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A "green" industrial revolution: Using chitin towards transformative technologies*

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Abstract: Even with the high costs of environmental exposure controls, as well as the chance of control failures, options for industries wanting to implement sustainability through frameworks such as green chemistry are not yet cost-effective. We foresee a "green" industrial revolution through the use of transformative technologies that provide cost-effective and sustainable products which could lead to new business opportunities. Through example, we promote the use of natural and abundant biopolymers such as chitin, combined with the solvating power of ionic liquids (ILs), as a transformative technology to develop industries that are overall better and more cost-effective than current practices. The use of shellfish waste as a source of chitin for a variety of applications, including high-value medical applications, represents a total byproduct utilization concept with realistic implications in crustacean processing industries.

Keywords: biopolymers; chitin; green chemistry; polysaccharides; sustainable chemistry.

The Industrial Revolution and the more recent technological revolutions have had extreme effects on the culture and quality of life. Without understanding the long-term environmental effects or drive to protect limited resources and the environment, there have been profound negative effects on the environment, which may be irreversible. Efforts creating this technology have led to a mindset directed towards the product, its properties, and its economic viability, leaving the industrial process an afterthought. Only recently have we begun to realize that focusing on the end product and not on the process is producing unsustainable industries. Since the mid-20th century, public concerns over environmental pollution have been increasing. Due to the public outcries, governments have started regulating emissions and waste disposal to limit the harmful effects to people and their surrounding environment (see, e.g., The Clean Water Act, CWA, [1] that establishes the basic structure for regulating discharges of pollutants into the waters of the United States). Unfortunately, virtually all of the approaches to reducing environment risk are focused on reducing exposure with controls that necessitate additional costs [2]. More importantly, these exposure controls can fail.

In the early 1990s, green chemistry was suggested as a design framework to achieve goals directed towards human health and the environment while producing profitable products [3,4]. Green chemistry stands on a foundation of 12 Principles such as "it is better to prevent waste than to treat or clean up waste" and "chemical products should be designed so that they do not persist in the environment" [4]. These principles guide the development of environmentally benign materials and processes, but are likely to have tradeoffs and balances when optimizing the application [5]. Nevertheless, and

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without broad acceptance, the impact of green chemistry can be seen in the numerous scientific advances, implementation, and educational outreach in its name [5]. This shift in rethinking the design and environmental impacts of products and processes is important for the sustainability of our planet.

Green chemistry is integral to sustainability and is at the intersection of three major crossroads: environmental integrity, social responsibility, and economic viability [6–8] (Fig. 1). Environmental integrity promotes efficient use of natural resources that minimize harm to the environment and reduce waste and byproducts from the system. Social responsibility is necessary to protect employees from harm, provide competitive salaries and benefits, and create a cultural identity to promote sustainability. The final crossroad, economic viability, yields a product that is competitive with current market prices. This is perhaps the most difficult, and least considered criterion as current industrial practice of adopting new methods are based on cost and demonstration of both viability and significant improvements. Producing sustainable, cost-effective products is most likely the biggest challenge facing green chemistry today.

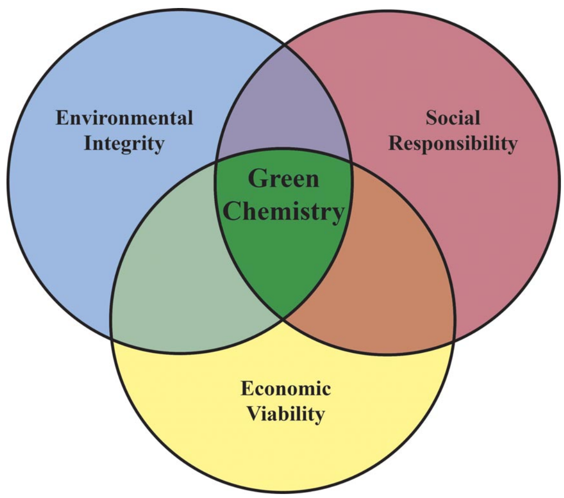

Fig. 1 Green chemistry intersects environmental integrity, social responsibility, and economic viability.

With every new revolution, a deeper focus on lowering the impact to the environment and being sustainable will become crucial. We should not wait for governments and legislation to start regulating these processes. *We propose to start a "green" revolution by developing new transformative technologies* from which various high-value products can emerge. This will result in a redefinition of green chemistry to one that while creating profitable products will also lead to *new business opportunities*. Therefore, we are implementing green chemistry by implementing "green" technologies; not because these technologies are "green", but because they are better. In this article we will focus specifically on one of the 12 Principles likely to lead to new competitive technologies and business opportunities. The principle states that a "raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable" [4].

Technology platforms based on renewable sources are a major step towards sustainability; however, a facilitated and efficient approach to access natural biopolymers (Fig. 2) is needed. For example, the pulping industry isolates cellulose from wood pulp for use in a wide variety of applications. Wood pulp contains 40–50 % cellulose, 20–40 % hemicellulose, and 18–35 % lignin, therefore, utilizing only this small percentage of the total biomass for applications and burning the remaining material results in an inefficient process [9,10]. The grand challenge of utilizing cellulosic biomass is the separation of these major components in a low-energy, cost-effective manner. These components could then provide

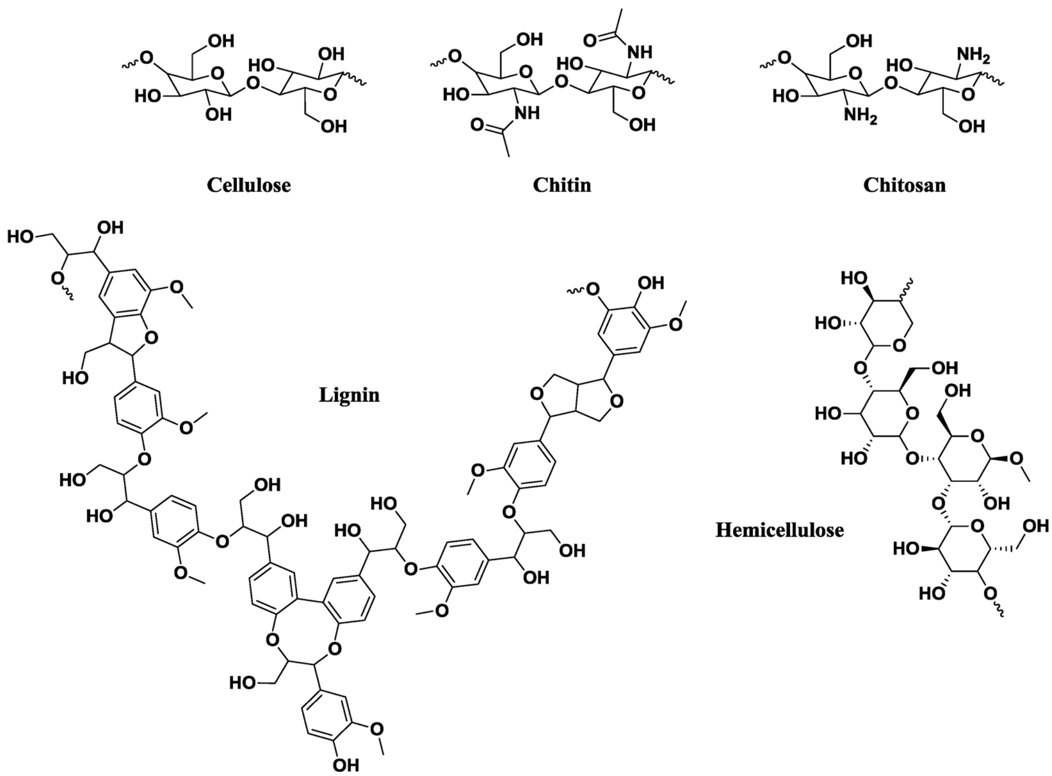

Fig. 2 Important biopolymers for renewable feedstocks (lignin representative only).

valuable feedstocks for new products, such as replacements for plastics derived from oil-based products, and allow for a more efficient use of cellulosic biomass. It has been demonstrated that biopolymers, particularly cellulose, can serve as feedstock for various types of biofuels (e.g., ethanol, butanol, and hydrocarbon fuels) [11,12]. To help unlock the promise of cellulosic biopolymers, we initiated a platform based on the use of ionic liquids (ILs) to dissolve and process lignocellulosic biomass.

ILs (Fig. 3; currently defined as salts that melt below 100 °C [13]) may have an important role in transformational technologies and platforms. ILs are "tunable" simply by varying the ion composition, which allows for the optimization of properties for specific applications. At present this tailoring is possible due to gained knowledge of how specific ions affect the resulting IL properties. ILs with properties ranging from energetic, pharmaceutical, agrochemical, and in combination with nanomaterials, have been developed, making ILs key materials in new technologies [14–20].

ILs for biopolymer dissolution is not a single concept, but rather a *very specific platform*. In 2002, we reported that cellulose can be dissolved in ILs [21], and in 2007 that wood can be completely dissolved in ILs [22]. A variety of researchers have also investigated other renewable feedstocks such as bamboo, cotton, bagasse, grass, corn, and others, as well as finding other ILs that will dissolve biomass (Fig. 3) [23,24]. The results have been promising, and the work has continued in many laboratories around the world. In our work, we have shown that ILs can not only dissolve cellulose but can partially delignify biomass [25] and that utilizing polyoxometalates allows catalytic enhancement of the delignification and dissolution of the biomass [26].

The IL platform represents a technology that changes our perspective on the grand challenge of the isolation of the major components from cellulosic biomass. It has also led to new business opportunities through the acquisition of patents [27] and the development of advanced biomaterials such as

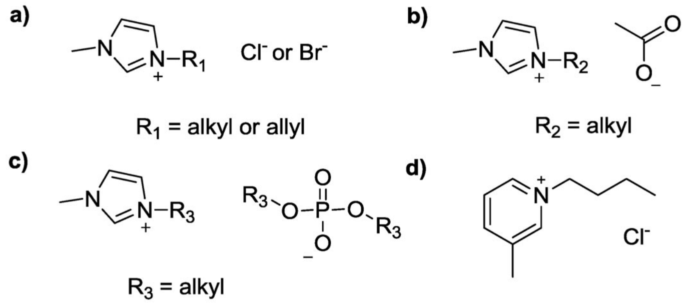

Fig. 3 Examples of ILs shown to dissolve biopolymers; (a) 1-alkyl(or allyl)-3-methylimidazolium chloride; (b) 1-alkyl-3-methylimidazolium acetate; (c) 1-alkyl-3-methylimidazolium dialkylphosphate; (d) 1-butyl-3-methylpyridinium chloride.

films [28], fibers [29], hydrogels [30], and membranes [31]. While a good beginning, the competitive cost advantage has not been proven yet, due to the current cheap price of oil. Though as oil reserves are depleted and prices rise, this technology might be further developed and become cost competitive. However, the IL approach might be used more quickly if it could be applied to a higher-value biopolymer such as chitin.

Chitin, the second most abundant biopolymer on earth after cellulose, is another abundant renewable resource [32]. Chitin is widely available from a variety of sources among which, the principal source is shellfish such as shrimp, crabs, and crawfish [33]. The annual synthesis of chitin in freshwater and marine ecosystems is roughly 600 and 1600 million tons, respectively [34]. Though obviously not all available as a resource, a recent report from the Food and Agriculture Organization of the United Nations in 2008 estimated the world shrimp catch to be 3.4 million tons per year and with shrimp farming, this production comes to 6 million tons indicating this is truly an abundant natural resource [35]. With the increase in production in farming, utilization of waste products, which contains valuable chemicals such as fatty acids, amino acids, pigments, as well as chitin, is needed [36].

Structurally, chitin is a linear amino polysaccharide composed of $\beta(1 \rightarrow 4)$ linked 2-acetamido-2-deoxy-β-D-glucose units, with the only difference between chitin and cellulose to be the acetylamine group in C-2 position of chitin instead of the hydroxyl (–OH) group found in cellulose [37]. The molecular weight of native chitin is usually larger than 1 300 000 Da [38] while commercial deacetylated chitin and chitosan have molecular weights in the range of 100 000 to 1 200 000 Da [39], depending on the isolation process. High temperature and concentrated acids treatment in the isolation of chitin from shellfish result in loss of molecular weight.

Commercial interest in chitin and chitosan is increasing due to its excellent properties including biocompatibility, biodegradability, adsorption, and chelating ability, therefore, it is interesting not only as an abundant resource but also as a key ingredient in novel functional materials. It can be manufactured into flakes, fine powders [40], films [25], membranes [31], fibers [29], sponges [41], hydrogels [30], and beads [42]. Applications of chitin and its derivatives include water treatment, nutrition, food processing, agriculture, cosmetics, and medical applications. Due to chitin's non-toxicity, non-allergenicity, biocompatibility, biodegradability, and bioactivity, diverse medicinal applications of chitin include both pharmacological and biotechnological materials and products [43,44].

The key property of chitin-derived products for application in various biomedical applications is the immuno-modulating effect and hemostasis through blood coagulation. Chitin-derived dressings for burns, surface wounds, and skin-graft donor sites accelerate healing and reduce pain compared to standard treatments. Other medical uses for chitin and its derivatives include vascular implants, structural surgical implants, artificial blood vessels, and tumor inhibitors [45,48]. Chitin and its derivatives are also used as a drug delivery agent in pharmacology [49–52]. Biotechnological applications include immobilization of cells and enzymes, matrixes for affinity and gel permeation, cell culture, membranes with permeability control, and as reverse osmosis agents. These applications represent the many factors that are converging to create an ideal opportunity for new business opportunities, for the introduction of high-molecular-weight sources of chitin into these fields. The applications of shellfish wastes as a source of chitin and chitosan represent a total byproduct utilization concept with realistic implications in other crustacean waste recovery industries.

Nowadays, the trend towards producing high-quality chitin for biomedical and pharmaceutical use emphasizes the chitin quality and physicochemical properties. The main reason for the current limited approaches being taken to utilize chitin is the difficulty in processing this material due to its insolubility in most aqueous and organic solvents [53,54] and the energy needed for its extraction from the shellfish waste. Specific physicochemical and functional properties of chitin that are affected by current extraction process protocols include the degradation of the chitin structure, including the decrease in molecular weight and resulting solution viscosity, as well as the degree of deacetylation [55]. As a result of the harsh alkaline treatment of the current process (discussed below), the degree of deacetylation increases thereby severely altering the structure of chitin and changing the properties of the polymer. Current extraction processes are the "bottleneck" in chitin production, resulting in severely limited chitin potential applications and market value. An IL extraction process can provide much improved functional properties of chitin and therefore act as a technology leading to better products.

The current industrial extraction of chitin from crustacean shell consists of two basic steps: (i) deproteinization by alkaline treatment (NaOH, 1 M, 1−72 h, 65−100 °C) and (ii) demineralization, separation of calcium carbonate/calcium phosphate, by acidic treatment (HCl, 0.275−2 M, 1−48 h, RT−100 °C) [55–57]. Such extreme conditions required for extracting chitin result in hydrolysis/degradation of the polymer [58], allowing for little control over the final product's physical characteristics such as crystallinity, purity, and polymer chain arrangement. The main factor to affect the polymer backbone of the chitin molecule is acid treatment, which cleaves the β-1,4-glycosidic bonds in chitin, resulting in a lower molecular weight and, upon dissolution, a lower viscosity. Strong acids used for the demineralization of chitin also affect the degree of acetylation [34], severely limiting chitin potential applications. Various chemical modifications of the above-mentioned industrial protocol have been applied to disrupt the inter- and intramolecular hydrogen bonds without cleavage of glycosidic linkages [59,60]. To produce 1 kg of partially deacetylated chitin or chitosan, from shrimp shells, 6.3 kg of HCl and 1.8 kg of NaOH are required in addition to nitrogen, process water (0.5 tons), and cooling water (0.9 tons) [61]. This process of chitin purification is not only energy-intensive, but damaging to the environment because of the disposal of high volumes of mineral acids and bases. Cost is also a concern for such large volumes of waste disposal.

To contrast this approach, an IL process has been proven to show that purified chitin with a high molecular weight can be extracted directly from crustacean shells to produce high-quality chitin materials with excellent efficiency and no need for extensive or harsh-condition processing [62,63]. It has also been shown that chitin can be directly electrospun into high-surface area nanofibers directly from a chitin extract solution [64]. Chitin-containing shells dissolve readily in ILs allowing for the coagulation of pure chitin by pouring the solution into a coagulation solvent, typically water. Dissolution of biopolymers in ILs is based on the disruption of the hydrogen bonds in the biopolymer followed by the formation of new hydrogen bonds between the polymeric hydroxyls and the IL anions [65,66]. It has been found that the best (so far) IL for extraction of chitin is 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]), but due to the fact that ILs have been recognized as "designer solvents" [67], it is anticipated that even better solvents will be found. Though at first this process seems quite simple, there are a variety of reasons that promote this technology over the current industrial process for chitin. This IL process has already shown to provide a higher-purity and higher-molecular-weight material than current industry practices, but it also provides:

- *Simple technology*: The IL process allows for the manufacturing of fibers, films, beads, and membranes *directly* from shrimp shell waste whereas the current system must process the material first (see Fig. 4).
- *Fast dissolution*: By utilizing current microwave technology, most dissolutions take between 2 min to 2 h.
- *Stronger materials*: In comparison to cellulose fibers processed in a similar way, chitin fibers and films provide a stronger material.
- *Minimal chemical and energy input*: The entire process only uses IL and coagulation solvent (water or alcohols) and the direct heating provided by flow-through microwave processing allows for a decrease in energy needed.
- *Solvent recycling*: ILs <u>are</u> recyclable, however, this is one area where process improvements and lower energy usage are needed [68].
- *Lower waste output*: Due to decreased chemical input, especially compared to the large volumes of mineral acids and bases needed for the current industrial process, there is high waste-to-volume minimization.
- *Chemical modifications*: With the solubility of chitin in ILs, there are opportunities to chemically modify the chitin before isolation with solution chemistry.
- *Broader impacts*: By repurposing a waste product we are salvaging it from being landfilled, which also saves shipping and disposal costs. This process could also create jobs by creating new business opportunities for the fisherman.

The IL process is still in its infancy, but it is clear that this process could make significant advances in the sustainability of the chitin extraction process. The repurposing of a waste product from the seafood industry into currently unavailable high-value products fits within the idea of our "green" revolution. These products not only integrate sustainability from the initial design of the process, but provide products that are better than the current processes allow. This possibility of manufacturing high-quality chitin products shows promise for new business opportunities. New start-up companies can use the developed process for chitin extraction, and, in turn, develop technologies for making chitin-based products. From the multitude of properties discussed above, novel high-value chitin products can find applications in biotechnology, medicine, dentistry, agriculture, food processing, environmental protection, textile production, and many other areas of science [69,70].

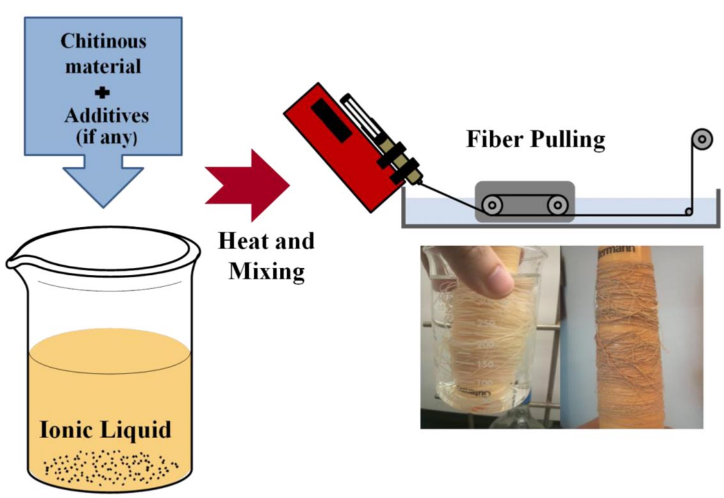

Fig. 4 Procedure for pulling chitin fibers directly from IL extracts of shrimp shells.

In the United States, the National Science Foundation-Small Business Innovation Research (NSF-SBIR) program provides ~$2 billion/year to small businesses, including start-ups for new technology and product development. This program represents one way that new "green" technology companies can demonstrate the viability of novel sustainable technologies. A new start-up company, 525 Solutions, Inc., being incubated at the Alabama Innovation and Mentoring of Entrepreneurs (AIME) [71] laboratories, is currently funded via an NSF-SBIR grant to develop antimicrobial chitin fibers which meet the specifications needed to make market entry. (525 Solutions has also won grants from the Department of Energy (DOE) SBIR program for lignocellulosic biomass processing.) However, chitin fibers for wound care are only a single example of the many chitin products the technology is capable of providing. The number of potential products may only be limited by one's imagination; however, each of these must be demonstrated to be cost-effective and have suitable markets before any new business opportunity can develop.

The chitin extraction process is currently the most costly step in the manufacturing of chitin-based products, and will therefore have a large impact on the overall production. The process will require large volumes of (currently) expensive ILs and in order for IL extraction to be economically feasible and a "green" process, recycle and recovery of the IL will be essential. Development of a single high-value product would allow starting with a higher-cost process and as the technology developed, cost would come down with process improvements.

Overall, the IL process platform allows a fuller exploitation of the potential of chitin and chitin-based products, and provides a safer, potentially environmentally neutral, and less-costly alternative pathway for the production of chitin and chitosan materials from seafood waste. Unlike the traditional processes, chitin compositions can be efficiently and reproducibly manufactured under environmentally friendly and sustainable conditions. These "better" products, designed using a green chemistry principle, might represent a transformative technology that has potential for creating many new business opportunities. We are currently pursuing these.

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