Green Chemistry

Cutting-edge research for a greener sustainable future

www.rsc.org/greenchem

Volume 15 | Number 4 | April 2013 | Pages 849–1080

ISSN 1463-9262

RSC Publishing

PERSPECTIVE

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Cite this: *Green Chem.*, 2013, **15**, 860

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Research into renewable chemicals, fuels and materials sourced from the oceans at Memorial University and elsewhere is employing green chemical technologies for the transformation of algae and food industry waste streams into useful products. A very small proportion of biomass utilization research is currently focused on these feedstocks and efforts focused in this area could reduce land space competition between food and chemical/fuel production. This perspective highlights some of the achievements and potential opportunities surrounding the use of algae and waste from shellfish and finfish processing. In particular, investigations in this field have used alternative solvents (water, supercritical carbon dioxide and methanol or ionic liquids) extensively. Supercritical Fluid Extraction (SFE) has been used to extract lipids and pigments from algae, and oils from fish-processing plant waste streams. Water can be used to isolate potentially high value biologically-active oligosaccharides from some seaweeds. Biotechnological approaches are showing promise in the separation of biopolymers from shellfish waste streams. Production of new nitrogen-containing bioplatform chemicals (*e.g.* 3-acetamido-5-acetylfuran) from aminocarbohydrates (chitin, chitosan and *N*-acetylglucosamine) is being pursued.

Received 9th December 2012,
Accepted 25th February 2013

DOI: 10.1039/c3gc36994c

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Introduction

Research in the area of renewable feedstocks has increased dramatically during the past decade (Fig. 1) and green chemistry has played an important role in the development of this field.[1–3] However, of the nearly 30 000 papers depicted in Fig. 1, only 2.5% are concerned with algae or oceanic biomass. Therefore, significant opportunities exist in terms of developing new technologies that use algae or waste from the fishing industry as feedstocks for the production of new chemical products.

Research on the development of valuable renewable chemicals from starch, lignocellulose and other materials has led to the identification of several key molecules – known as platform chemicals.[2,3] These chemicals (including levulinic acid and substituted furans) normally contain only C, H and O and have potential uses as is (*e.g.* solvents, fuels) or as starting materials for new bio-derived products (*e.g.* polymers, flavour enhancers). They have typically been accessed from land-based biomass (Fig. 2) but there are opportunities to use these existing technologies with oceanic biomass. Such diversification of feedstocks could be important, as concerns have been voiced over the use of food crops and valuable land for the production of biofuels and chemicals, *e.g.* starch from corn/maize to yield bioethanol.[4] These concerns have been minimized by considering alternatives to food crops,[5] including (i) *Miscanthus* and other rapid growth biomass,[6] (ii) wood and forestry waste,[7] and (iii) municipal waste.[8–10] Recently, significant advances have been made in obtaining high value chemicals from food industry waste streams.[11,12] For example, pectin and D-limonene are two marketable products, which can be obtained from waste citrus peels. Nevertheless, just as the oceans have been used to take some of the pressure off land use in terms of renewable energy production *e.g.* off-shore wind farms,[13] we

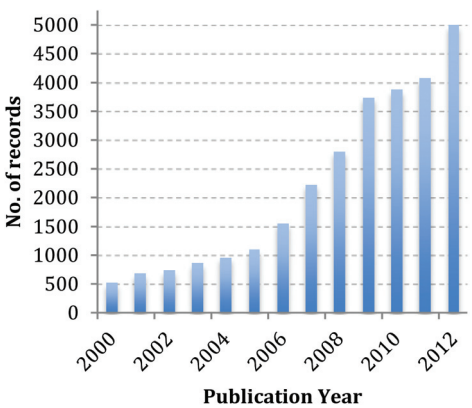

Fig. 1 Number of publications per year concerned with renewable feedstocks. (Data obtained using Web of Knowledge (14/11/2012): Topic = Biomass OR Renewable, AND feedstock).

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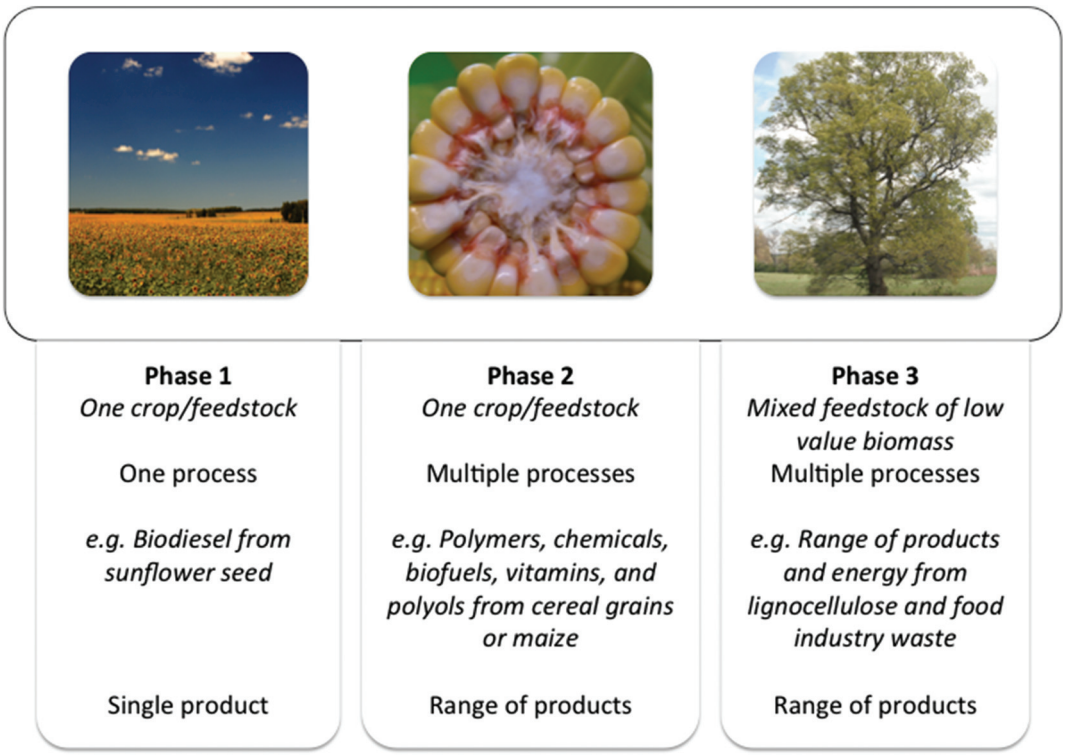

Fig. 2 Overview of existing biorefinery concepts.

can also look to the oceans as a source of valuable chemicals. After all, oceans account for 71% of the earth's surface.

The oceans are home to a wide range of biota, which can provide biomass for a range of products and applications:

1 Plants: Macro- and microalgae,[14] which can act as a source of lipids (for biodiesel), cellulose, agar (agarose), and more complex chemicals (secondary metabolites incl. bioactive carbohydrates, pigments and vitamins).

2 Vertebrates: In particular, waste from fish farms and processing plants can yield fish oils and other potentially valuable chemicals.

3 Invertebrates: Shellfish (crustaceans and molluscs) processing produces waste shells/exoskeletons, which can be used as a source of chemicals and materials (incl. minerals, pigments and chitin).

Importantly, at present, waste from fishing industries and algae are mainly used as low cost fertilizers or dumped at sea. In Canada, legislation is being introduced to prevent dumping food industry waste at sea. Furthermore, many areas of the globe do not have fertile soil for the production of land-based biomass and, through exploitation of ocean-sourced feedstocks, people in these regions would have access to renewable materials without sacrificing valuable space on land needed for food crops. It should, however, be noted that valorization of fish processing waste would be a greater challenge than using algal crops. Greater sanitary risks (*e.g.* bacterial contamination) would need to be considered. Having said this, it is not without hope. Shellfish waste is already being used as a feedstock to produce chitosan and glucosamine sulfate (GlcN sulfate) for a wide range of applications especially in the biomedical field.

This perspective aims to highlight opportunities for future research, discoveries in this field and to redress the balance between land-based and oceanic biomass utilization. In order to develop an ocean-based biorefinery, multidisciplinary research will be essential to tie together waste characterization and processing, product separation, and end use to afford a cradle-to-cradle process. Through such research aimed at valorization of marine by-products,[15] there are opportunities to develop methods and systems that will benefit many coastal regions of the world. Due to the geographical location of the authors, particular focus is placed on plant and animal species that can be harvested in the North Atlantic region.

Sea plants

The production of plant biomass in the oceans is often overlooked as a feedstock for future biorefineries but many opportunities surround the use of both micro- and macroalgae (commonly known as seaweeds) in this regard.[14] Seaweed is a very versatile product widely used for food in parts of Asia and research into its use as a nutritional supplement is ongoing around the world. In Newfoundland and Labrador (NL), seaweed has traditionally been used for animal feed and fertilizer. In North America, Atlantic macroalgae such as *Palmaria palmata* (Dulse) are rapid growing with a short natural growth cycle and are a potential source of valuable chemicals. For example, *Palmaria palmata* is known to contain skin-hydrating water-soluble xylans[16] and antiviral bioactive carbohydrates.[17]

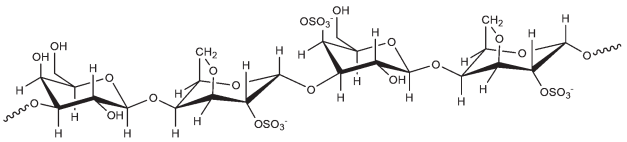

Fig. 3 Carrageenan consists of alternating 3-linked-β-D-galactopyranose and 4-linked-α-D-galactopyranose units.

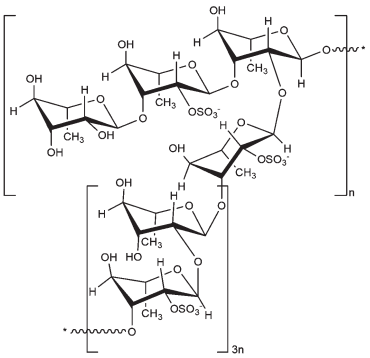

Fig. 4 Sulfated polysaccharide composing of rhamnose units, thought to be active in the treatment of diabetes.[19]

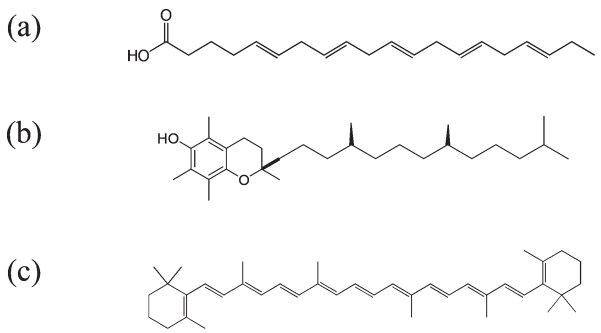

Fig. 5 Some of the valuable secondary metabolites that can be extracted from algae: (a) eicosapentaenoic acid (EPA), (b) vitamin E, and (c) β-carotene.

In 2003, the total annual value of global seaweed production was estimated at almost US$6 billion, of which food products for human consumption represented US$5 billion.[18] As the tradition of eating seaweed is not widespread in this region of the world, 'green' processing of *Palmaria palmata* and other macroalgae could provide opportunities for economic growth and the development of new products. As the oceans account for a large proportion of the earth's surface, non-food applications of seaweed should not unduly affect the existing food industry uses and market.

The use of seaweeds as a source of iodine is well known, however, additional complex molecules are also present. These include hydrocolloids (Fig. 3), biologically active polysaccharides (Fig. 4), fatty acids, vitamins and pigments (Fig. 5). Therefore, sea plants could potentially yield the following high-value products: medicines, nutraceuticals, natural colours, aromas/flavours, anti-oxidants, water-soluble biopolymers and cellulose fibres. These could find applications in the food, nutraceutical, pharmaceutical, biomaterials and cosmetics industries.

A number of variables need to be studied in order to determine which plants and products would be of highest economic value including algal species, pre-extraction processing and extraction methods (Fig. 6). Of relevance to green chemistry, supercritical fluid extraction (SFE) using carbon dioxide could play an important role.[20] SFE has been used on an industrial scale in coffee decaffeination for many years and smaller factories are also in operation.[21] Continuous subcritical water extraction is also used in the field of natural product chemistry[22] and could yield a different extract profile for a particular plant compared with organic solvents, room temperature water or SFE using carbon dioxide. In whole crop usage of algae, it would be important to separate high value lipids, vitamins and pigments, which can be extracted using SFE from the water-soluble carbohydrates (bioactive components and hydrocolloids) and cellulose. Furthermore, it would be crucial, in terms of pollution prevention, to isolate cellulose free from sulfur-containing species (*e.g.* rhamnose derived polysaccharides) in order to minimize potential SO_x emissions. Due to the different sugar-profile for carbohydrates within algae compared with land-based feedstocks, their transformation *via* fermentation or chemical processing will yield a different suite of products.[14]

Several patents on the extraction of high-value biologically active materials from macroalgae have been published, including treatments for diabetes,[19] antiviral treatments,[17] and anticoagulants.[23,24] Generally, the active components have not been fully characterized and they have not been produced using a whole plant approach. Therefore, as chemists, we need to determine whether such bioactive materials can be isolated as co-products in a process yielding hydrocolloids, pigments, lipids, vitamins and cellulose from sea plants. It has been proposed by others that the initial extraction of high-value chemicals present in biomass will play an important part of future biorefinery operations.[25,26] This would also apply to ocean-sourced biomass feedstocks.

As 'green' and 'natural' solvents, supercritical carbon dioxide ($scCO_2$) and subcritical water are well suited to the extraction and fractionation challenges in this field. Also, by using such approaches, the bioproducts produced would be free from harmful organic solvent residues. In contrast, the use of organic solvents (*e.g.* hexane) is less selective, more polluting, more hazardous and would likely produce an additional waste stream. Unfortunately, the use of SFE at remote, rural locations is unlikely to flourish due to high costs and the need to employ experts in the use of such equipment. This means that the algae may need to be dried and transported to a centralized facility in order for fractionation of products to occur. Clearly, there is a need for a more in-depth life cycle assessment (LCA) of such whole plant approaches in this field.

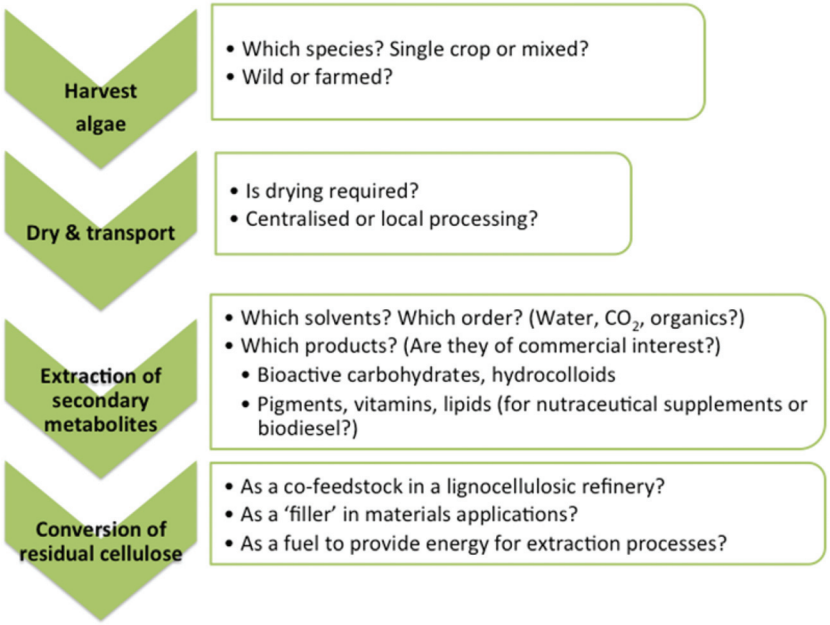

Fig. 6 Decision making flow chart for 'green' processing of algae into chemical products.

Products from sea plants

Hydrocolloids (alginate, agar and carrageenan – hexose-derived polysaccharides) (Fig. 3) are produced globally on a large scale from red and brown seaweeds [including *Laminaria longicruris* (Kelp) and *Ascophyllum nodosum* (Rockweed)]. They are important ingredients in the food[27] and cosmetics industries. The primary difference between agar and carrageenan is the replacement of some OH groups with sulfate groups. Alginates and alginic acids are used in a wide range of food, pharmaceutical and specialty applications for thickening, stabilizing, gelling and film forming. Carrageenans are also used for thickening, suspending and gelling in the food and pharmaceutical industry. The solvent used industrially in the isolation of biopolymers from algae is water. The pH of water is adjusted to encourage dissolution; carrageenans are soluble in basic media, whereas alginic acid is extracted using acidic solutions.

Bioactive carbohydrates are typically pentose-based and extracted using neutral water as the solvent. Rhamnose-based polysaccharides can be obtained from a range of seaweeds, including *Ascophyllum nodosum* and are potentially useful in the treatment of diabetes (Fig. 4).[19] Other extracts have been identified as having antiviral properties.

Lipids, fatty acids and secondary metabolites. Data have been reported on SFE of brown (*Sargassum hemiphyllum*)[28] and red seaweeds (*Hypnea charoides* and *Liagora boergesenii*).[29,30] Total crude lipid contents were found to be between 5 and 20% on a weight/weight basis. The fatty acid profile of the lipid extract obtained from these macroalage was found to vary with the density of the $scCO_2$ used. For example, the ratio of saturated : unsaturated fatty acids was found to decrease with increasing pressure at a constant temperature. These results demonstrate that the properties of the $scCO_2$ extract from algae can be varied through the tunable density of the SCF phase. Eicosapentaenoic acid (Fig. 5), or EPA, is a major component of fish oil supplements and also a major component in the lipid extract from algae. Therefore, extracts from algae obtained using SFE could be used as food supplements for vegetarians and others who do not obtain these essential fatty acids in their diet. SFE has also been used to extract a range of pigments from microalgae including astaxantine, phycocyanin,[31] β-carotene, canthaxanthin and zeazanthin.[32,33] Interestingly, other pigments including chlorophyll-a and myxoxanthophyll were not co-extracted and this speaks to the selectivity of the SFE method.[32] It has also been reported that in the extraction of fatty acids and carotenoids from *Spirulina maxima*, adjusting the temperature and pressure allowed the fatty acids and pigments to be extracted separately.[34] Therefore, SFE offers the potential to fractionate these valuable components from sea plant feedstocks. Perhaps the most advanced studies on SFE and algae have been targeted at biodiesel production. In one such study,[20] SFE was used to extract components of interest from the microalgae *Scenedesmus dimorphus*. The algae could be harvested by centrifugation and SFE performed without the need for prior dehydration. Although extraction yields were improved if drying was performed.

In a recent LCA study concerned with potential industrial production of algal biodiesel,[35] a supercritical methanol based method (250 °C, 8.3 MPa)[36] was determined to be the most efficient of those assessed (including the use of $scCO_2$). The use of methanol allowed both the extraction and direct transesterification to take place in a single process without the need for an added catalyst. Biodiesel production from algal lipids could be a viable option for fuel production if other high-value components of algae, *e.g.* bioactive carbohydrates and vitamins, could be isolated and marketed. However, further

research and LCA exercises are needed, as an optimum process for one species of algae may be significantly different to another.

Fishery waste

The fish processing industry is an important part of rural and remote coastal communities around the world. Waste generated from fish processing plants is approximately 50% of the weight of harvested fish depending on the type of fish,[37] product and processing techniques. As a percentage of total landed weight, only 40% of prawns, 39% of crustaceans, 14% of mussel, 32% of crabs, 35% of brown shrimp and 35–45% of catfish harvested are used for human consumption. Waste generated in Atlantic Canada fish plants has been estimated at 418 000 t yr^{-1}.[38] In 2004, it was estimated that the availability of salmon by-products from filleting plants (heads, bone, skin, viscera) was 38 000 tonnes in Canada.[39] This material consists mainly of heads, backbones, and skin with 15–26% lipid content and 11–20% protein content. Constituents of the aqueous waste streams varies with fish type, season and the processing systems, however high BOD, total suspended solids and high nitrogen content due to the presence of blood and slime are common to all wastewaters.[38] There is a tremendous opportunity to recover valuable by-products from fish processing waste, ranging from fuel for on-site use to high value nutraceuticals. This opportunity is further driven by the significant costs associated with transporting the waste material to disposal sites. The challenge in remote regions is developing recovery and separation methods that are economically viable. However, there are many benefits to such an approach (Fig. 7).

Significant research efforts are needed to identify by-products[40] (Fig. 8) from fish plant and seafood processing wastes. Methods of recovery and extraction appropriate to the scale and infrastructure of the region need to be developed. At present, effluent processing occurs at fish plants in some regions but this is not the case in many remote communities. In many locations, solid waste is transported to landfills and wastewaters are typically discharged to the marine environment.[38] When waste effluent is utilized, products include fishmeal/oil, silage, and organic fertilizer.[40]

1. Development of new industries e.g. nutraceuticals, fish feed
2. Improved economic viability of procressing plant
3. Minimize environmental impact of processing plant
4. Optimizing energy balance through biofuel use

Fig. 7 Benefits of a by-product recovery market to the fisheries.

1. Fish feed for aquaculture (fishmeal and oil)
2. Silage
3. Fertilizer
4. Biofuel
5. Fish protein hydrolysate and concentrate
6. Pigments (e.g. astaxanthin)
7. Biopolymers (e.g. chitin)
8. Food additives and nutraceuticals

Fig. 8 Possible products from fishery waste.

Finfish processing waste

In both the fishing and aquaculture industries, oil and fats represent a significant fraction of finfish processing waste. Therefore, extraction of this waste component would decrease waste volumes and offer an energy resource for the processing plant. Lipids constitute up to 60% of fish waste. The oil is predominantly triacylglycerol (TAG) made up of more than 50 fatty acids (FAs). Research has indicated that unsaturated FA levels are approximately two to four times those of the saturated FA levels.[41,42] This differs from other waste oils (*e.g.* tallow) and impacts (i) the stability of the oil with respect to oxidation, (ii) the cold flow properties of any biofuel produced, and (iii) NO_x emissions associated with fuel use. A LCA has demonstrated that by blending extracted fish oil with lower grade petroleum fuels, emissions associated with the extraction, production, and use of the blended fuels is decreased when compared with petroleum.[41,42] In terms of alternative solvents, hydrolysis of fish waste streams has been performed under sub- and supercritical conditions using water,[43,44] and $scCO_2$ has been used to extract fish oil from fish waste.[45,46] At present, LCA studies on the use of such methods in fish waste processing have not been performed. The infrastructure required for large-scale implementation of SFE in a fish plant is likely not feasible but could be part of a larger central by-product facility. Oil quality from such a by-product isolation plant would need to be assessed. Properties to be monitored would include density, viscosity, acidity, lipid analysis, free fatty acid content, melting points, specific heat capacities and decomposition temperatures. This would help determine the end uses of said oil. After separation of oil from the fish waste, various valuable by-products might also be isolated (Fig. 9).[42] Further work is needed to identify and quantify these.

In the Faculty of Engineering at Memorial University, the wastes associated with the processing of salmon and cod from aquaculture facilities have been characterized. Studies are ongoing to determine the waste stream characteristics for processing plants associated with other fish species. Characterization of the waste is key to determining options for oil extraction and yields of oil from it. A lab scale process has been developed at Memorial University to maximize oil extraction from finfish processing waste and minimize energy used and waste generated.[41] The development of oil recovery processes that take into account the infrastructure of the existing fish processing plant and the region represent opportunities to enhance sustainability. However, there are several important issues, which need to be addressed in order to achieve this goal: (i) Characterization of processing plant waste (oil content, stability, lipid analysis and physical properties) and oil recovered. (ii) Development of a flexible extraction method. The oil extraction process will need to be subtly varied according to type of fish and season of harvest, as these will impact the oil content of processing plant effluents. For example,

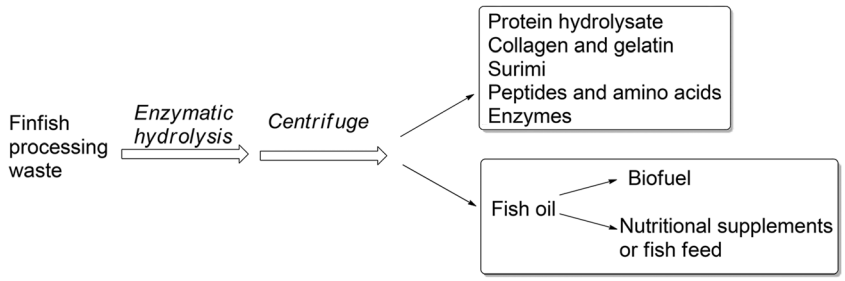

Fig. 9 Possible scheme for isolating valuable by-products from finfish waste streams.

research at Memorial University has shown that fresh salmon viscera-containing effluents tend to be higher in total lipids and lower in impurities than effluent from cod processing. The purified salmon oil was determined to be suitable for use as a fuel (and not suitable for nutraceutical or fish feed purposes). The composition and properties of purified oil from frozen and raw salmon viscera by-products were, on average, not different; therefore, processing the effluent after short-term storage is an option. However, further research is needed. For example, the oil extracted by physical methods has a high water content. This leads to the formation of water in oil emulsions and decreases the heating value of the oil, complicates downstream processing, and poses a corrosion risk. Another option for recovering chemicals from fish waste is to perform a fermentation process (enzymatic hydrolysis) to recover proteins. After such a step, the oil is typically separated by centrifugation (Fig. 9). In addition to using the oil as a fuel, it can also be used as a food supplement for humans or in the aquaculture industry. Both the protein and the oil by-products could help to significantly improve sustainability within the aquaculture sector. Aquaculture continues to be the fastest-growing animal-food-producing sector with an average annual growth rate of 6.6% and accounts for 46% of total food fish supply.[47] A key ingredient in the fish feeds used within this industry are long-chain omega-3 polyunsaturated fatty acids [eicosapentaenoic acid (EPA: 20:5ω3) and docosahexaenoic acid (DHA: 22:6ω3)], which are essential fatty acids providing beneficial health effects to fish and to their human consumers. Fish remain the major food source of EPA and DHA so extraction of oil from fish waste is critical with fish feeds now consuming as much as 90% of global fish oil supplies.[48] Development of 'green' methods to use in this field will be essential to the long-term stability of the aquaculture industry.

Shellfish waste

Approximately 39 000 t y^{-1} of shellfish waste (incl. northern shrimp and snow crab) is generated in NL which represents ~35% of the commercial harvest. The waste from most processing plants is either dumped back into the sea or transported to special landfills. This means that for some species, *e.g.* mussels, it is not economically viable to process them into a higher value food product because of the waste that would be generated. However, that is primarily due to the technologies employed and the current value of said waste. Mussel shells

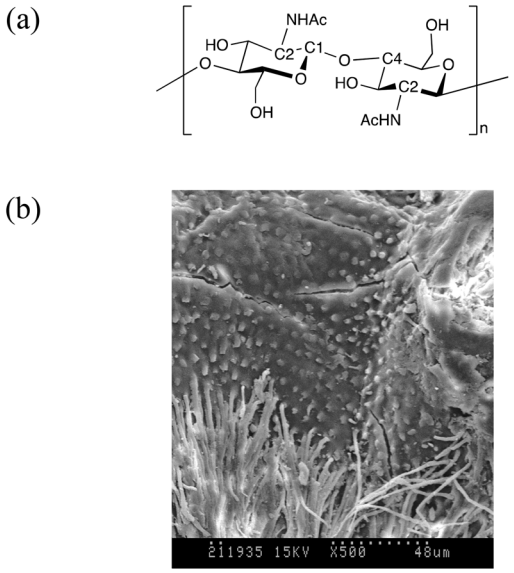

Fig. 10 (a) The molecular formula of chitin showing β-linkages and *N*-acetamido functionality. (b) SEM micrograph of chitin from shrimp shells.

are primarily composed of calcium carbonate (95–99 wt%) and the shells could potentially be ground to yield a material with useful absorbent properties. Waste from crab and shrimp shells consists of protein (~40%) and chitin (~20–25%) along with a calcium carbonate matrix (~30%) and is rich in lipids (5–10%) and astaxanthin. When crustacean waste is utilized it is chiefly for the chemical production of chitin (Fig. 10), a valuable biopolymer with many uses.[49,50] Previous studies have demonstrated that shrimp shell proteins are well balanced in amino acid composition for use as aquaculture feed.[51] Currently, chitin production releases toxic chemicals such as HCl and NaOH into the aquatic ecosystem as harmful by-products and does not allow for co-product isolation (*e.g.* proteins). Furthermore, traditional chitin plants and their associated chemical transportation/storage are not always suitable near rural processing plants where most of the industry is located. Microbial fermentation of shellfish waste would potentially allow the recovery of protein, lipids, pigments to be used in aquaculture fish feed and at the same time the isolation of chitin.[52] Fermentation has been envisaged as one of the most eco-friendly, safe, technologically flexible, and economically viable alternative methods for chitin production.[53,54]

Ultimately, one could envisage small microbial fermentation plants alongside the food processing units. At the fermentation plants, proteins, lipids and pigments could be isolated and used in such products as fish feed, whilst simultaneously allowing the isolation of chitin for industrial applications. This would lead to maximum utilization of the shellfish and minimize environmental impacts by decreasing both the volume and contaminant load in waste streams.

Production of chitin

Chitin typically has a molecular weight in the region of 10^5 g mol^{-1} and 50–80% of the nitrogens are *N*-acetylated. The production of chitin (Fig. 11) involves three main steps after initially grinding the dry shells. These are demineralization, deproteination and decolouration. In the first step, an acid such as hydrochloric acid, sulfuric acid, nitric acid or acetic acid is used to remove the minerals, particularly calcium carbonate.[15,16,55,56] Chitin hydrolysis also takes place in this acid demineralization step. However, ethylenediaminetetraacetic acid (EDTA) can be used instead of more conventional acids in this step to minimize hydrolysis of the biopolymer.[16,56] The second step is protein removal, which is achieved using a basic medium such as sodium or potassium hydroxide or carbonate, sodium sulfide, calcium hydrogen sulfite or sodium phosphate.[56] In the shells of many crustaceans, a carotenoid pigment (astaxanthin) is present and in combination with a macromolecular protein complex called crustacyanin, it is responsible for giving the typical orange-red colour to these animals. A bleaching agent such as hydrogen peroxide or potassium permanganate is typically used in the last step to oxidize these pigments to produce colorless chitin. Strong acids, bases and oxidizing agents are all hazardous chemicals and could contaminate the environment if not handled carefully. An alternative process for chitin production would use (i) a protease enzyme to remove protein, and (ii) bacteria to remove minerals.[55] The bacteria produce lactic acid as a by-product, which could potentially be used as a chemical and polymer feedstock. Green oxidation catalysts could be used in the final pigment removal step if required. Ideally, the pigments would be isolated as part of the valorisation process.

Recently, it has been reported that chitinous biomass can be purified using ionic liquids (ILs), in particular 1-ethyl-3-methylimidazolium acetate [EMIm]OAc (Fig. 12).[57] Chitin was recovered from the IL by adding water to the mixture, as water is able to dissolve the IL but not the chitin. Microwave heating could be used to greatly reduce the time needed in this process compared with conventional heating. The growth in knowledge and development of new products based on IL processing of cellulose[58] could be applied to new chitin-derived products in the coming decade.

Production of chitosan

Chitosan is prepared through deacetylation of chitin using alkaline treatment, *e.g.* 50–55% (w/v) sodium hydroxide at 95–110 °C followed by neutralization, filtration and washing steps.[59] However, biochemical approaches are showing promise. For instance, a chitin deacetylase enzyme has been obtained from the fungus *Mucor rouxii*, and use of such an enzyme could be an alternative method for deacetylating chitin to give chitosan.[60] The process of removing the acetyl group from chitin to leave an amino group (NH_2) in place of an *N*-acetylamido group (NHAc) does not proceed to 100%

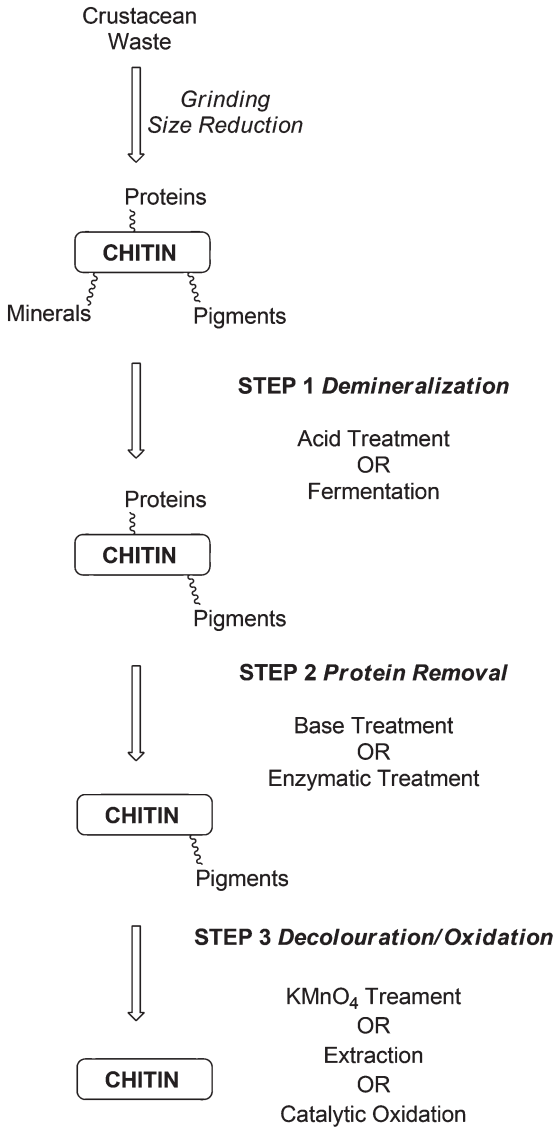

Fig. 11 A schematic diagram of the chitin purification process involving 3 steps.

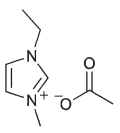

Fig. 12 1-Ethyl-3-methyl-imidazolium acetate, an ionic liquid which is able to dissolve chitinous biomass.

completion. Therefore, chitosan typically has acetyl groups at some sites within the polymer. The Degree of Deacetylation (DD) value is an important factor when describing chitosan in terms of physical, chemical and biological properties.[61]

Uses of chitin and chitosan

As functional materials, chitin and chitosan have been used in a range of areas.[36,37,45] Chitosan has been used as is or modified for applications in catalysis including base-catalysed reactions, in combination with metals for a range of transformations,[62] and as a support for enzymes.[63] More recently, hydrothermal treatment of chitosan and glucosamine has led to the preparation of interesting nitrogen-doped carbons with potential applications in sequestration of carbon dioxide and catalysis.[64,65] Chitosan is used widely in the biomedical field (drug delivery applications and tissue engineering),[66] and in agriculture (*e.g.* seed coating, fertilizer, feed additive, films and sponge materials). It has also found additional uses in food processing,[67] materials, paints and textiles.[68] Chitosan has been used in water purification in the food industry and elsewhere *e.g.* to remove pesticides and polychlorinated biphenyls (PCBs) from contaminated water.[67] It is likely that use of a 'natural' material in the food and water industries would be highly desirable with consumers and, therefore, allow uptake of such technologies in these industries even if the cost of chitosan was slightly more than current approaches (*e.g.* activated charcoal). Of particular relevance to this perspective, Beach *et al.* recently showed that chitosan can be used in the processing of algae.[69] Chitosan was a superior flocculant compared with ferric sulfate for the processing of a green algae, *Neochloris oleoabundans*, and it was also noted that alum (a traditional flocculant in many fields) did not work at all for the species under investigation. Therefore, there is synergy between different types of ocean-sourced materials in the production of chemicals and materials.

For additional uses and transformations of chitin, it is important to consider its solubility. Unfortunately, chitin is insoluble in most solvents, Table 1, including dilute acid solutions and organic solvents. In α-chitin, the carbohydrate rings (hydrophobic faces) in the structure are arranged over each other and this results in its low solubility.[70] The sheets of chitin interact with each other *via* non-covalent linkages such as hydrogen bonding between C═O amide···HN.[71] However, chitin is soluble under harsh and non-environmentally friendly conditions such as in hexafluoroisopropanol, and hexafluoroacetone.[72] Chloroalcohols, including 2-chloroethanol, 1-chloro-2-propanol, and 3-chloro-1,2-propanediol, can be used in combination with acids to dissolve chitin. β-Chitin is the only polymorph of chitin that is soluble in anhydrous formic acid and will precipitate when water is added to dilute the formic acid solution.[72] Chitin is also soluble in hot concentrated solutions of some salts including CaI_2, $CaBr_2$ and $CaCl_2$.[50] Recent results have shown that suitably designed ionic liquids can be used to dissolve chitin.[57] In general chitosan is more soluble than chitin under many conditions, Table 1. Chitosan is soluble in acidic aqueous solutions of pH less than 6.0,[73] because of protonation of NH_2 groups in the polymer. When the pH is increased up to *ca.* 6.0, chitosan starts to precipitate. In general, chitosan is insoluble in neutral or basic media. Its solubility depends on DD. The solubility of chitosan in water increases with a decrease in its molecular weight.[73] Chitosan is commercially available with molecular weights between 10^3 and 10^5 g mol^{-1}. 1-Butyl-3-methyl-imidazolium chloride ([BMIm]Cl) is an IL which can dissolve both chitin and chitosan biopolymers.[74] They also dissolve in mixtures of ILs including 1-butyl-3-methylimidazolium acetate, 1,3-dibutylimidazolium acetate, and 1,3-dimethylimidazolium acetate.[57] ILs are able to dissolve polysaccharides by disrupting their inter- and intra-molecular hydrogen bonding between chains.[57,74]

Production of chemicals from chitin, chitosan and their monomers

Although solubility is a problem in processing these polysaccharides, chitin and chitosan can potentially be used to produce useful chemicals. Hydrolysis of chitin and chitosan to yield mono-, di- and oligosaccharides has been studied previously. Reported yields vary from low to moderate. Some examples include: (i) Hydrolysis of colloidal chitin using *Vibrio furnissii* chitinase (*chi* E, 89 kDa) in DMSO–LiCl (buffered NH_4HCO_3, pH 7.9) to yield chitobiose, a dimer of *N*-acetylglucosamine – $(NAG)_2$, selectively (8.3 g from 20 g chitin).[75] Diafiltration was used to continuously remove the product from the reaction mixture, as the presence of $(NAG)_2$ inhibits the activity of the enzyme. (ii) Hydrolysis of β-chitin using cellulase *Trichoderma viride* to yield NAG in yields of up to 76%.[76] The conditions employed were [Chitin] = 10 mg mL^{-1}, pH = 4.8 (AcOH buffer solution), T = 37 °C, t = 8 days, [enzyme] = 20 mg mL^{-1}.

Table 1 Solubility of chitin and chitosan

	Soluble in	Insoluble in
Chitin	ILs incl. [EMIm]OAc	Water
	Hexafluoroisopropanol and hexafluoroacetone	Basic media
	Chloroalcohols incl. 2-chloroethanol, 1-chloro-2-propanol, and 3-chloro-1,2-propanediol, with mineral acids (*e.g.* HCl(aq)) or organic acids (*e.g.* AcOH)	Dilute acid solutions including HCl and AcOH
	Hot concentrated solutions of some salts including CaI_2, $CaBr_2$ and $CaCl_2$	Organic solvents including acetone and acetonitrile
Chitosan	ILs incl. [EMIm]OAc	Water
	Acidic organic or aqueous solutions (pH less than 6.0)	Basic media

(iii) Concentrated HCl has been used to produce 40.5 g NAG from 300 g chitin in 3 h at 45 °C.[77] After reaction, the mixture was diluted and neutralized using NaOH, and the NAG purified *via* recrystallization. NAG and glucosamine (GlcN) salts are well-known for their biological properties (treatment of osteoarthritis). Chitin and chitosan oligomers are also bioactive and possess antitumorigenic, antifungal and antibacterial properties.[67] Therefore, pursuit of greener industrial methods for the hydrolysis of chitin and chitosan are highly desirable as the products are potentially of high commercial value.

In terms of accessing small organic molecules from these N-containing feedstocks, few studies had been performed prior to our investigations in this area. Most examples, until 2012, had focused on pyrolytic methods[78,79] (Fig. 13) and were aimed at food chemistry audiences. For example, pyrolysis of NAG under vacuum gave a tar from which 3-acetamidofuran, 3-acetamido-5-acetylfuran and acetamidoacetaldehyde could be isolated in 5%, 2% and 3% yields respectively. GC-MS provided evidence for the formation of several other compounds that were tentatively assigned as 3-acetamido-5-methylfuran, acetamido-substituted 2- and 4-pyrones and hydroxydihydropyran-4-one.[78] In the work of Franich *et al.*, a mechanism of dehydration proceeding *via* an anhydrosugar intermediate was proposed. In our research,[80] we have proposed a mechanism that proceeds through an open-chain aldose form of the hexose in line with mechanisms proposed for dehydrations of fructose. In 1998, Chen *et al.* pyrolyzed NAG at 200 °C for 30 min. They identified a range of volatile compounds as products including pyrazines, pyridines and furans.[79] Once again 3-acetamido-5-acetylfuran was found to be the major degradation product and in order of decreasing quantity 2-acetylfuran, 3-acetamidofuran, pyrazine, pyridine, ethylpyrazine, methylpyrazine, 2-ethyl-6-methylpyrazine, 2,3-dimethylpyrazine, and acetamide were identified as the minor products. Taking these pyrolysis studies as a starting point and due to demands for new N-centered chemistry,[81,82] we wondered if using a N-containing carbohydrate, can N-containing renewable chemicals be made?

In our initial studies on chemical transformations of these N-containing carbohydrates, we obtained moderate yields of levulinic acid from chitosan and GlcN using water as the reaction medium.[83] However, when reactions were performed in dipolar aprotic solvents or in some imidazolium ionic liquids in the presence of chloride ions and boric acid, 3A5AF was obtained.[80,84] In both studies, under optimized conditions, 60% yield of 3A5AF could be obtained, which is approximately 30 times greater than the yields *via* pyrolysis. In reactions performed in organic solvents, the highest yields were obtained in DMA, DMF and DMSO, however, we also noted that significant conversion levels could be achieved in the 'greener' solvents ethyl lactate and PEG.[84] We also discovered that trace impurities (containing boron and chlorine) affected the outcome of the reactions and further studies are on-going in our group to understand the role that Cl and B play in these dehydration processes. In the studies described above, ethyl acetate was used to extract 3A5AF from the reaction phase. We have previously shown that 5-hydroxymethylfurfural is moderately soluble in $scCO_2$ and that many platform chemicals are soluble in modified $scCO_2$.[85] Therefore, we hope to use $scCO_2$ in the future to extract 3A5AF from the reaction mixture. It is also worth noting that carbon dioxide can have a favourable impact on the outcome of some reactions of platform chemicals in carbon dioxide. In 2011, Leitner, Klankermayer and coworkers showed that catalytic decarbonylation reactions of 5-hydroxymethylfurfural proceeded with greater selectivity in the presence of compressed carbon dioxide.[86] Therefore, one can see that carbon dioxide will be a useful solvent in both extracting platform chemical molecules and their further reactions.

In summary, we feel there is significant scope to use green chemistry tools in the valorization of waste from crustacean fisheries. In the processing of such waste (Fig. 14), new methods need to be developed to reduce the environmental impact of step 1. In particular, new extraction or oxidation methods are needed to remove the pigment components from chitin, and further investigation of biological methods for the demineralization and deproteination steps will also be necessary. Once chitin is isolated, in step 2, cellulase or chitinase enzymes could be used to produce NAG. Then, new chemical

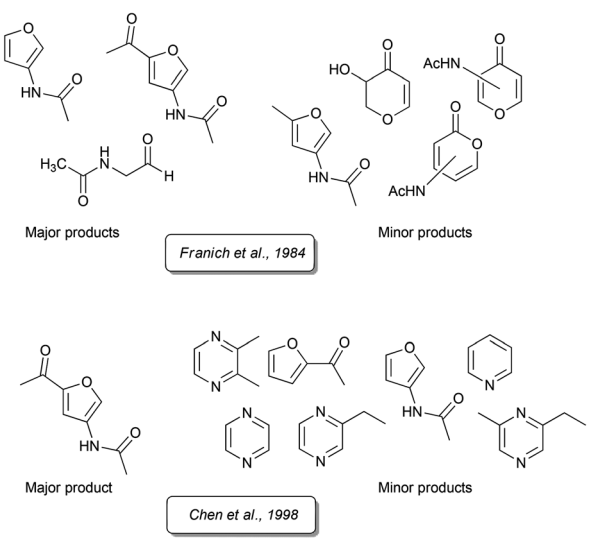

Fig. 13 Small molecules detected from pyrolysis of aminocarbohydrates.

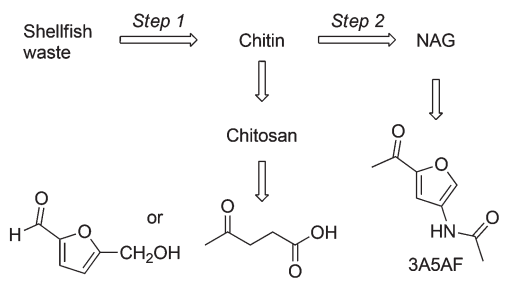

Fig. 14 Schematic flow diagram representing the production of platform chemicals from shellfish waste.

methods might be utilized to produce N-containing platform chemicals such as 3A5AF. It should be noted that the production of such N-containing platform chemicals is not reliant on shellfish waste, as GlcN and NAG can be produced from fructose or glucose.[87,88] The synthesis and reactivity of 3A5AF is being studied in more detail in our group at present. A LCA study is required to compare routes to 3A5AF from ocean-sourced NAG and from glucose.

Conclusions

During the past decade, research concerned with the valorisation of land-based resources (*e.g.* forestry and municipal waste) *via* the production of useful fuels, chemicals and materials has grown dramatically. However, given competition for land space both in terms of food production and habitats for humans and wildlife, it is not unreasonable to look at the oceans as a source of valuable materials. This perspective highlights some of the achievements made to date with regards to the use of algae and waste streams from fish processing. Potential products are summarized in Fig. 15. As detailed in the introduction, only a limited number of publications have appeared in this field compared with the area of renewable feedstocks as a whole (Fig. 1). There is enormous scope to employ green chemistry methods in this area to produce chemicals sustainably. However, teamwork is needed to bring together the necessary skills (biochemical, chemical and engineering) to develop benign, economically viable processes for the future. It should be noted that the N- and S-containing carbohydrates present in chitin and in seaweeds should be processed in such a way to avoid NO_x and SO_x emissions. Wherever possible the high-value heteroatom-containing carbohydrate should perhaps be used in its polymeric form *e.g.* chitosan in biomedical applications and bioactive sulfur-containing oligosaccharides as medicines. If depolymerisation is desirable, *e.g.* to produce new, renewable heteroatom-containing chemical building blocks, the possibility of gaseous emissions should not be ignored.

At present, only a limited number of researchers are working in this area and efforts are suffering from a fragmented approach toward utilization of these feedstocks. For example, green methods exist for many of the steps involved with isolation of chitin from crustacean waste. However, no approaches combining fermentation (for demineralization), enzymatic hydrolysis (for protein removal) and pigment extraction or 'green' oxidation have been reported. Researchers are studying the production of biodiesel from algae but they are not attempting to isolate valuable co-products including hydrocolloids and cellulose. In short, green methods could be used to maximize the number of products obtainable from algae or fish waste rather than producing a single chemical substance or material. In many cases, LCA studies are lacking and the economic value of the new products is unknown. Many opportunities, not limited to those mentioned above, are awaiting ingenious teams of researchers in order to sustainably produce chemicals and materials from oceanic biomass.

Acknowledgements

Dr C. Bottaro, Dr R. Helleur (Memorial University) and Darrell Green (Newfoundland Aquaculture Industry Association) are thanked for valuable discussions. We also acknowledge the funding agencies of our research programs including Memorial University, NSERC of Canada, Canada Foundation for Innovation and the Research & Development Corporation of Newfoundland.

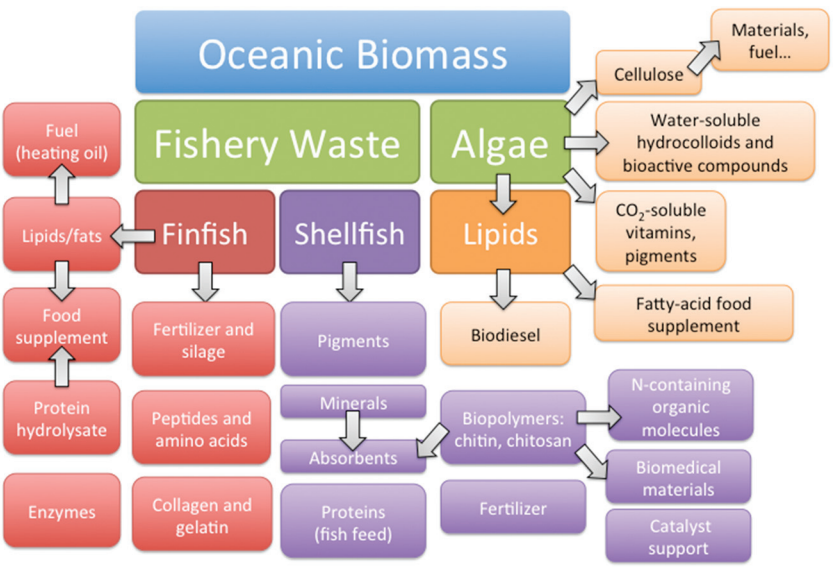

Fig. 15 Potential products from oceanic biomass (excluding fish/shellfish use as meat and direct use of algae as a foodstuff).

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