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Short Review

# Shell biorefinery: A comprehensive introduction

Max J. Hülsey\*

Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Blk E5 #04-02, Singapore 117585, Singapore

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#### Abstract

Biomass refinery is considered to be a key technology in the 21st century due to the importance of the sustainable production of various bioderived fuels and fine chemicals. Besides the synthesis of oxygen-containing chemicals mainly from lignocellulosic biomass, nitrogencontaining chemicals belong to some of the most important commodity and fine chemicals. In this introductory short review, the main similarities and difficulties between petroleum oil- and biorefinery will be discussed and future challenges will be highlighted. As a particular example, recent developments in the shell biorefinery – the utilization of shell waste – will be reviewed. Particular emphasis will be placed on the structure of shell biomass, the current and emerging fractionation methods and the conversion of chitin and chitosan to various heteroatomcontaining chemicals. This review is meant to provide an introduction to beginners in the field of biorefinery as well as a comprehensive discussion of recent proceedings in the field of shell biorefinery. An outlook on the future potential and challenges will be given. © 2018, Institute of Process Engineering, Chinese Academy of Sciences. Publishing services by Elsevier B.V. on behalf of KeAi Communications Co., Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

# 1. Introduction

Due to the inevitable depletion of fossil fuels and rising greenhouse gas concentrations in the atmosphere associated with surging temperatures, ocean acidification and rising sea levels among many other adverse effects, the utilization of renewable resources for the generation of energy and production of chemicals becomes a major imperative in the 21st century [1-3]. Until so far, chemicals are produced almost entirely by classical petroleum oil refinery associated with the emission of carbon-based greenhouse gases thus exhibiting an open carbon cycle. In contrast, employing biomass as raw material could close the carbon cycle and therefore, the future chemical industries might increasingly rely on 'biorefinery'. Although general characteristics of oil and biorefinery are very similar, the differences are one of the main reasons for the slow implementation into current industries (Fig. 1) [4].

Refinery generally means the conversion of raw materials into a product with a higher value. In terms of tradition petroleum oil refinery, the raw product is crude oil, a complex mixture of compounds predominantly containing carbon and hydrogen. The separation of crude oil is achieved by continuous fractional distillation, a process to separate a wide range of components. This step requires a considerable amount of energy but can be easily intensified to yield high volumes of each fraction in a relatively short time using little space. In contrast to that, the immense complexity of biomass alongside the polymeric nature of most of its constituents make mono- or biphasic wet-chemistry-based fractionation almost inevitable. This might not require high temperatures but relies on the use of solvents and possibly even includes the utilization of some reactants that inevitably generate waste and is difficult to intensify.

Petroleum oil extraction is highly localized; the crude product is transferred from huge offshore oil or drilling rigs to giant oil production plants where primarily inorganic components such as sulfur, salts and heavy metals are removed before further treatment. The opposite is the case especially for waste biomass such as bagasse or corn stover that is widely distributed over a large area thus posing a major logistic challenge [5,6]. In the case of biofuel, it is mostly considered more cost-effective to convert the low energy-density biomass into a biofuel in a decentralized manner and then transporting the products with a higher energy density to a centralized facility for further upgrading or blending [7].

E-mail address: m.huelsey@u.nus.edu.

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<sup>\*</sup> Corresponding author.

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Fig. 1. Schematic comparison of petroleum oil and biomass refinery.

Fractions of the purified oil often need to be further upgraded by either carbon–carbon bond formation to generate fuels with a higher boiling point or higher octane number or fluid catalytic cracking if shorter chain products are desired. Besides the generation of fuels, further functionalization of the oil fractions is necessary to form precursors for fine chemicals. In biorefinery, the opposite is required. First, pretreatment steps are employed to reduce the crystallinity and thus recalcitrance of the biopolymers and then, carbon–carbon and carbon–oxygen bonds need to be cleaved to form monomeric units for commodity and fine chemicals. The generation of fuels can be achieved by defunctionalization of biomass products to decrease the boiling point and enhance the stability of the biofuels [8,9].

In most cases, the products of oil refinery can be separated by distillation. However, it has to be noted that other technologies might be necessary in certain cases such as for ethylene and acetylene and the separation of the three isomers of xylene. Porous adsorption materials [10,11] as well as selective hydrogenation in case of the unsaturated  $C_2$ products [12] are promising approaches to obtain pure products. Product purification after biorefinery mostly relies on chromatography or continuous liquid–liquid extraction, associated with an immense use of organic solvents. Crystallization or even distillation of the final product is preferred, and has been shown before but needs to be further developed for a broader range of compounds [13–15].

In recent decades, the conversion of biomass into biofuels or value-added fine or commodity chemicals has garnered a tremendous amount of interest [16,17]. Lignocellulosic biomass, primarily consisting of cellulose, hemicellulose and lignin is by far the most extensively studied material due to its sheer abundance in plants and plethora of accessible *O*-containing chemicals [18–34]. Biomass conversion and utilization still suffer from several problems such as vastly complex

product mixtures that require thorough purification steps and the occurrence of those biomaterials in a complex and often recalcitrant matrix. Moreover, some of the current utilization schemes for platform chemicals aim at the reductive defunctionalization of biomass followed by the reintroduction of functional groups containing heteroatoms such as nitrogen and oxygen [35–39]. All those drawbacks render recent biorefinery technologies economically rather unfeasible.

Thorough analyses of the environmental impact of biorefinery need to be considered in order to assess whether it is economically and environmentally beneficial. One of those studies for glycerol, a major by-product of biodiesel production has been reported previously (Fig. 2) [40]. From this casestudy some key requirements for biorefinery can be observed. Firstly, the entire biomass stream should be utilized appropriately in order to minimize the produced waste. Furthermore, the feed should be split into different pathways for chemicals guaranteeing sufficient flexibility to adjust to changing demand. Heat integration throughout the different upgrading routes was predicted to benefit substantially to the overall greenness of the biorefinery. Another key point is that the products from a biorefinery scheme should be easily implementable into the existing chemical production framework and should ideally have a high market value and volume. This analysis is particularly applicable to glycerol because sufficient effort has been devoted to developing and optimizing catalytic and process technologies. The realization of efficient biorefinery streams is encouraging and should be developed for a range of other waste biomass streams and a multitude of different products.

Generally, one of the most important differences between classical crude oil- and biorefinery is that the former has been in development for more than 150 years whereas the latter is much younger and therefore less well developed and established. Differences become obvious when comparing the



Fig. 2. Schematic overview over a heat-integrated process for the conversion of glycerol into a variety of common chemicals. Reprinted from Ref. [40], copyright Royal Society of Chemistry.

structure of petroleum oil and biomass and thus further technological advancements are required to develop the full potential of biomass resources. However, as most utilized commodity and fine chemicals have a complex structure carrying multiple heteroatom-containing functional groups, it should be appealing to carry out slight modifications on biomass resources instead of massively functionalizing hydrocarbons. Although this has been shown for oxygencontaining chemicals from lignocellulosic biomass, there are both a potential for the utilization of ocean-based biomaterials as well as the need for the development of routes to obtain nitrogen-containing chemicals from renewable biomass resources [41–43].

#### 2. Shell biorefinery

One of the possible solutions can be the utilization of chitin, the second most abundant biopolymer on earth and most abundant in the ranks of nitrogen-containing biopolymers. The concept for the conversion of chitin into various nitrogencontaining chemicals was termed 'shell biorefinery' because chitin is a major component in the shells of crustaceans besides its occurrence in the exoskeleton of insects and the cell walls of fungi and microorganisms where it is commonly mixed with protein and/or several minerals. Although chitin is not mixed with minerals in fungi and microorganisms, it coexists with several other biopolymers rendering the separation of them a difficult endeavor. Both crustaceans and insects contain high amounts of relatively pure chitin mixed with protein and calcium carbonate [44–46]. Much previous work was devoted to developing shell biorefinery starting from shrimp or crab shell due to the sheer abundance of seafood waste (an estimated 6-8 million tonnes per year worldwide) and its current

underutilization. In fact, most of the seafood waste is disposed into landfills or back into the ocean where the decomposition products can pose a major environmental issue especially in coastal regions [47,48]. Shell biorefinery, in which crustacean shells are fractionated and further upgraded into value-added chemicals and materials, could be utilized to exemplify the unique features of biorefinery. Crustacean shells normally consist of 20-50% calcium carbonate, 20-40% protein and up to 15-40% chitin (Fig. 3). Protein can be used as fertilizer and feedstock for animals whereas calcium carbonate can find application as filler or pigment in various industries. As discussed before, chitin's possible applicability ranges from the production of pharmaceuticals and cosmetics to the use of materials for water treatment [49]. Besides those major components, the value of astaxanthin - a red coloring agent and dietary agent with antioxidant activity - and lipids inside crustacean shells should not be underestimated. Shrimp shells, for example, contain up to 1-2% extractable fats with a high content of  $\omega$ -3 and other valuable unsaturated fatty acids [50,51].



Fig. 3. Main components of shell waste biomass and their utilization. Reprinted from Ref. [52], copyright Nature Publishing Group.



Fig. 4. Chemical structure of (a) chitin and (b) cellulose.

The main focus in the following, however, will be on the conversion of chitin which consists of long *N*-acetylglucosamine (GlcNAC) chains bound by  $\beta$ –(1  $\rightarrow$  4)–glycosidic bonds (Fig. 4a) similar to cellulose (Fig. 4b). Due to its high amounts of biologically fixed nitrogen (~7 wt%), chitin can act as a sustainable and abundant source for various *N*-containing compounds and materials [52]. Besides that, the nitrogen atoms can benefit the adsorption of for example heavy metal atoms and upon cleavage of the amide group, then obtained free amine renders the polymer soluble in acidic solution and more biocompatible.

# 3. Fractionation of crustacean shell biomass

The occurrence of minerals and protein alongside chitin create the requirement for a fractionation scheme that facilitates or at least does not hamper further separations and conversions. In the case of crustacean shell, this is not a trivial endeavor due to the complex structure as depicted in Fig. 5 with the strictly hierarchical combination of chitin nano-fibrils that form fibers arranging in a helicoid manner. The extensive covalent and hydrogen-bonding between chitin and protein together with embedded calcium carbonate benefits the mechanical strength required to protect the soft body of crustaceans but also accounts for the difficulties associated with separating the components [53].

The currently used procedure for the fractionation of crustacean shell biomass involves the demineralization, deproteinization and subsequent decoloration to obtain pure and colorless chitin. Prior to that treatment, astaxanthin can be obtained as a high-value pigment. Due to the very limited solubility in water and low accessibility in the chitin-protein network, harsh conditions involving the use of strong mineral acids such as hydrochloric or sulfuric acid, elevated temperature (up to 100 °C) and long reaction times (around 2 days) are required. Subsequently, the protein is removed by treating the demineralized biomass with strong bases such as sodium hydroxide again at elevated temperatures up to 100 °C and for long times of up to three days [55]. This step also hydrolyzes and removes lipids which can then be separated from the protein. Oxidative bleaching is required if a colorless product is desired. Overall, this procedure is neither environmentally benign nor does it yield clean products in their native structure. Consequently, the price of chitin is relatively high and the production is limited by environmental regulations in most countries, hampering its wider application for the synthesis of materials or chemicals. Methods relying on the selective extraction with various solvents such as ionic liquids [56,57] or deep-eutectic solvents [58,59] and biocatalytic processes [60] have been developed and assessed but are currently not competitive on an industrial scale.

Recently, the fractionation process was shown to be successful in a one-step procedure where the acid treatment was sufficient for both the demineralization and deproteinization. However, this process still requires relatively concentrated acid and even higher temperatures and similarly long times compared to the conventional industrial process [61]. A rather unconventional approach relies on the use of atmospheric-pressure dielectric discharge



Fig. 5. The chemical composition and structure of shrimp shell primarily composed of chitin, protein and calcium carbonate. Adapted with permission from Ref. [54], copyright Elsevier.

plasma under a nitrogen or mixed oxygen-nitrogen atmosphere for the deproteinization of shrimp shell biomass. Highly reactive nitrogen or oxygen species are responsible for the decomposition of proteins and by fine-tuning the amount of oxygen and other process parameters, most of the polysaccharide biomass can be retained. Although this could represent a viable, environmentally more benign and rapid process, calcium carbonate cannot be removed by plasma treatment and the protein components are almost entirely destroyed by this treatment [62]. It has been shown that a short (around 5 min) pre-treatment of prawn shell waste in glycerol at 200 °C facilitates the subsequent demineralization and deproteinization which can then be carried out in a single step by employing the significantly weaker and environmentally friendlier citric acid and water. The resulting chitin has a higher purity and a higher crystallinity as compared to the harsher conventional process [63]. Besides those recent developments, even simpler and environmentally more benign methods should be developed, ideally based on a catalytic system rather than by using stoichiometric amounts of reagents such as acids or bases.

#### 4. Chitin conversion into chemicals

The conversion of chitin into materials for biomedical, environmental or agricultural applications has been well investigated previously [64–70] but the direct conversion of chitin into valueadded chemicals represents an alternative pathway for the utilization of such shell waste-derived materials. It has been shown recently that a plethora of oxygen- and nitrogen-containing chemicals are accessible from chitin and its deacetylated derivative chitosan (Fig. 6). Although the full potential of the high natural nitrogen weight content can only be utilized by the synthesis of nitrogen-containing compounds, oxygen-containing compounds are often easier to be implemented into already existing (bio)refinery schemes.

Direct oxidation of crude shrimp shell waste with oxygen gas using a copper oxide catalyst in basic water led to the production of close to 50 wt% acetic acid and 12 mol% pyrrole with addition of ammonia in a single-step reaction. Besides those two main products, other acids such as lactic, formic, oxalic and glycolic acid can be obtained in yields higher than available when cellulose is used as starting material [71]. Levulinic acid can be produced by microwave treatment of sulfuric acid-pretreated chitin with a yield of around 37% at 190 °C within 30 min [72]. Dehydration of a chitin-derived furanic amine yields levoglucosenone using a combination of Brønsted and Lewis acidic catalysts such as hydrochloric and boric acid [73]. 5-HMF - one of the most prominent biomass-derived platform chemicals - can be either obtained from the monomeric sugar or directly from chitin by treatment with Lewis acid catalysts such as zinc or iron chloride or recyclable ionic liquids in polar solvents [74-76]. Noble metal catalysts can be used to hydrogenate chitin and chitin-derived sugars into N-acetylmonoethanolamine and nitrogen-containing polyols with total yields close to 85% at temperatures below 180 °C [77]. By using a combination of acid, mechano- and noble metal-hydrogenation catalysis, 2-



Fig. 6. Broad chemical space of highly *O*- and *N*-functionalized compounds accessible from shell biomass *via* chitin and chitosan as key intermediates. AA, acetic acid; FA, formic acid; LA, levulinic acid; LG, levoglucosenone; 5-HMF, 5-hydroxymethylfurfural; GlcNH<sub>2</sub>, glucosamine; 3A5AF, 3-acetamido-5-acetylfuran; NMEA, *N*-acetylmonoethanolamine; GlcNAc, *N*-acetylgluco-samine; HADP, hydroxyethyl-2-amino-2-deoxyhexopyranoside; MEA, monoethanolamine.

acetamido-2-deoxysorbitol was obtained without any purification step. Remarkably, the amide group was retained during this treatment whereas the glycosidic bonds were selectively hydrolyzed [78]. Much effort has been devoted to the depolymerization of chitin to obtain its monomeric sugar unit N-acetylglucosamine among which the use of co-solvent mediated depolymerization [79], the use of mechanical grinding together with a cheap and natural clay [80] and biocatalytic breakdown of enzymatically pretreated chitin [81] represent some of the most recent advances. Upon liquefaction of chitin biomass with sulfuric acid in ethylene glycol, several monomeric-sugar-derived compounds such as hydroxyethyl-2-amino-2-deoxyhexopyranoside and hydroxyethyl-2-acetamido-2-deoxyhexopyranoside can be obtained with a chitin conversion of 75% at 165 °C after 90 min [82]. The hydrolysis of chitin can be almost completely avoided by using formic acid for the depolymerization of the biopolymer. Several steps include the solubilization by partial formylation of chitin residues followed by the non-hydrolytic cleavage of glycosidic bonds. Further hydrolysis occurs when sufficient water is formed during the reaction yielding up to 60% monomeric products at 100 °C after 12 h [83].

3A5AF is a furan derivative with potential use in the synthesis of other small organic building blocks and biologically active compounds such as proximicin A, B and C [84,85]. Although functionalizations on the 2 and 5 position of the furan ring are frequently reported [86–88], the two other positions are less easily available for chemical modification. This is one of the reasons why the synthesis of 3A5AF through conventional pathways is lengthy, generates a large amount of chemical waste and starts from a relatively expensive precursor [84]. Employing a direct one-step process for the synthesis of 3A5AF from cheaper and renewable starting materials thus represents an ecologically and probably even economically more feasible access to this compound. The conversion of N-acetylglucosamine into 3A5AF has been reported earlier [89,90] but more recently, the direct conversion of chitin into 3A5AF has been demonstrated as well [73]. This conversion was further refined by replacing the initially used organic solvents with ionic liquids and the reaction was shown to occur more rapidly at a lower temperature [91]. The reaction probably occurs after partial hydrolysis of chitin into its monomeric subunit followed by acid-catalyzed isomerization of the hexose into a pentose which then eliminates water and forms the corresponding ketone. After elimination of two additional water molecules, the aromatic compound with the unusual substitution pattern is formed (Fig. 7).

The complete synthesis of proximicin A has been achieved recently from biomass-derived 3A5AF and represents the first synthetic procedure to produce a pharmaceutically relevant nitrogen-containing compound from chitin. Besides relying on a biorenewable starting material, the authors paid much attention to the principles of green chemistry by avoiding harmful reagents and solvents and by reducing the amount of separation steps necessary to obtain the final product (Fig. 8) [92].



Fig. 7. Proposed reaction mechanism of the acid-catalyzed formation of 3A5AF from chitin.



Fig. 8. Comparison between the recently reported biomass-based and traditional petroleum oil-based synthetic pathway toward proximicin A. Reprinted from Ref. [38], copyright American Chemical Society.

Apart from proximicin A, a plethora of other compounds have been synthesized from 3A5AF by various chemical transformations (Fig. 9). Among them is the renewable amine 1 which can be obtained by basic hydrolysis or alcohol 2 accessible by catalyzed transfer hydrogenation or reduction with sodium borohydride. The produced alcohol 2 can then spontaneously eliminate water to form alkene 3 [93]. The reaction of 3A5AF with several carbonyl compounds under acid catalysis yields a range of compounds (4, 5) among which the dihydrofuropyridine scaffold (6) represents one of the most interesting examples (Fig. 9) [94].

It can be envisioned that a large chemical space of oxygenand especially nitrogen-containing compounds can be synthesized from chitin. 3A5AF will probably play a significant role but further efforts should be devoted to explore the full potential of the first chitin-derived platform chemical and the development of other platform chemicals. Existing synthetic procedures should be improved and scaled up to show economic viability and environmental benefits. Furthermore, materials from sources other than waste shell biomass and the valorization of side products should be considered in future studies.

# 5. Production of chitosan and its conversion into chemicals

Another attractive polymer accessible from chitin is chitosan, where the majority (>50%) of sugar monomer units is deacetylated. The remaining free amine group renders



Fig. 9. Recently widened chemical space accessible from the chitin-derived platform chemical 3A5AF. Reprinted from Ref. [38], copyright American Chemical Society.

Table 1	
Comparison of different methods for the deacetylation of chitin to chitosan.	

	DD <sup>a</sup> [%]	M <sub>w</sub> [kDa]	Solvent <sup>b</sup>	Base <sup>c</sup>	Time [h]	Temp [°C]	Ref.
Traditional industrial	92 <sup>d</sup>	120-160	Water, 1:50	>20	1-4	100-130	[101]
Mircrowave-assisted	98 <sup>e</sup>	127.7 <sup>f</sup>	Water, 1:50	50	3	150	[102]
Mechanochemical	83 <sup>e</sup>	7.7	None	1	12	NA	[103]
Glycerol-mediated	85 <sup>g</sup>	30.9	Glycerol, 1:40	12	12	180	[63]

<sup>a</sup> DD: degree of deacetylation.

<sup>b</sup> Weight ratio between chitin and solvent.

<sup>c</sup> Based on weight ratio between chitin and sodium hydroxide.

<sup>d</sup> Determined by potentiometric titration.

<sup>e</sup> Determined by <sup>1</sup>H NMR and FTIR.

<sup>f</sup> After 6 h reaction.

<sup>g</sup> Determined by pH titration.

chitosan water-soluble and thus much easier to process than chitin [95–100].

Various methods have been reported for the deacetylation of chitin to chitosan [101–104], a comparison of which is shown in Table 1. As mentioned previously, the traditional industrial method heavily relies on the use of inorganic bases to achieve a satisfactory degree of deacetylation (DD) [101]. Among all, the microwave-assisted method is the only one that cleaves the amide bonds almost quantitatively but even harsher reaction conditions for a similar amount of time are required [102]. Recently, two additional methods were developed in order to reduce the amount of base required. The first relies on a solventless ball-milling procedure where only one equivalent of base is required and no external heating is necessary (Fig. 10). Besides the efficient deacetylation, a depolymerization into low molecular weight chitosan is achieved with a polydispersity index around 1.1 [103], which is often better for material syntheses [105] and biomedical applications [106]. The second employs glycerol - a coproduct of the biodiesel production - for the deacetylation lowering the requirements for the use of base and yielding a significantly lower molecular weight compared to the starting material [104]. Besides the commonly used sodium hydroxide, a mixture of potassium and lithium hydroxide has been demonstrated to facilitate the dissolution and deacetylation of chitin simultaneously. Based on <sup>15</sup>N and <sup>13</sup>C NMR spectroscopy, potassium was shown to break the carbonyl-based hydrogen bonding whereas lithium binds to amine groups thus breaking the NH<sub>2</sub>-based hydrogen bonds in chitosan [107].

The conversion of chitosan into value-added chemicals is less explored than for chitin but several studies have reported the synthesis of different nitrogen- and oxygen-containing compounds. Similar to the conversion of cellulose, 5-HMF and levulinic acid belong to the most commonly observed products which can be obtained from chitosan under various conditions. Low-temperature hydrothermal treatment at 174 °C with 2.2% sulfuric acid yielded up to 12% 5-HMF after slightly above half an hour reaction time [108]. Similarly, treatment of chitosan with tin chloride under microwaveirradiation produced up to 10 wt% 5-HMF or 24 wt% levulinic acid after 30 min at 200 °C [109]. The use of Brønsted or Lewis acidic ionic liquids, methanesulfonic or sulfamic acid were explored more recently and those systems produce 5-HMF with yields up to 45% [110–113]. The comparatively higher yield of levulinic acid from chitosan as compared to cellulose was explained by the efficient quaternization of the amine group by acidic ionic liquids, followed by hydrolysis and elimination of ammonia to produce the final product [114]. The relatively mild treatment of chitosan with acids or enzymes leads to the depolymerization into oligomers and finally glucosamine monomers [115]. Similar to the treatment of chitosan, the monomeric sugar can be converted into levulinic and formic acid by hydrothermal treatment with methanesulfonic and sulfamic acid or zirconium oxychloride under suppression of 5-HMF formation [116–118]. Due to the structural similarity with cellulose, the range of compounds obtained from chitosan can possibly be expanded much further



Fig. 10. Comparison between the conventional method (top) using a two-step procedure and the developed one-step, mechanochemical method (bottom). Reprinted under the terms of the CC BY-NC 3.0 license [103]. Copyright 2017, The Authors, published by Royal Society of Chemistry.

to typical *O*-containing platform chemicals and even some *N*-containing equivalents.

### 6. Summary and perspective

In this introductory review, particular emphasis was placed on the similarities and differences between crude oil- and biorefinery providing a general overview. As a specific example, the conversion of chitin or raw shrimp shell into several heteroatom-containing organic building blocks was chosen as an in-depth example to demonstrate the potential of (shell) biorefinery making using of an almost entirely untapped abundant resource. A holistic overview in all the steps necessary to convert crude biomass into a highly-value added product is given. The efficient use of chitin as starting material, however, is so far limited by the detrimental environmental impact of the fractionation process and the deacetylation of chitin. Further improvements on this side can attract more attention to developing technologies for the industrial-scale production of chitinand chitosan-derived materials and chemicals. As insects are frequently considered an attractive alternative nutrition source due to their low feed conversion ratio of sometimes below 1.5 [119] for soldier flies or crickets (beef has a common feed conversion ratio of around 6) and an improved food security compared to traditional domestic animals, another ubiquitous source for chitin might emerge soon. First preliminary studies on the composition and fractionation of potential insect sources such as the black soldier fly prepupae reveal that indeed there is a huge potential in the use of insects as sources for chitin and other components [120].

Overall, this review should help students and researchers develop an improved understanding and appreciation for abundant, renewable and easily available materials.

# **Conflict of interest**

The author declares no competing financial interest.

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