

Marine biorefinery: an environmentally sustainable solution to turn marine biomass and processing wastes into value-added products and profits

Trung Nguyen, Niki Sperou, Peng Su and Wei Zhang (Flinders University, Australia)

A major shift from a fossil fuel-based economy, dependent upon finite resources, towards a renewable biomass-based bioeconomy is occurring rapidly due to growing awareness and global demand for sustainable energy, food and a myriad of other products. While terrestrial biomass is perhaps the obvious feedstock for a 'green bioeconomy', largely untapped marine biomass presents greater potential to drive sustainable products development via a 'blue bioeconomy'.

Untapped marine bioresources and biorefinery

Covering more than 70% of the Earth's surface, with a depth reaching beyond 10,000 m, the marine environment is habitat to over 1bn microorganism species and a million macroscopic species. Marine organisms make up approximately one-half of global biodiversity and are comprised of viruses, bacteria, fungi, algae, sea plants, finfish, shellfish and many others. Their excellent adaption to the wide-ranging variations in the marine environment such as temperature, salinity, pressure, light and darkness has stimulated the evolution of a marine biomass with diverse biochemical composition useful for nutraceutical enriching profiles and outstanding bioactivities. Over 1000 marine compounds are discovered annually and approximately 30,000 marine-derived bioactive compounds have been described thus far. These serve as valuable sources

of bioactive ingredients for food, cosmeceuticals, nutraceuticals, pharmaceuticals and numerous other important industry applications.

To achieve sustainability metrics, the measurable goals for environmental, social and economic benefits such as resource renewability, carbon neutrality, energy saving, water conservation and profitability, biorefinery is the key enabling technology platform. Biorefinery is a cascading sustainable processing technology for the translation of whole or part biomass into multiple products. Marine biorefinery refers to the refinery of marine biomass. Sustainability metrics for marine biomass are measured as a percentage of useful mass recovery, zero-waste generation via green/clean processing technologies, maximum water and energy efficiency and optimal return on investment. The goal of marine biorefinery is to boost the establishment of a circular bioeconomy. As a model of production and consumption, a circular bioeconomy is based on the enhancement of strategies to reuse, reproduce and recycle to optimize economic, social, and environmental benefits and to ultimately achieve greater harmony between human society and the world we live in.

Sustainable production of marine biomass at scale is critical to build a blue bioeconomy, an economy which relies on renewable and living aquatic resources to deliver a wide variety of products, processes and services. The supply of marine biomass is primarily from wild harvesting (quantity of species caught from the wild environment) and aquaculture-based production

(quantity of species farmed or cultured in an aquatic environment). Wild harvesting is limited and unlikely to meet growing industry demand. At present, many marine species can be efficiently cultivated without arable land, freshwater, antibiotics, pesticides and added fertilizers. Further to this, they yield much higher biomass as compared to terrestrial cultivars. The 5m² region of ocean utilized for seaweed production (approximately 0.3% of the ocean's surface) was estimated to efficiently produce as much biomass as all of annual global agriculture. Furthermore, microalgae are spatially more productive than both macroalgae and terrestrial plants. Biomass production per hectare of *Spirulina*, e.g., was reported to be 10 times higher than that of high-yielding corn hybrids. Indeed globally, 210.9 million tons (MT) of all types of seafoods was harvested in 2018 with over 114.5 MT contributed via aquaculture production. Approximately, 32.4 MT of these were algae while the rest included finfish, shellfish and other marine aquatic animals. Production of seaweed and microalgae could be efficiently integrated with water treatment, bioremediation and CO₂ biofixation for considerable reduction in pollution and greenhouse gas emission. Therefore aquaculture-based production of marine biomass of either existing or new species via continuous R&D is feasible, scalable, profitable, renewable and ultimately sustainable to feed marine biorefinery industry development.

Challenges in the utilization of marine biomass seafood processing waste and eutrophication

The use of marine biomass has also raised some challenges. Securing sustainable marine bioresources for biorefinery can exacerbate pressure upon wild stocks. Over-exploitation of wild species can threaten marine biodiversity and their future supply. Therefore, developing methods for sustainability such as regeneration strategies, minimal impact harvesting, aquaculture and processing waste management is important. Harvesting marine biomass for biorefinery is challenging because it is unlikely to harvest only target species without interrupting their associated communities. Multispecies rather than mono-species utilization can be a strategy to reduce waste. However, the diversity in type, size, shape, cellular structure and biochemical profiles which require different processes and costly classification for efficient processing are further challenges. Further to this, handling logistics is difficult as the collection and utilization of marine biomass is challenging due to its perishable nature.

Seafood processing by-products (SPB; or side streams or wastes) and fisheries by-catch are also valuable feedstocks to marine biorefinery that can turn/translate environmental wastes from 'the cost centre' into valuable products as 'the profit centre'. Not all harvested species are suitable for processing into human food. Some species are too small in size, high in fat content, and have an unpleasant muddy taste or unattractive meat colour. Such species often account for a significant

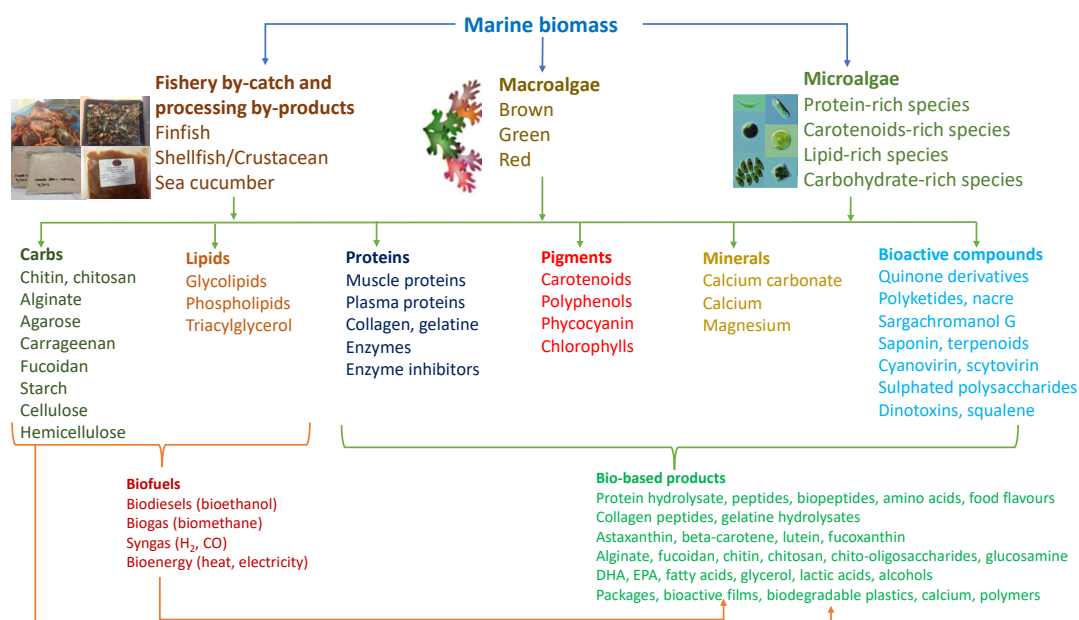


Figure 1. Marine biomass with diverse valuable components for biorefinery of multiple value-added products.

portion of the total global harvest and are treated as by-catch with poor utilization. Additionally, seafood processing generates a major proportion of biowastes such as shells, heads, tails, frames, bones, skins, scales, viscera, blood and other residues. More than 32 MT of fishery processing waste and underutilized marine biomass are produced globally each year costing around AU\$150 per ton for waste treatment. Similarly, costly is the overabundant growth of seaweed in shallow water, beaches and coasts, which results in problematic waste in several places around the world. The associated eutrophication processes, the nutrient-induced increase in phytoplankton productivity, can damage marine ecosystems and impair local tourism.

Marine biorefinery with multiple value-added products

Marine biorefinery enables the production of multiple products from marine biomass which are enriched with diverse valuable components including proteins, carbohydrates, lipids, small molecules, minerals and their derivatives (Figure 1). Optimizing marine biorefinery configurations is critical to achieve sustainability metrics for various marine biomasses. The cascading product flow generally starts with the highest value, or the most fragile products extracted first, and finishes with lowest value and largest volume of products. Biofuels and other energy options are produced last as these require the complete destruction of the biomass. There are many



Figure 2. Algal caviar developed from marine polysaccharides

product options produced through marine biorefinery and a few are highlighted in the discussion below.

Protein-based products are commonly produced from marine animals and protein-rich algae. Protein is the principal component of marine wastes accounting for 29–54.4% of some dry SPBs and algae species. Protein levels are relatively low in green algae (9–26%) and brown algae (3–15%). Marine protein can be efficiently recovered in the form of protein concentrates, protein isolates, protein hydrolysates, biopeptides, amino acids, food flavours, enzymes, enzyme inhibitors, collagen and gelatine. Many of these proteins have demonstrated excellent nutritional values, functionalities and

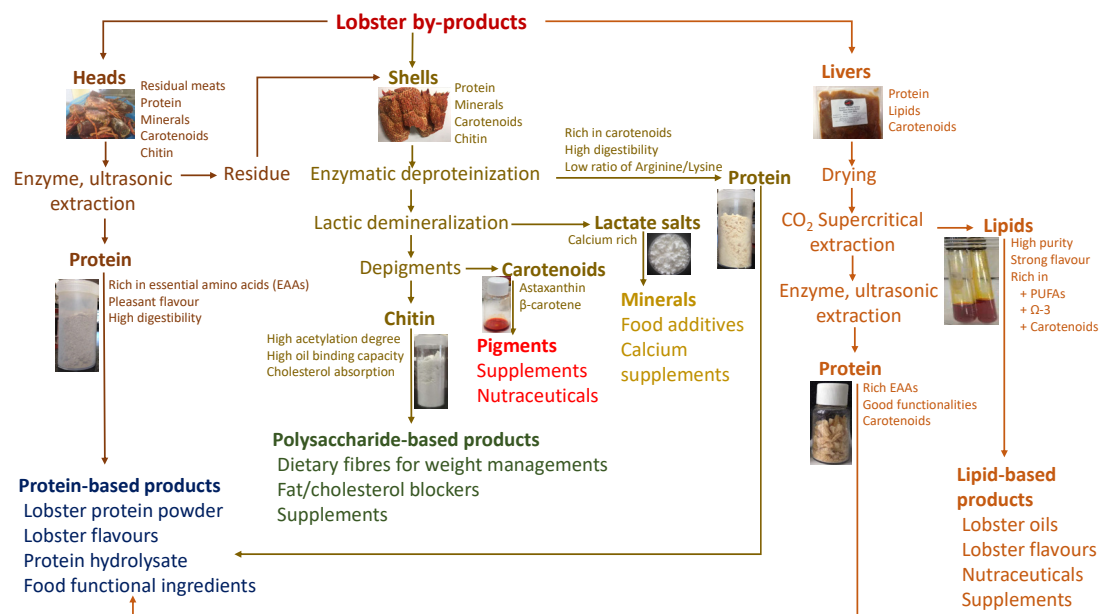


Figure 3. Example of a multi-product biorefinery of lobster processing by-products with their potential value-added products

bioactivities. In feed, food, cosmeceutical, nutraceutical and pharmaceutical products they provide nutrients, functional ingredients, antihypertensive, antioxidative, anticoagulant and antimicrobial components. Proteins recovered from Southeast Asian crustacean shells alone, for the production of protein-rich animal feeds, could reach an annual market value of US\$100m. Notably, the increasing demand for marine collagen for healthcare and nutraceutical supplements is driving a market valued at US\$581.3m in 2017 and is expected to reach US\$897.5m by 2023. Hydrolysates and peptides derived from marine collagen and proteins have also been developed for value-added products. For instance, fish collagen peptide is exceedingly used in dietary supplements and cosmetic products. Popular for use in haircare and skin-care applications, fish collagen achieved market revenue from nutraceuticals which exceeded US\$405m in 2020 and is expected to register over 5.5% compound annual growth rate (CAGR) between 2021 and 2027.

Marine polysaccharides-based products are commonly derived from macroalgae, microalgae and crustacean by-products. Polysaccharides can account for a large proportion of marine biomass depending on type and species. Chitin, chitosan, alginate, agarose, carrageenan, fucoidan, laminarin, porphyrin, Maurn, and ulvan are among the different polysaccharides produced through marine biorefinery. Many of these have attracted great commercial interest as they exhibit a wide spectrum of biological activities (antioxidant, antithrombotic, anti-inflammatory and neuroprotective), functionalities (gelling, thickening, stabilizing and protein-binding agents), and rheological properties. As the second most abundant natural biopolymer on Earth after cellulose, chitin could be annually produced towards 100bn tonnes. Currently, chitin and its derivatives have a wide variety of applications in water treatment, agriculture, textiles, food, cosmetics and biomedicine. Noteworthy, its applications and potentials have increased exponentially as several nitrogen-containing chemicals (ethanolamine (ETA), pyrazine, pyrrole and pyridine) have recently been produced from chitin in a simple single-step extraction process. Nitrogen-containing chemicals have huge global market potential with about 2m tonnes of ETA consumed yearly and with annual sales around US\$3.5bn. Agar, alginate and carrageenan are other high-value hydrocolloids used as gelation and thickening agents in food, pharmaceutical and biotechnological applications (Figure 2). Their annual global production recently reached 100,000 tons with a gross market value just above US\$1.1bn. In 2021, the world market for fucoidan was predicted to grow at a CAGR of 3.8% over the next five years and to increase to US\$37m in 2024, from US\$30m in 2019.

Marine lipids are a third group of products produced through marine biorefinery. Their content and

composition within marine biomass vary widely and is dependent on the type and species. Wastes of mackerel and catfish are particularly rich in lipids with 52.3–67% dry weight, while some microalgae could accumulate as high as 85% of their weight under certain cultivation conditions. Fish oils have 25.2–48.2% polyunsaturated fatty acids (PUFAs) in which eicosapentaenoic acid (EPA) ranges from 4.23% to 7.02% and docosahexaenoic acid (DHA) 11.7% to 36.01%. Nearly half of macroalgal lipids are PUFAs with the ratio of ω -6/ ω -3 and PUFAs/SFAs (saturated fatty acids) favourable for human health. Noticeably, DHA accounts for 25–60% of the total fatty acids derived from *Cryptocodinium cohnii*, while EPA makes up 75.9% of the lipid profile derived from *Nitzschia laevis*. Currently, over 1m tonnes of global marine oil production is used for aquaculture feed, pet food, functional food, supplement and pharmaceuticals, and was valued at US\$1.905bn in 2019.

Other valuable products include pigments, polyphenols, minerals and biofuels. Algae and some SPBs (crustaceans' shells, livers and eggs) contain three main classes of pigments including chlorophylls, carotenoids and phycobilins (phycocyanin and phycoerythrin). Chlorophylls range between 0.5% and 1.5% of microalgae dry weight and have applications as food and pharmaceutical colourants. Chlorophylls and their derivatives have been used in wound healing, anti-inflammatory and calcium oxalate controlling crystals, and internal deodorization. Carotenoids such as β -carotene, violaxanthin and neoxanthin occur in all microalgae while astaxanthin can only be found in some species. Unlike green and red algae species, brown algae are rich in polyphenols: 3–12% of *Fucus* algae based on dry weight, in which phlorotannin accounts for 3.72–7.18% of the biomass. Phenolic extracts are excellent functional and/or therapeutic agents and are highly valuable for food and pharmaceutical industries. Natural pigments are valuable commodities that have many applications in pharmaceutical, food and cosmetic products. In 2019, astaxanthin and β -carotene from algae had a market size of US\$664m, while that of phycobilins was US\$60m.

Minerals constitute a major proportion of marine biomass, particularly as dry fish bones and shells (50–80%). These are plentiful sources for calcium production. Calcium carbonate is a dominant component of crustacean and mollusc shells and has extensive applications in the pharmaceutical, agricultural, construction and paper industries. Calcium is mainly produced from plentiful geological sources with the advantage of easy accessibility. However, geological-derived calcium might contain heavy metals that are difficult to decontaminate for advanced industry applications. Production of calcium from marine bioresources would be more suitable for human consumption and advanced manufacturing than that from rocks. Potentially, the utilization of Southeast Asian

crustacean shells alone for the processing of coarse calcium carbonate particles, the cheapest form of calcium carbonate, could deliver an annual market value of up to US\$45m. Potentials for higher value calcium supplements derived from marine sources have recently been highlighted when consumption of marine mineral supplements was reported to increase bone turnover and aid in the prevention of injuries and repair of damaged bone in humans.

To maximize benefits of marine biorefinery and considerably improve its economic feasibility, multi-product biorefinery has been applied for different types of marine biomass. Recovery and developing variety of bioproducts from lobster processing by-products (LPBs) illustrated in Figure 3 is one practical example of the marine biorefinery.

Summary

Marine biomass is a sustainable, but largely underutilized resource which has great potential in addressing global food security and energy needs and to balance health and nutrition disparity. Multiple challenges could be better reconciled within a circular blue bioeconomy. Sustainability metrics evidence the profound significant benefits of utilizing marine biomass, particularly SPBs and undervalued sources, for multi-product recovery and development. Marine biorefinery has already demonstrated social, economic and environmental benefits and will continue to be the enabling technology platform to provide innovative next-generation solutions. ■

Further reading

- Daniotti, S.; Re, I., Marine biotechnology: Challenges and development market trends for the enhancement of biotic resources in industrial pharmaceutical and food applications. A statistical analysis of scientific literature and business models. *Mar. Drugs* 2021, 19, (2), 61.
- Bjerregaard, R.; Valderrama, D.; Radulovich, R.; Diana, J.; Capron, M.; Mckinnie, C. A.; Cedric, M.; Hopkins, K.; Yarish, C.; Goudey, C. Seaweed aquaculture for food security, income generation and environmental health in tropical developing countries; The World Bank: 2016
- Dismukes, G. C.; Carrieri, D.; Bennette, N.; Ananyev, G. M.; Posewitz, M. C., Aquatic phototrophs: efficient alternatives to land-based crops for biofuels. *Curr. Opin. Biotechnol.* 2008, 19, (3), 235–240.
- Venugopal, V., Valorization of seafood processing discards: Bioconversion and bio-refinery approaches. *Front. sustain. food syst.* 2021, 5, 132.
- Nguyen, T. T.; Heimann, K.; Zhang, W., Protein recovery from underutilised marine bioresources for product development with nutraceutical and pharmaceutical bioactivities. *Mar. Drugs* 2020, 18, (8), 391.
- Yan, N.; Chen, X., Sustainability: Don't waste seafood waste. *Nature News* 2015, 524, (7564), 155.
- De Jong, E.; Higson, A.; Walsh, P.; Wellisch, M. J. I. B., Task42 Biorefinery, Bio-based chemicals value added products from biorefineries. 2012, 34.
- Kim, S.-K., Marine proteins, and peptides: biological activities and applications. John Wiley & Sons: 2013.
- Salvatore, L.; Gallo, N.; Natali, M. L.; Campa, L.; Lunetti, P.; Madaghiale, M.; Blasi, F. S.; Corallo, A.; Capobianco, L.; Sannino, A., Marine collagen, and its derivatives: Versatile and sustainable bio-resources for healthcare. *Mater. Sci. and Eng. C* 2020, 113, 110963.
- Sierra Lopera, L. M.; Sepúlveda Rincón, C. T.; Vásquez Mazo, P.; Figueroa Moreno, O. A.; Zapata Montoya, J. E., Byproducts of aquaculture processes: development and prospective uses. *Review Vitae* 2018, 25, (3), 128-140.
- Kim, S.-K., Chitin, chitosan, oligosaccharides, and their derivatives: biological activities and applications. CRC Press: 2010.
- Huiying, Y.; Ning, Y., Transformation of seafood wastes into chemicals and materials. *Enc. Sustain. Sci. and Technol.* 2018.
- Nguyen, T.T., et al., Lobster processing by-products as valuable bioresource of marine functional ingredients, nutraceuticals, and pharmaceuticals. *Bioresour. and Bioprocess.*, 2017. 4(27): p. 1–19.
- Nguyen, T.T., et al., Significant enrichment of polyunsaturated fatty acids (PUFAs) in the lipids extracted by supercritical CO₂ from the livers of Australian rock lobsters (*Jasus edwardsii*). *J. Agric. and Food Chem.*, 2015. 63(18): p. 4621–4628.
- Nguyen, T.T., et al., Microwave-intensified enzymatic deproteinization of Australian rock lobster shells (*Jasus edwardsii*) for the efficient recovery of protein hydrolysate as food functional nutrients. *Food Bioproc. Tech.*, 2016. 9(4): p. 628–636.
- Nguyen, T.T., et al., Application and optimization of the highly efficient and environmentally-friendly microwave-intensified lactic acid demineralization of deproteinized Rock lobster shells (*Jasusedwardsii*) for chitin production. *Food and Bioprod. Process.*, 2017. 102: p. 367–374.



Dr Trung Nguyen obtained a PhD in medical biotechnology from Flinders University in 2017. He successfully developed an intensive biorefinery process for the recovery of multiple valuable products from underutilized marine biomass. He joined the Flinders Centre Marine Bioproducts Development in 2019 to develop technologies for algae biorefinery. Recently, he has held a research associate at ARC Industrial Transformation Training Centre – Green Chemistry in Manufacturing to lead research on advance marine biorefinery. His research interest is towards green and sustainable production of intensified biorefinery processes to recover functional bioactive compounds for health product development. Email: trung.nguyen@flinders.edu.au



Niki Sperou has engaged in science and art collaboration for over 20 years. She has worked as the artist in residence and science communicator with the Centre for Marine Bioproducts Development, Flinders University, since 2009. She aims to demystify science to make it accessible to a broader audience. In 2020, she collaborated with professor Wei Zhang and Peng Su to research societal trends and develop sustainable biodegradable marine algal biopolymers that have the potential to replace petrochemical plastics for a more sustainable future. Email: niki.sperou@flinders.edu.au



Peng Su achieved his Master of Biotechnology, Flinders University, in 2009 and Diploma in Project Management in 2013. He began working at Flinders University in the field of scientific research and commercialization. He is currently Research Officer for Centre for Marine Bioproducts Development (CMBD). The centre has a focus on integrated biotechnology processes to transform materials into high-yielding commercial products, while reducing costs, waste and pollution. He specializes in algal bioprocessing technologies and focuses on advanced extraction and high-value bioproducts development. He has been involved in the development of several industry and government partnerships playing an important role in project management and industry implementation. Email: peng.su@flinders.edu.au



Professor Wei Zhang is a biochemical engineer with globally leading expertise in industrial and marine biotechnology. He has founded the Centre for Marine Bioproducts Development at Flinders University since 2009 to pioneer the industry-driven R&D towards the development of Australian third-generation marine bioproducts industry. He has initiated and succeeded in securing 10-year funding of \$270m to establish Marine Bioproducts Cooperative Research Centre. His vision is to grow, promote and connect marine bioproducts research and industry sectors internationally for green production and sustainable development. Email: wei.zhang@flinders.edu.au