J. of Supercritical Fluids 96 (2015) 211–216

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Green processes and sustainability: An overview on the extraction of high added-value products from seaweeds and microalgae

Miguel Herrero, Elena Ibáñez*

Laboratory of Foodomics, Bioactivity and Food Analysis Department, Institute of Food Science Research (CIAL-CSIC), Nicolás Cabrera 9, Campus UAM Cantoblanco, 28049 Madrid, Spain

ARTICLE INFO

Article history:
Received 22 May 2014
Received in revised form 2 September 2014
Accepted 7 September 2014
Available online 16 September 2014

Keywords:
Environmentally-friendly processes
Sustainability
Green chemistry
Compressed fluids
Biorefinery
Seaweeds
Microalgae

ABSTRACT

The present contribution is based on a presentation given at the Workshop on Supercritical Fluids and Energy (SFE'13), in the Panel devoted to Green Chemistry and Sustainable Technologies, and on the discussions that occurred in the panel. Through the discussion of some selected examples related to the extraction of bioactives from marine sources (specifically seaweeds and microalgae) combining green solvents and compressed fluids conditions, several ideas are presented as a way to improve processes towards sustainability.

The role of compressed fluids is discussed and emphasized together with the development of a green processing platform able to fulfil the requirements for a sustainable framework in which processes can fit more efficiently, basically through a biorefinery approach.

1. Introduction

At present, there is an enormous interest in giving new answers to one of the main societal challenges: sustainability. Sustainability can be understood as a rational way of improving processes to maximize production while minimizing the environmental impact or, in the words of the Environmental Protection Agency (EPA), "sustainability creates and maintains the conditions under which humans and nature can exist in productive harmony, that permit fulfilling the social, economic and other requirements of present and future generations" [1]. Bearing this in mind, many aspects can be considered in this framework, ranging from the rational use of resources to the modern concept of biorefinery which, undoubtedly, may change our perception of the industrial processes in this century. A biorefinery involves biomass conversion processes and equipment to produce fuel, power, and added-value chemicals from organic material. This facility is analogous to modern petroleum refineries, which produce multiple fuels and products from crude petroleum [2]. Integration of the emerging biorefinery concept with other industries can bring many environmental deliverables while mitigating several sustainability-related issues with respect to greenhouse gas emissions, fossil fuel usage, land use change for fuel production and future food insufficiency. A new biorefinery-based integrated industrial ecology encompasses the development of different value chains in order to generate new products, coproducts, and services from the biorefinery industries [3]. Considering this framework, the production of high added-value products from natural sources is of high interest since it can allow consolidating the idea of sustainable processes.

Within the Food Science and Nutrition field, the finding of new bioactive compounds able to confer with additional health benefits beyond the nutritional and energetic requirements in order to maintain and promote consumers' health and prevent chronic diseases is, at present, a hot-topic. Considering the tremendous market value of the functional food industry, valued in 168 billion dollars just in the US in 2010 [4], it is easy to understand the enormous interest in new compounds, extracts and products that, once its efficacy has been proved with scientific evidence, can be produced at a larger scale. A good example is, for instance, compounds such as antioxidants, which consumption has been associated to a lower risk of certain diseases as heart disease and cancer [5,6]. Although some bioactive compounds have been already widely studied, and some evidence about their activity collected, further research efforts are needed to prove their real efficacy in human beings. In this sense, Foodomics, a new discipline defined recently by our group as a platform that studies the Food and Nutrition

* Corresponding author. Tel.: +34 910017956; fax: +34 910017905.
E-mail addresses: elena.ibanez@csic.es, elena@ifi.csic.es (E. Ibáñez).

http://dx.doi.org/10.1016/j.supflu.2014.09.006
0896-8446/

domains through the application of advanced -omics technologies to improve consumer's well-being, health, and confidence [7,8], can be an adequate strategy to investigate the complex issues related to prevention of future diseases through food intake.

As the search for new bioactive compounds continues, the search for new natural underexploited sources of these bioactives is also pushed forward. In this sense, a particular niche of under-studied organisms is the marine environment.

1.1. Marine resources

The long evolution period of marine life compared to terrestrial has generated a huge diversity in terms of genes, species, etc. [9]. This diversity, together with the ability of adaptation and survival at different and extreme environmental conditions (in terms of temperature, salinity, radiation, light, nutrients, etc.) makes marine organisms an important and almost unlimited field of basic and applied research. Moreover, they can synthesize unique chemical structures, most of them with potent bioactivities [10]. Interestingly, some marine organisms, such as microalgae, may be used as natural bioreactors potentiating the synthesis of valuable compounds depending on the cultivation conditions. These molecules have a high potential to be used in pharmaceutics, cosmetics, as nutritional supplements and as functional food ingredients [11].

Among marine sources, microalgae are indeed one of the most promising feedstocks for sustainable supply of commodities and specialties for both food and non-food products [12,13]. Microalgae use light energy and carbon dioxide with higher photosynthetic efficiency than plants for the production of biomass; they do not need to be grown on arable land thus alleviating food versus fuel conflicts. Moreover, microalgae cultivation may become advantageous for regions with limited biomass availability, extreme climatological conditions and land unusable for agriculture, such as desert areas. Microalgae can use residual nutrients and CO_2 from flue gas; their cultures have a high areal productivity, and the produced biomass is an excellent source for oils, proteins, polysaccharides (including starch, xylans, pectins, β glucans, extracellular polysaccharides (EPS)) and other high-added value compounds present in smaller amounts such as carotenoids, pigments, antioxidants, sterols and other unsaponifiables, antimicrobials or minerals. Moreover, microalgae are a potential source of triacylglycerides (TAG) which may contain high amounts of long chain poly unsaturated fatty acids (LC PUFA) such as omega-3 fatty acids EPA and DHA [14].

1.2. Algae-based biorefinery concept

The algae-based biorefinery concept relies on the complete process optimization from biomass production to generation of different products; in fact, the idea behind this concept is the development of a platform able to offer a multitude of different products, from bulk chemicals, food supply (proteins, fibre), bioactives to be used for food ingredients and oil for biofuel. Optimization in terms of the input or use of energy, water, land and nutrients is needed. Recently, the European Union FP7 programme project MIRACLES "Multi-product Integrated bioRefinery of Algae: from Carbon dioxide and Light Energy to high-value Specialties" (based on the topic KBBE.2013.3.2-02: The CO_2 algae biorefinery) was approved with the main aim to develop integrated, multiple-product biorefinery technologies for production of high value specialties from algae for application in food, aquaculture and non-food applications including development of novel products for these markets. The generation of these products altogether can lead to a feasible and sustainable process in which other technologies are expected to be implemented in order to apply CO_2 concentration from the air for algal growth. Since algae are, at present, mostly used for a particular target application, technologies for extraction, isolation and fractionation into multiple products (lipids, proteins, polysaccharides, bio-actives and other products) and steps into integrated approaches for multi-product biorefinery of algae require further research (http://miraclesproject.eu/) [15].

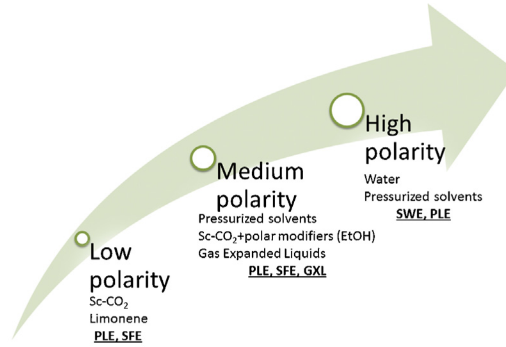

Fig. 1. Green solvents and environmentally friendly technologies used to extract high added-value products from natural sources.

1.3. Green processes

Nevertheless, for the development of these integrated processes, the 12 principles of Green Chemistry [16] have to be closely examined, considering that effectively provide a framework for designing and/or improving materials, products, processes and systems from an environment protection perspective.

In this sense, researchers are facing new challenges in the development of new extraction processes to obtain valuable products from natural sources. Up to now, traditional extraction methods (mainly solid–liquid extraction) have been used to extract bioactives; these methods have several drawbacks like they are time consuming, laborious, have low selectivity and/or low extraction yields. New challenges involve the development of fast, selective, efficient, sustainable, green (without using toxic organic solvents), with high yields and at lower costs. The techniques able to meet these requirements are, among others, those based on the use of compressed fluids such as supercritical fluid extraction (SFE), pressurized liquid extraction (PLE) and subcritical water extraction (SWE), which are among the more promising processes [17,18]. Depending on the polarity of the green compressed fluid, different "green" or environmentally clean technologies can be used, as can be seen in Fig. 1.

The green and sustainable solvents referred to in this manuscript lie between simple gases and ionic liquids and have been described in a very recent review by Pollet et al. [19] in relation to their possible use in chemical processes. Fig. 2 shows the relative position of the mentioned solvents in a 2 axis diagram that relates the transport properties of a solvent (expressed as diffusion coefficient, DA) and solvation (expressed as Kamlet–Taft dipolarity/polarizability parameter, π^*). As it is widely known, gases exhibit high diffusion coefficients but are poor solvents, as indicated by their low π^*. In contrast, at the other extreme, ionic liquids are good solvents with poor transport properties. The gap existing between gases and ionic liquids can be filled by green and sustainable solvents (defined as a solvent that addresses environmental issues, contributes to the optimization of the overall process, and is cost-effective) such as supercritical fluids, gas-expanded liquids (GXLs), near-critical water, pressurized solvents and common organic solvents (organic liquids). The different systems that can be seen in Fig. 1 offer a quite unique set of properties in terms of transport properties, solvation power, viscosity, etc. and are the basis for the processes proposed in this article.