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Research review paper

Marine algal carbohydrates as carbon sources for the production of biochemicals and biomaterials

Cesário M. Teresa[a], da Fonseca M. Manuela R.[a], Marques Mafalda M.[a], de Almeida M. Catarina M.D.[a,b,*]

[a] Institute for Bioengineering and Biosciences (iBB), Bioengineering Department, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[b] Centro de Investigação Interdisciplinar Egas Moniz (CiiEM), Instituto Universitário Egas Moniz, Quinta da Granja, 2829 – 511 Monte de Caparica, Portugal

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ABSTRACT

The high content of lipids in microalgae (> 60% w/w in some species) and of carbohydrates in seaweed (up to 75%) have promoted intensive research towards valorisation of algal components for the production of biofuels. However, the exploitation of the carbohydrate fraction to produce a range of chemicals and chemical intermediates with established markets is still limited. These include organic acids (e.g. succinic and lactic acid), alcohols other than bioethanol (e.g. butanol), and biomaterials (e.g. polyhydroxyalkanoates). This review highlights current and potential applications of the marine algal carbohydrate fractions as major C-source for microbial production of biomaterials and building blocks.

1. Introduction

The biorefinery concept is currently under hot debate. The biorefinery that relies on terrestrial crops to obtain liquid biofuels, namely bioethanol and biodiesel, impacts the economy and competes for water and energy. It is thus necessary to develop biorefineries that do not constitute an environmental burden in terms of feedstocks and of components extraction and processing.

For millennia, the sea has been a source of valuable commodities (Chew et al., 2017; Wei et al., 2013). However, intensive harvest and irresponsible human actions can cause environmental unbalances and affect the survival of marine species. Marine resources are worldly exploited for different end uses, ranging from food, food additives and nutritional supplements, to agro fertilizers, cosmetics and pharmaceuticals (Cardoso et al., 2014). A conscious biorefinery concept applied to marine algae effectively improves its commercial feasibility by directing every fraction/stream towards high added value products, hence providing an environmentally sustainable approach to the exploitation of marine algal resources. Indeed, after the extraction of biomolecules (such as bioactive compounds, proteins, gel polymeric materials, pigments), the cellulose-rich fraction remains may be processed towards monomeric sugars, which can then be converted into a wide range of products by fermentation. In the last decades, research efforts have been aimed at decreasing the world's dependency on petrochemicals and petrofuels. As a consequence, many of the bioprocesses developed so far, both from marine and freshwater algae, have focused on the production of biofuels (de Jong and Jungmeier, 2015; Wijffels et al., 2010). Algal biomass is worldwide being considered as a sustainable source of simple sugars for bioethanol fermentation. The present review doesn't intend to detail or highlight ethanol processes from algae biomass, as this has been done extensively elsewhere (Alam et al., 2015; Borines et al., 2013; Choi and Lee, 2016; Goh and Lee, 2010; Harun et al., 2011; Harun et al., 2010; Jambo et al., 2016; Kim et al., 2011; Kraan, 2013; Shukla et al., 2016). In particular, bioethanol production from macroalgae has been recently reviewed by Varejão and Nazaré (2017) (Varejão and Nazaré, 2017). Instead, this review addresses the applications of carbohydrates from both marine micro- and macroalgae directly from biomass, and after biorefinery approach for the production of biochemicals and biomaterials. Although several uses of macroalgae-derived sugars as C-sources in biological processes have been reported in the literature, high-scale marine algal carbohydrates saccharification is still to be explored.

2. Marine microalgae

Microalgae, the major eukaryotes in phytoplankton, are unicellular plants that live individually, aggregated, or in a filamentous form in marine, freshwater and terrestrial environments (Metting, 1996). They perform over 50% of the primary photosynthetic productivity on earth (Chisti, 2007), producing approximately half of the atmospheric oxygen

* Corresponding author at: Centro de Investigação Interdisciplinar Egas Moniz (CiiEM), Instituto Universitário Egas Moniz, Quinta da Granja, 2829 – 511 Monte de Caparica, Portugal.
E-mail addresses: calmeida@egasmoniz.edu.pt, catarina.almeida@tecnico.ulisboa.pt (M.C.M.D. de Almeida).

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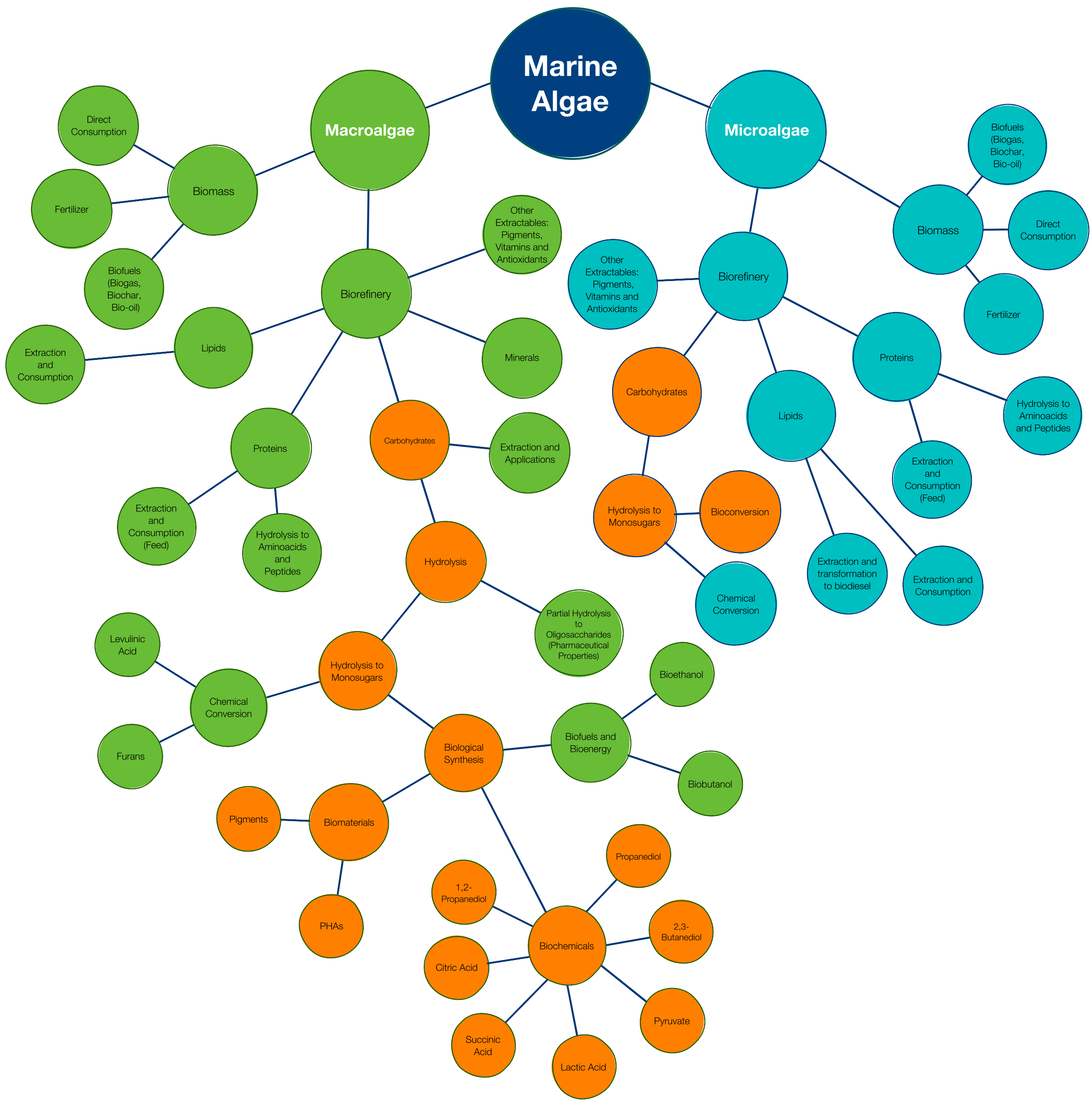

Fig. 1. Marine algae - a renewable feedstock for a myriad of products (in orange, biochemicals and biomaterials from carbohydrates).

(http://www.abc.net.au/radionational/programs/scienceshow/microscopic-algae-produce-half-the-oxygen-we-breathe/5041338). Some species are particularly tolerant to high carbon dioxide concentrations and can thus play an important role in the capture of CO_2 from flue gases. The marine green alga *Chlorococcum littorale* is an example of extreme resilience to CO_2 stress since it can grow under 40% CO_2 (Kodama et al., 1993). Microalgae are also invaluable synthesizers of omega-3 and omega-6 fatty acids which climb the food chain and are accumulated higher up, namely by the "fat fish".

There are over 50,000 microalgae species described, but only a few are being cultivated. Other than for biofuel purposes, marine microalgae are currently produced around the planet (Japan, China, India, North America, Europe, Australia) for direct consumption (human and animal nutrition) or use (e.g. as organic fertilizer) and for extraction of proteins, lipids, sugars, antioxidants, pigments and nutraceuticals (Fig. 1). The present review does not include information with regard to cyanobacteria, which are often called "blue-green algae". This is indeed a misleading designation because, even though cyanobacteria are unicellular, aquatic and photosynthetic, they are prokaryotic organisms (*Cyanophyta*).

Microalgae are also a source of unique enzymes and it is likely that a large number of further, still untapped, microalgal compounds will be identified in the near future. Novel products from microalgae have also been announced, like the formulation of sustainable algae inks, a project for the development of biodegradable inks and print products to be carried out jointly in the U.S. by Cellana Inc. (San Diego) and Living Ink Technologies (Colorado) (www.livinginktechnologies.com). Table 1 presents some of the marine microalgal species commercially exploited for purposes other than bioenergy, soil amendment, bioremediation, and wastewater treatment.

At large-scale, species of microalgae that have environmental selective advantages are usually cultivated in open raceway ponds (Milledge, 2011). However, due to the variations in yield, to the difficulties of maintaining a monoculture and also to the risk of microbial contamination, a lot of effort has been dedicated to the design of efficient closed bioreactors in recent years. These become also invaluable for the growth of species with selective advantages. A comprehensive review on enclosed vessels for microalgae cultivation was published by