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Review article

# Harvesting of microalgae within a biorefinery approach: A review of the developments and case studies from pilot-plants



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#### ARTICLE INFO

Article history: Received 10 May 2015 Received in revised form 10 June 2015 Accepted 27 June 2015 Available online xxxx

Keywords: Microalgae Harvesting Biorefinery Review Pilot scale

#### ABSTRACT

Microalgae are a promising renewable feedstock for a diverse number of products such as fuels, fine chemicals, nutraceuticals, and cosmetics. The extraction and processing of biochemicals from microalgae require the handling of large volumes of feedstock, largely due to the small biomass to liquid ratio, typically <0.1% solids. This work reviews the developments in microalgae harvesting and details the underlying phenomena of each technology in relation to key physical parameters such as: size, morphology, surface charge, and density. A critical appraisal of each method is given in relation to biomass concentration, biomass recovery, energy consumption and integration into a biorefinery approach. Finally, we detail four microalgae harvesting case studies from pilot-plants across Northwest Europe. The case studies are: (1) membrane filtration of *Scenedesmus* sp. used for protein, carbohydrate and lipid extraction; (2) synergetic harvesting of cyanobacteria by autoflocculation and passive capillary dewatering for the production of bioactive extracts; and, (3) bioflocculation and filtering of wastewater-grown microalgae for the production of shrimp feed, biogas and fertilizer. Overall, this review highlights that there is considerable scope for further innovation in harvesting processes, especially with synergistic interactions that exploit multiple physical and chemical properties simultaneously.

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#### 1. Introduction

The majority of commercial biodiesel is currently derived from the trans-esterification of terrestrial-feedstocks (soya, rapeseed, palm, sunflower and other edible oil seeds) which are produced by intensive agricultural practices. The bioethics behind biofuels are currently a contentious issue as terrestrially-derived biofuels, particularly palmoil, have been linked to deforestation, reduced biodiversity, farmland loss, increase in food prices, and increase in CO<sub>2</sub> and N<sub>2</sub>O emissions [3, 4]. However, the currently anticipated global shortages of petroleumderived liquid fuels, have led corporate and political energy agendas to put a high priority on the development of renewable sources of fuel and energy. The European Commission proposes an objective of increasing the share of renewable energy to at least 27% of the European Unions' (EU) energy consumption by 2030 [5]. Similarly, countries such as China, Australia, Canada, Russia, Korea, Egypt and Chile have also committed to specific targets by 2020. Others, such as the USA and India, have not committed to any deadlines, yet their current national renewable energy targets are 20% and 35%, respectively [6]. As a consequence of the renewable energy targets, a significant number of worldwide research calls have been commissioned over the last decade, challenging the research community to provide sustainable and economical solutions for energy production. These projects aim to reduce CO<sub>2</sub> emissions and dependency on unsustainable energy sources. Scientists believe that such a reduction will be achieved by the development of sustainable technologies for bioenergy and greenhouse gas mitigation taking these technologies from pilot facilities to market-place products and services [7].

Microalgal biomass is a promising renewable feedstock for a diverse number of products such as fine chemicals, nutraceuticals, aquaculture feed, and cosmetics. From a bioenergy perspective microalgae could be, in theory, a highly attractive route for sustainable production of biofuels [1,2]. When grown phototrophically, microalgae require light, nutrients (nitrogen, phosphorus and trace metals) and a carbon source which is most commonly CO2. These are incorporated into the cell's tissue as proteins, carbohydrates, lipids, and silica nanomaterials (in the case of diatom species) [10,11]. This very favorable biochemical composition indicates that microalgae biomass can be processed for marketable products, across a wide range of applications, and values. Lipids can comprise one of the largest fractions of microalgae where biodiesel production is favored by the presence of triglycerides. High volumes of products such as proteins and carbohydrates can also be co-produced for use across a range of different industries [9,12]. Low-volume high value products such as the antioxidant astaxanthin [13],  $\beta$ -carotene [14], and poly-unsaturated fatty acids such as eicosapentaenoic acid and docosahexaenoic acid [15] have also been extracted from microalgae biomass, and have significant market demand. The productivity of microalgae can surpass that of any other terrestrial feedstock used in renewable energy and biorefinery [9]. In addition, the production of microalgae bioproducts can be integrated with bioremediation such as CO<sub>2</sub> mitigation (to a certain extent) [16], and the removal of nutrients and metals from waste effluents [17]. Combining the bioremediation potential with the production of valuable products, microalgae is set to become an important feedstock in the biotechnology sector.

#### 2. The biorefinery approach

Despite significant research into the production of biofuel from microalgae, it has been demonstrated that fuel-only algal systems are currently unable to compete on the open market against traditional fossil fuels [18–21]. This is largely due to the dilute nature of autotrophic microalgae cultures, to the order of 0.3–5 kg/m<sup>3</sup> [22,23], leading to time and energy intensive cell harvesting stages. Indeed, harvesting has often been cited as one of the major factors preventing a scalable industry [18,24–26]. Consequently, the algal research community has shifted from a one-product focus to multiple-product extraction

strategies [27–30]. Similar to a traditional petroleum refinery, multiple fuel products and chemicals may be produced from microalgae. Nonetheless, in order to preserve the microalgal products along the several extraction steps, the technologies selected for the processing of the algal biomass must be mild so that the integrity and value of each subsequent product extracted are preserved [8,9]. Several authors have introduced the microalgal biorefinery concept, which can be defined as a methodical approach which exploits up- and downstream processes for the production and conversion of microalgal biomass.

A microalgal biorefinery should combine all the technologies required for harvesting, fractionating, and hydrolyzing algal biomass with conversion steps to produce and then recover intermediates and final products [31]. This therefore enables its conversion into valuable commodities while minimizing energy inputs, waste generation, and maximizing product output [32]. The development of such a holistic system is reliant on the multi-process crossover regimens of several steps: conditioning of waste effluents, cultivation, harvesting, extraction, purification, and recycling pathways [31,33–37]. Setting aside the tailored biochemical composition through specific cultivation strategies, such as nutrient composition of the growth media or light [38, 39], harvesting of microalgae biomass is a determinant process which directly impacts the subsequent downstream processing technologies [40,41]. Dilute concentrations of microalgae, commonly found in large scale production facilities, require cumbersome processing of large volumes leading to high production costs (Fig. 1). Decreasing the processing volume is vital for the feasibility of product extraction technologies which increase the range and value of algal products in a microalgal biorefinery. Most, if not all, dewatering methodologies exploit the physical properties of microalgae such as size, charge and density. Owing to the variety of microalgae species with different properties and its existence in different environments, dewatering technologies are very likely to perform differently across the different microalgae species. The knowledge of these properties is an important criterion in the selection of appropriate dewatering and downstream processing technologies.

#### 3. Key physical properties of microalgae

A wide range of brown, red, and green microalgae, diatoms and cyanobacteria have been commercialized for the production of feedstock for fuel, food and fine chemicals [42]. These microalgae, diatoms and cyanobacteria have cell sizes ranging from 0.5–200 µm and adopt various shapes and forms: elongated, filamentous or spherical (Fig. 2). The *Scenedesmus* species, which has been highlighted as a potential source of high value carotenoid, and lipids for biodiesel production [43,44] normally exhibit long spines in colonies of 4 cell coenobia (Fig. 2A), whereas other species such as *Chlamydomonas reinhardtii*, a well-known species used for genetic manipulation [45], are flagellated and mobile within the medium. These physical characteristics have the potential to disturb the efficiency of the adopted separation process. For example, flagellated cells could avoid flocculation or swim out of flocs, or if a mechanical harvesting method is used the cell can easily become damaged and the integrity of the spines could be jeopardized.

Another key cell characteristic of an algal cell that influences downstream processing is the cell surface charge, i.e. zeta potential. Microalgal cells are negative, however the zeta potential can fluctuate considerably depending on the chemical functional groups present in the surface which change with cell age, and culture conditions from -2 mV to - 75 mV [33,46]. Broadly speaking, the charge and stabilization of microalgae suspensions are due to the ionization of certain functional groups at the cell surface, such as the carboxyl and amino-groups. The highly pH-dependent ionization of these functional groups has a significant impact on the physical-chemical characteristics of algal cells [47].

The cell density of green algae and diatoms varies from 1070 to 1140 kg/m<sup>3</sup>, respectively [48]. Solid–liquid density differences highly influence gravity based separations, such as sedimentation. However,

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