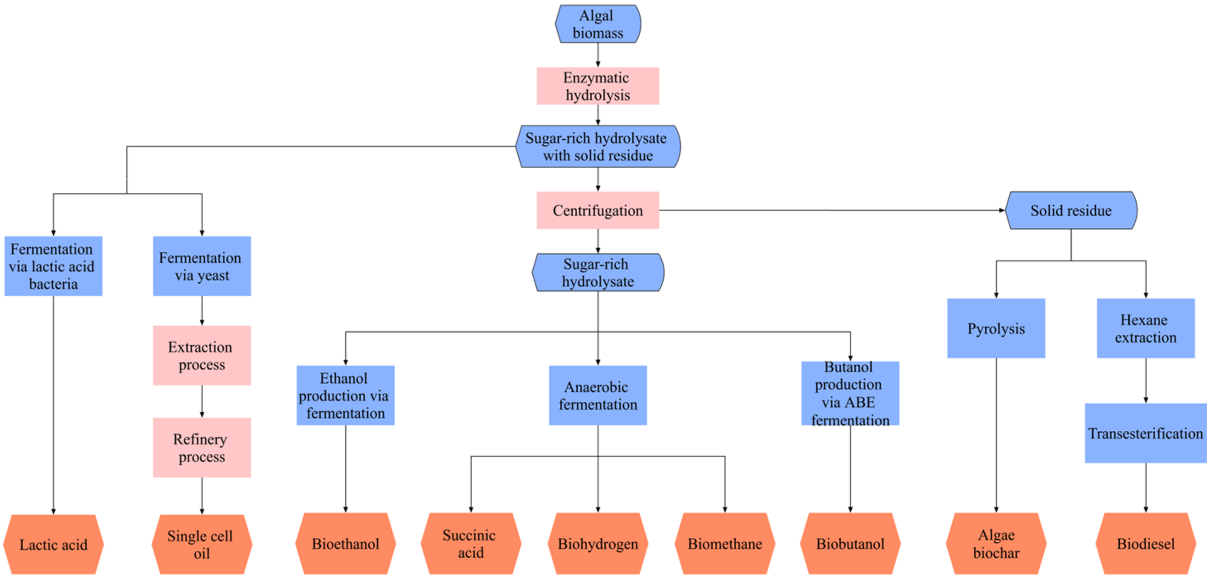

Fig. 2 Bio-based products from algae biomass.

Algae are composed of three primary components, which are carbohydrates, proteins, and lipids. The composition analysis of various macro- and micro-algae, as presented in Table 1 demonstrated that the biochemical composition (wt%) is species-specific, which varies with the type of algae. According to Dave et al. [12], environmental factors such as wind, temperature, salinity, nutrient, and photoperiod concentration as well as the seasonal effect also leading to differences in biochemical composition of algae.

Table 1 Biochemical composition of different algae species

Algae	Composition (wt %)					References
	Carbohydrate	Protein	Lipid	Ash	Others	
Macroalgae						
Chondrus crispus	21.8 ± 1.57	19.9 ± 0.27	0.48 ± 0.25	19 ± 1.02	-	[9]
Palmaria palmata	39.4 ± 1.00	2.29 ± 0.16	3.3 ± 0.60	25.7 ± 0.31	-	[9]
E. denticulatum	65.82	4.90	0.10	17.30	11.88	[10]
Laminaria digitata	46.6	12.9	1.0	26.0	-	[11]
Ulva rigida	53 ± 1	23.4 ± 0.51	1.2 ± 0.2	21.7 ± 1.12	-	[13]
Sargassum latifolium	20.1	5.7	4.2	25	-	[14]
Ulva lactuca	19.87	4.9	5	35	-	[14]
Jania rubens	11.6	16.9	6.5	30.3	-	[14]
Halimeda macroloba	32.63	5.4	9.89	-	-	[15]
Microalgae						
Spirulina maxima	14.6 ± 1.5	65.5 ± 5.5	6.5 ± 0.5	-	-	[15]
Synechococcus sp.	63	15	11	-	-	[15]
Scenedesmus obliquus	27.7 ± 0.02	31.8 ± 0.01	42.6 ± 0.01	-	-	[16]
S. bibraianum	38.2 ± 0.02	44.7 ± 0.00	9.4 ± 0.02	-	-	[16]
Laminaria japonica	7.4	45.2	1.1	-	-	[17]
Chlorella vulgaris	17.3-19.2	52.0-56.44	12.4-15.7	-	-	[17]
Dunaliella tertiolecta	21.69	61.32	2.87			[17]
Tetraselmis maculate	15	52	-	-	-	[18]
Prymnesium parvum	25-33	28-45	-	-	-	[18]

In general, algae biomass contains carbohydrates that can be used as a carbon source in the biological transformation process. Algae biomass is thereby proposed as the potential substrate for commercial production of lactic acid thru microbial fermentation.

3 Recent technologies for lactic acid production

In general, lactic acid could be manufactured by two pathways: (1) chemical synthesis, and (2) fermentation. Unfortunately, the chemical pathway would convert a racemic mixture acid (DL-lactic acid) at most of the time, whereas microbial fermentation can be used to produce two different optical isomers (L- and D-lactic acid) [19]. Also, the consumption of high doses of D-lactic acid is harmful to the human body; therefore, L-lactic acid is preferably in the food and pharmaceutical industry. Thus, nearly 90% of the global production of lactic acid is derived through fermentation processes as it provides better beneficial results in terms of economic and environment compared to the chemical synthesis pathway [20,21]. Basically, lactic acid bacteria can be grouped into homofermentative and heterofermentative, as shown in Fig. 3. Homofermentative lactic acid bacteria produce lactic acid from glucose via the Embden-Meyerhof-Parnas (EMP) glycolytic pathways, whereas heterofermentative lactic acid bacteria use both EMP and Phosphoketolase (PKP) pathway that will produce by-products such as acetate, carbon dioxide, ethanol, or mannitol in the case of fructose metabolism [22].

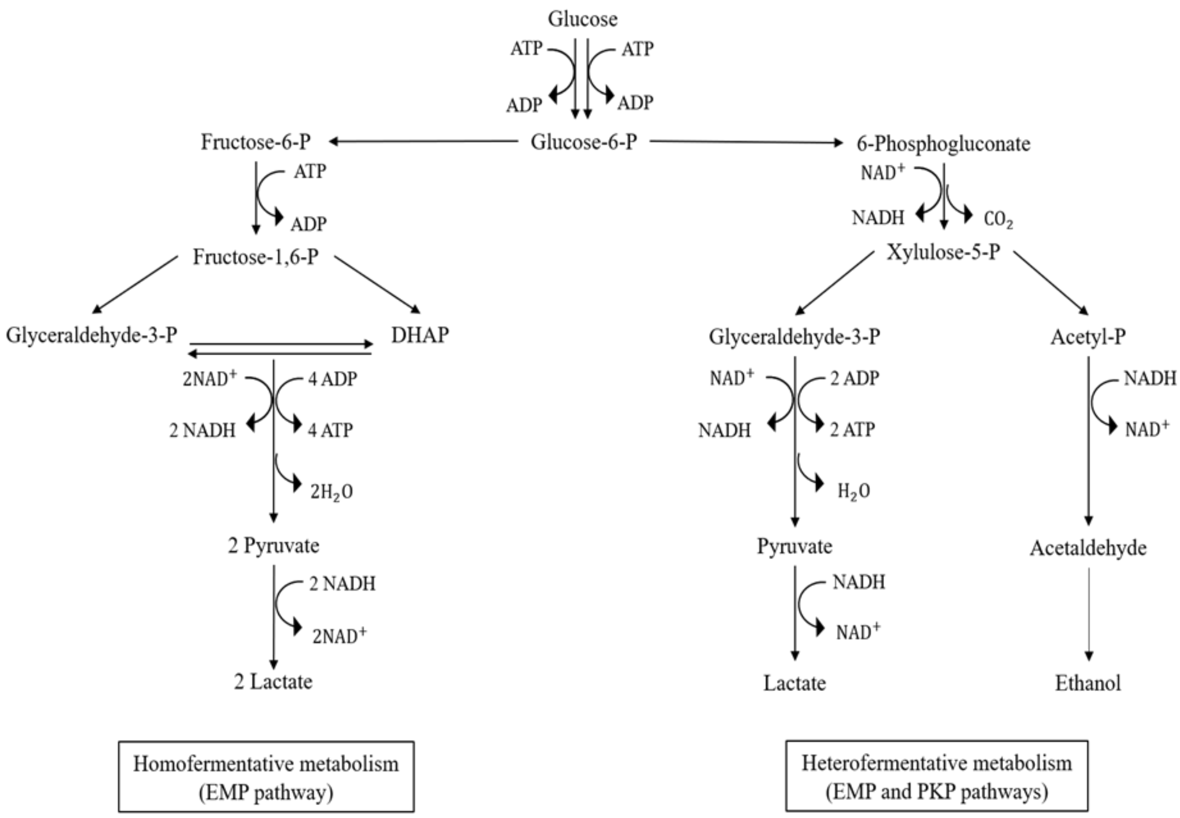

Fig. 3 Metabolism for lactic acid bacteria (homofermentative and heterofermentative pathways) [22].

In addition, lactic acid bacteria (LAB) strains using the EMP pathway were recommended for commercial lactic acid production [23]. Thus, strains selection for industrial-scale lactic acid production was limited to a few important genera of LAB, such as Lactobacillus, Lactococcus, and Enterococcus [24]. Commonly, Lactobacillus strains have been widely used for the production of lactic acid in industry, as they are highly acid resistance and able to be altered to produce D/L – lactic acid selectively. [25]. The details of some studies for the synthesis of lactic acid by using different microorganisms (wild and engineered) are tabulated in Table 2. Overall, recent research has investigated and proved the feasibility of using carbohydrate-rich feedstock to produce lactic acid through microbial fermentation.

Table 2 Parameters of lactic acid fermentation from different LAB

Strains	Substrate	LA produced (g/L)	D, L type	Optical purity (%)	Productivity (g/L·h)	Reference
Lb. plantarum $\Delta ldhL1$	Corn stover	15.9	D	99.6	0.26	[26]
Lb. plantarum $\Delta ldhL1$	Sorghum stalks	12.5	D	99.2	0.21	[26]
Lb. plantarum $\Delta ldhL1 - pCU - PxylAB$	Corn stover	19.7	D	99.3	0.27	[26]
B. coagulans (NBRC 12714)	Corn stover hydrolysate	92	L	99.5	13.8	[27]
B. coagulans strain H-1	Lignocellulosic corncob residue	68	L	99.5	1.89	[28]

4 Perspective on novel cascading macroalgae biorefinery systems

Recently, algae biomass has been investigated by the researchers as a sustainable feedstock to produce biofuels such as bioethanol, biogas, and biomethane. However, it is known that a better economic benefit and more employment should be created while converting algae biomass to chemicals or other valuable products such as polymer resin [29]. Therefore, lactic acid is the bioproduct to be featured in this review as the market for lactic acid continuous to grow rapidly in recent years due to the high demand of PLA polymers [30].

Biochemical conversion such as fermentation is considered as an environmentally friendly route to produce valuable products from biomass. Therefore, lactic acid production through fermentation using sustainable algae biomass is proposed as an alternative to chemical synthesis pathway. According to Tan and Lee [31], cellulose extracted from algae after several steps of pre-processing are subjected to enzymatic hydrolysis to produce sugars by the action of hydrolytic enzymes. Then, the sugars are converted by bacteria to produce lactic acid during fermentation [25]. The steps involved in the processing routes are (1) pretreatment of algae biomass, (2) enzymatic hydrolysis, (3) fermentation. The overview process flow of lactic production through fermentation using algae biomass is presented in Fig. 4.

Prior to enzymatic hydrolysis, algae biomass can be subjected to pretreatment to enhance cellulose accessibility. There is a variety of pretreatment, such as microwave-assisted, hydrothermal, ultrasonication and electron beam [32,33]. The pretreatment reduces the crystallinity and degree of polymerization, leading to efficient interaction of enzymes or microbes and enhance enzymatic digestibility of the cellulose. Several reports have revealed that pretreatment of biomass enhanced the production yield in contrast to untreated biomass [31,34-38]. The complex sugars extracted from algae biomass is further degraded into monosaccharides through hydrolysis process (e.g. acid or enzyme hydrolysis). Acid hydrolysis is likely to produce inhibitors such as furfural, phenolic compounds (vanillin), and hydroxyl methyl furfural. The presence of these inhibitors could affect the microbial growth in fermentation and reduces the production yield of lactic acid [39]. On the other hand, enzymatic hydrolysis may be preferable as it also reduces chemical usage and biodegradable [40]. Enzymatic hydrolysis can be carried out either simultaneously or in a separated stage with fermentation. Separated hydrolysis and fermentation (SHF) allows enzymatic hydrolysis and fermentation to be carried out under their optimum conditions. However, simultaneous saccharification fermentation (SSF) which combines both enzymatic hydrolysis and fermentation simultaneously offers advantages such as short processing time, better tolerance to inhibitors and reduces the risk of contamination in the same vessel if compare to SHF [41,42]. Recent studies are mainly focused on the application of SSF to produce lactic acid [27,28,43,44]. The details of some studies of the production of lactic acid from algae are tabulated in Table 3. As an example, both components (Carrageenan and Cellulose) in red algae, Eucheuma denticulatum are good sources to produce lactic acid as they contain high concentration of reducing sugar after hydrolysis steps [37,38].

Table 3 Recent studies on the production of lactic acid from different types of algae

Algae	Hydrocolloid	Pretreament Technique	Type of Hydrolysis	Concentration of Reducing Sugar (g/L)	Type of Fermentation	Concentration of Lactic acid (g/L)	Reference
Macroalgae							
Eucheuma denticulatum	Carrageenan	-	Microwave assisted dilute acid hydrolysis	27.9 ± 1.64	Separate hydrolysis and fermentation (SHF)	22.5 ± 0.07	[37]
	Carrageenan	-	Microwave assisted hydrothermal hydrolysis	26.3 ± 0.33	Separate hydrolysis and fermentation (SHF)	22.5 ± 0.07	[37]
Eucheuma denticulatum	Cellulose	Microwave pretreatment	Enzymatic hydrolysis	19.3	Prehydrolysis and simultaneous saccharification and fermentation (PSSF)	14	[38]
Glacilaria sp.	Agar	Dilute acid pretreatment	Acid hydrolysis	23.32 ± 0.26	Separate hydrolysis and fermentation (SHF)	14.21± 0.16	[45]
Microalgae							
Nannochloropsis salina	Lipid extracted residue	Acid pretreatment	Acid hydrolysis	25	Separate hydrolysis and fermentation (SHF)	23	[46]

Furthermore, to promote the zero-waste concept in biorefinery processes, the remnant biomass from the lactic acid production can be utilized for algae-biochar production through pyrolysis process. According to De Bhowmick et al. [47], algae-biochar contains higher nitrogen content, pH value, and inorganic elements (P, Ca, K and Mg), but have lower carbon content than terrestrial biomass. Thus, algae-biochar was recommended as the fertilizer for plant growth as it could provide different nutrients and reduce the soil acidity.

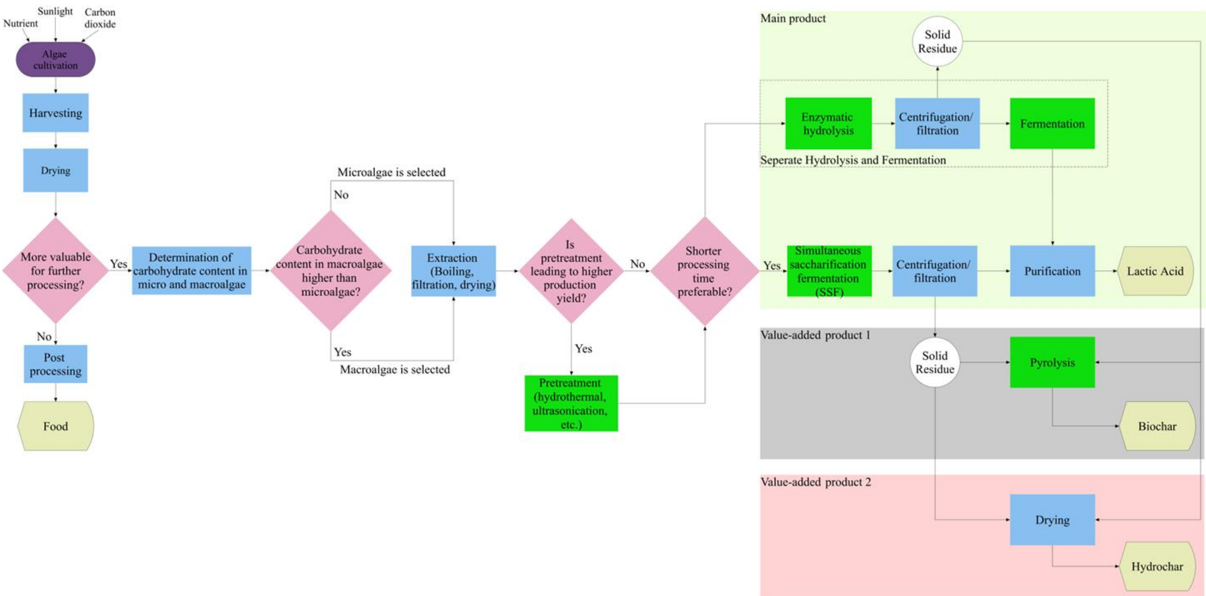

Fig. 4 Process flow of lactic acid production from algae biomass.

5 Concluding remarks: Opportunities and potential pathways for further study

First and second-generation biomass is still insufficient to satisfy the global requirement for biofuel and biochemical production. High reliance on these feedstocks may also influence the global carbon cycle. In this case, algae, a photosynthetic living microorganism, are the emerging feedstock for lactic acid production due to their unique physicochemical properties. Rich carbohydrates in algae can be processed into lactic acid through biochemical conversion. In this review, various examples of algae, lactic acid bacteria, and fermentation technology have been discussed. Also, the ability of algae as feedstock to produce lactic acid has been introduced in the proposed mechanism. Moreover, the biomass of red macroalgae, Eucheuma denticulatum had high potential to replace first and second-generation feedstocks for commercial lactic acid production as recent studies reported that both of its components (cellulose and carrageenan) can be converted to high concentration of reducing sugar and lactic acid after applying different hydrolysis and fermentation methods. However, production of algae-based lactic acid is still limited by some challenges such as selection of algae, algae cultivation system, pre-treatment technology, microorganism performance, fermentation technology and productivity of lactic acid. Although some researchers have investigated different technologies to overcome the challenges addressed above, there is still a huge gap to achieve economic and energy feasibility for commercial applications. Therefore, novel R&D works are still required to meet consumer's demands and to overcome the barriers of lactic acid production systems from algae biomass.

Declaration of Conflict of Interest

The authors declared that there is no conflict of interest with any other party on the publication of the current work.

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