McGill Green Chemistry Journal

Volume 2 - 2016

Table of Contents

Fuels and Energy

Recycling

Synthesis

Chemical Processes

Letter from the Editors

It is a great honour to carry the torch of yesteryear's editors and publish the 2016 edition of the McGill Green Chemistry Journal. Green chemistry is both a field of research and a philosophy; one that values sustainability, renewability and efficiency as paramount within the context of a rapidly industrializing world. Although fewer in number, this year's collection of articles, fostered from the fresh minds of the McGill Green Chemistry class, continue to explore the many possible avenues where green chemistry may improve the world we live in.

Moreover, this year's articles span an especially wide gamut of current topics that are well worth developing, perhaps by readers like yourself: energy production, rare resource recovery and retention, green alternatives for petrochemicals, among others.

As green chemistry continues to grow in prominence, we hope that this journal can serve as a starting point for interested readers, be they scientists or the general public, to gain an interest and contribute to a more sustainable future.

We hope that you enjoy the read.

From the editorial team, thank you,

Editor in Chief - Arnold Downey

Associate Editors - Jill Bachelder, Joseph Marrett, and Pierre-Olivier Ferko

Making green fuels: algae as a feedstock for biodiesel

Karlie Potts*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada, H3A 0B8

KEYWORDS: Biodiesel, biofuel, algae, fossil fuels, feedstock

ABSTRACT: Given the rapidly decreasing accessibility of fossil fuels, an alternative feedstock for oil must be found. The replacement must be sustainable, economically viable, and abundant enough to meet the growing demand of fuels. There is a considerable amount of research encouraging the adoption of algae as a biomass feedstock for fuel. Algae have shown great potential due to their accessibility, abundance, and affordability. This article will aim to review the issues with first generation biofuels, the current processes in place for the production of algae biofuel, and the economic viability of its production.

INTRODUCTION

One of the largest impending threats today, is the scarcity of fossil fuels. Fossil fuels are used to fuel cars and airplanes, power electricity plants, and heat our homes[3]. As well, there are many subtle but critical uses like pharmaceuticals, cosmetics, plastics, and fabrics[3]. Today, it is predicted that fossil fuels will be extinct in 60 years[4]. Although this number is controversial, there is strong support for the development for of alternative technology. The scientific community has been looking towards natural sources of sugars and lipids, which may be converted to fuels by simple chemical reactions. A promising platform for the replacement of diesel is algae based biodiesel.

The term "algae" covers many different unicellular and multicellular organisms, which have one uniting feature; they lack true roots, stems and leaves, and a vascular system to regulate water and nutrients through their bodies[5]. Despite having a simple structure, algae have the ability to produce complex organic compounds from basic inorganic molecules using energy from photosynthesis, inorganic chemical reactions, and heterotrophic fermentation. The majority of algae live in aquatic habitats, thriving in both freshwater lakes and saltwater oceans. However, they have also been found on land in soil, snow, and desert crusts[6]. Algae were among the first organisms on Earth, dating back 2.7 billion years, playing a crucial role in the development of oxygen. Today algae produce between 75-80% of all oxygen on Earth. For the past 2.7 billion years algae have honed their ability to produce and store energy in the form of oil in the most efficient way.

Biodiesels are a type of biofuel, which can replace traditional fossil fuel based diesels. Algae are an attractive option because of their abundance, and the variation of how and where they can grow. Even under harsh, unfavorable conditions, algae can produce significant amounts of lipids[7]. Algae have been predicted to give a yield of 200 barrels of oil per hectare of land used to grow algae[7-8]. This is approximately 200 times the amount oil that corn can produce (1.08 barrels)[9]. The theoretical yield for algae is far larger than any other biodiesel feedstock[10]. Algae-based fuels have many advantages:

1) Algae can grow in all environments, allowing there to be minimal competition with agricultural land.
2) Algae have the largest potential yield of oil due to its rapid growth rate.
3) Algae consume carbon dioxide (CO_2) as they grow, releasing oxygen. This CO_2 could be provided by industrial sources.

Much of the past decade has been spent on determining the viability of algae biofuel, and acquiring the technology to scale up to industrial levels.

THE ISSUE WITH CURRENT FIRST-GENERATION BIOFUELS

First generation biofuels (FGBs) are made from the sugars and vegetable oils found in arable crops (sugar cane, corn, etc.). Despite being easily extracted using conventional technology they have important limitations[11]. FGB are unable to produce enough biodiesel without threatening food supply and biodiversity[12]. Also, they are not economically feasible. Current FGB depend on subsidies and are not cost competitive with existing fossil fuels[13]. These limitations prompt the development of second-generation biofuels (SGBs). SGBs focus on preventing agricultural competition and providing a cost effective method for the production of fossil fuels. Typically manufactured from various types of biomass, the extraction process is much more complex than FGBs.

VARIOUS CULTIVATION METHODS OF ALGAE

Algal biomass is made up of three main components: carbohydrates, proteins, and lipids. Their lipid content is between 16 and 75% (Table 1) dry weight, which is much higher than terrestrial plants, containing about 5% dry weight of oil[14].

Table 1: Oil Content of Algae Suitable for Biofuel Production

Microalga	Oil Content (% dry wt)
Botryococcus braunii	25-75
Chlorella sp.	28-32
Crypthecodinium cohnii	20
Cylindrotheca sp.	16-37
Nitzchia sp.	45-47
Phaeodactylum tricornutum	20-30

The bulk of natural oil made by algae is in the triglyceride form. These oils are long carbon chain molecules, which serve as a structural component of the algal cell membrane. There are optimal conditions that will maximize the production of lipids[15]. Algae require light, carbon dioxide, water, and inorganic salts to grow. Adequate amounts of nitrogen, phosphorus, and sulfur, as well as silica and iron are important nutrients for growth[16]. These nutrients can be monitored in one of the two main microalgal culture systems available.

Algae can be cultivated in either open ponds or photobioreactors. Open ponds are the most common system for algae cultivation, especially those with high oil content[8]. They are shallow ponds or tanks, which are circular and designed in a racetrack configuration (Fig. 1)[1], called parallel raceway ponds (PRPs)[17]. In this system, algae are cultured under conditions, which are similar to their natural environment. These systems are operated in a continuous mode, meaning that the water and nutrients are circulated and not left stagnant. This kind of system is economical, as it simple to set up, and does not require excessive maintenance. However, there are major drawbacks to an open system. There is often a lack of control, which results in poor light utilization by microalgal cells, evaporative losses, and poor uptake of CO_2[8, 14]. Open ponds often require a significant amount of land, which leaves it susceptible to environmental fluctuations[8], which can be difficult to control[18]. Finally, microorganism contamination restricts the size and productivity of open pond systems[19].

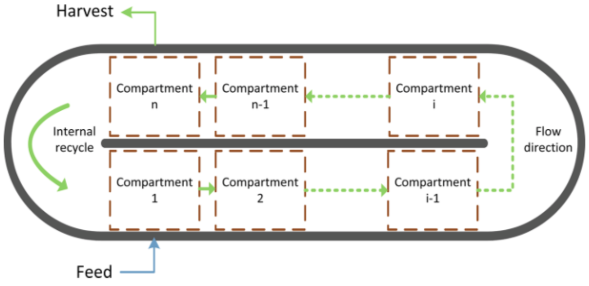


Figure 2: Typical Parallel Raceway Pond Design[1]

The second kind of microalgal culture system is photobioreactors (PBRs). This is often the choice of scientific and commercial algae production, as it is a closed system. PBRs were designed to overcome the contamination and evaporation problems which are encountered in open pond systems[18]. Environmental factors such as amounts of CO_2 and water, temperature, sunlight exposure, and pH, can be regulated for ideal growth conditions[20]. These systems are typically made of tubular transparent plastic vessels, which have a high surface area-to-volume ratio (Fig. 2)[2]. This allows increased exposure to the sun, encouraging elevated rates of photosynthesis[20]. The media is pumped through these tubes, ensuring all algae acquire the needed nutrition. PBRs require more maintenance than open ponds; oxygen and CO_2 levels must be monitored. The algal broth is periodically pumped into a degassing zone, which removes excess oxygen. Then before returning to the tubular vessels, CO_2 must be directed into the system.

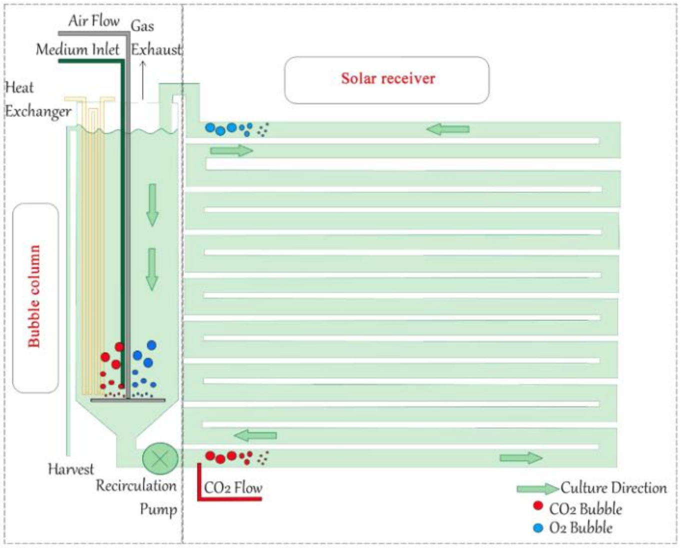


Figure 1: A Typical Photobioreactor Design[2]

Although the initial investment of a PBR is larger than an open pond, the productivity of a PBR is approximately 13 times larger than the open pond set-up[14]. Algae is produced in much larger concentrations in a PBR and is more economical to harvest[14]. Upon scale up of algae production, it would be best to integrate both systems features[7, 14].

FROM ALGAE TO BIOFUEL: THE PROCESS

Upon maturation of the algal colony, it must be harvested for further development into biofuel. There are two efficient methods to separate the algae; centrifugation or filtration[21]. Centrifugation is a process, which applies the centripetal force for the sedimentation of heterogeneous mixtures. It forms a pellet of algae biomass at the bottom of the solution. This method is extremely reliable and works for all kinds of algae[21]. The drawback of this method is its difficulty to scale up, and the amount of energy input required[21].

Filtration is an economical way to separate large algae from the medium it was grown in. It can be adapted to the larger forms of algae[22], by varying the pore size of the filter. However, it is difficult to ensure the algal mixture does not clog the filter.

Once the algae have been separated from its medium, it can be efficiently turned into oil. The most economical method is by means of an oil press. The oil press alone can extract up to

75% of oil from the algae being pressed[23]. The remaining algae biomass will be combined with hexane, which will extract another 20% of oil, in combination with the press removing 95% of oil[23]. These fractions will be combined and then filtered and washed. The obtained oil must then be refined through transesterification (Fig. 3). In transesterification, the triglyceride is combined with a mixture of methanol and sodium hydroxide, leading to methyl esters and glycerol[24]. The base used in transesterification deprotonates the alcohol, making it more nucleophilic. The carbonyl then undergoes attack by the incoming alkoxide, giving a tetrahedral intermediate. This can then proceed to the trans-esterified product, as it is energetically favorable. This is an efficient method, with high recovery of biofuel[14]. Considering transesterification does not require extremely harsh conditions (i.e. minimal temperature elevation), it is realistic to assume scale-up is possible. There is also the potential of catalytic conversion[25] to convert the triglyceride to methyl esters. Catalytic conversion can convert the lipids to a mixture of hydrocarbons very similar to that of gasoline[25]. However, this is not as well studied, and would likely cost more than simple transesterification[25].

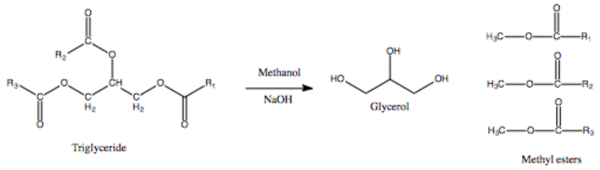


Figure 3: General Transesterification Scheme

ECONOMIC FEASIBILITY OF ALGAE BIOFUEL

In order to be a viable fuel option, algae biofuel must be competitive with the price of petroleum. Out of all renewable resources, algae shows the greatest potential for the production of renewable fuels[8]. Currently, there is no established plant, which can produce biofuel at an industrial scale (100 million gal/year). Therefore, the projected cost of algae based biofuel is speculative. The majority of the cost (65-70%) lies in the growth of the algae, with the chemical conversion processes accounting for the rest (35-40%)[26]. The cost is also highly dependent on the both the technique used to cultivate the algae and to separate it from the broth.

Solazyme Inc. is a renewable oil and bio-product company, based in San Francisco, which transforms a range of low-cost-plant-based sugars into oils. Solazyme's lead microalgae strains producing oil for fuels have achieved key performance metrics that they believe would allow them to manufacture oils today at a cost below $3.44 USD per gallon[8], if produced in an industrial setting. This is comparable and competitive to the cost of fossil fuel based oil at $3.01 USD per gallon.

There is hope that this value will continue to decrease as technology evolves and becomes more accessible. It is important to also consider the benefits of employing algae based fuels; reducing waste-water and consuming CO_2 from industrial applications. These two processes cost additional money and could be eliminated as a byproduct of algae growth.

CONCLUSION

The impending threat of the extinction of fossil fuels demands a solution. It is a problem, which cannot be neglected. Green chemistry aims to improve environmental impact in sustainable ways. Algae as a feedstock for biofuel have been shown to be greener than traditional fuel synthesis. They have demonstrated the ability to be economically viable, sustainable, and do not compete with agricultural production.

ACKNOWLEDGMENT

I would like to thank Dr. Audrey Moores and Dr. Robin Rogers for their guidance and support in the writing of this article. Also, Joe Marrett, and Jill Bachelder for the editing of this paper.

ABBREVIATIONS

First generation biofuels (FGBs), Second generation biofuels (SGBs), Parallel raceway ponds (PRPs), Photobioreactors (PBRs)

REFERENCES

(1) Malek, A.; Zullo, L. C.; Daoutidis, P., Modeling and Dynamic Optimization of Microalgae Cultivation in Outdoor Open Ponds. *Industrial & Engineering Chemistry Research* **2016,** *55* (12), 3327-3337.

(2) Fernández, I.; Acién, F. G.; Berenguel, M.; Guzmán, J. L., First Principles Model of a Tubular Photobioreactor for Microalgal Production. *Industrial & Engineering Chemistry Research* **2014,** *53* (27), 11121-11136.

(3) Association, N. M. O. a. G. What are fossil fuels used for? https://http://www.nmoga.org/what-are-fossil-fuels-used-for (accessed Dec. 1).

(4) Ecotricity The End of Fossil Fuels. https://http://www.ecotricity.co.uk/our-green-energy/energy-independence/the-end-of-fossil-fuels (accessed Dec. 2).

(5) Sheehan, J.; Dunahay, T.; Benemann, J.; Roessler, P., A look back at the US Department of Energy's aquatic species program: biodiesel from algae. *National Renewable Energy Laboratory* **1998,** *328*.

(6) Bold, H. C.; Wyynne, M. J., *Introduction to the algae: structure and reproduction*. Prentice Hall: 1978.

(7) Hu, Q.; Sommerfeld, M.; Jarvis, E.; Ghirardi, M.; Posewitz, M.; Seibert, M.; Darzins, A., Microalgal triacylglycerols as feedstocks for biofuel production: perspectives and advances. *The Plant Journal* **2008,** *54* (4), 621-639.

(8) Menetrez, M. Y., An Overview of Algae Biofuel Production and Potential Environmental Impact. *Environmental Science & Technology* **2012,** *46* (13), 7073-7085.

(9) Kurki, A.; Hill, A.; Morris, M.; Lowe, A., Biodiesel: The Sustainability Dimensions. *ATTRA- National Sustainable Agriculture Information Service* **2010**.

(10) Simmons, B. A.; Loque, D.; Blanch, H. W., Next-Generation biomass feedstocks for biofuel production. *Genome Biology* **2008,** *9* (242).

(11) Evans, G., International Biofuels Strategy Project. Liquid Transport Biofuels. *National Non-Food Crops Centre* **2008,** (Technology Status Report).

(12) Mohr, A.; Raman, S., Lessons from first generation biofuels and implications for the sustainability appraisal of second generation biofuels(). *Energy Policy* **2013,** *63*, 114-122.

(13) Eisentraut, A., Sustainable Producttion of Second-Generation Biofuels. *International Energy Agency* **2010**.

(14) Chisti, Y., Biodiesel from microalgae. *Biotechnology advances* **2007,** *25* (3), 294-306.

(15) Doucha, J.; Lívanský, K., Outdoor open thin-layer microalgal photobioreactor: potential productivity. *Journal of Applied Phycology* **2009,** *21* (1), 111-117.

(16) Grobbelaar, J. U., Factors governing algal growth in photobioreactors: the “open” versus “closed” debate. *Journal of Applied Phycology* **2008,** *21* (5), 489.

(17) Briggs, M., Widescale Biodiesel Production from Algae. *University of New Hanpshire Biodiesel Group* **2004**.

(18) E., M. G., Microalgae, mass culture methods. . *Encyclopedia of bioprocess technology: fermentation, biocatalysis, and bioseparation* **1999,** *3*.

(19) Sukenik, A.; Levy, R. S.; Levy, Y.; Falkowski, P. G.; Dubinsky, Z., Optimizing algal biomass production in an outdoor pond: a simulation model. *Journal of Applied Phycology* **1991,** *3* (3), 191-201.

(20) Lee, C.-G., Calculation of light penetration depth in photobioreactors. *Biotechnology and bioprocess engineering* **1999,** *4* (1), 78-81.

(21) Milledge, J. J.; Heaven, S., A review of the harvesting of micro-algae for biofuel production. *Reviews in Environmental Science and Bio/Technology* **2013,** *12* (2), 165-178.

(22) E, M. G.; EH, B.; FG, A. F.; A, R. M.; Y, C., Recovery of microalgal biomass and metabolites: process options and economics. *Biotechbol Adv.* **2003,** *20* (7).

23. Newman, S., How Algae Biodiesel Works. *How Stuff Works* **2008**.

(24) Anastopoulos, G.; Zannikou, Y.; Stournas, S.; Kalligeros, S., Transesterification of vegetable oils with ethanol and characterization of the key fuel properties of ethyl esters. *Energies* **2009,** *2* (2), 362-376.

(25) Beranek-Collins; G., A. Algae biofuels. https://wiki.uiowa.edu/display/greenergy/Algae+Biofuels (accessed Nov. 30).

(26) Howell, K., Exxon Sinks $600M Into Algae-Based Biofuels in Major Strategy Shift. *The New York Times* 2009.

Powering the future: a look at solid oxide fuel cell technology

Pierre-Olivier Ferko*

Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montréal, Québec H3A 0B8

KEYWORDS: Solid Oxide Fuel Cell, SOFC, Solid Oxide Electrolysis Cell, SOEC, Reversible, Hydrogen Gas, Yttrium-Stabilized Zirconia, YSZ

ABSTRACT: The staggering energy demands of the modern world will only intensify as the economies of developing countries grow. In this review, we introduce solid oxide fuel cell (SOFC) technology as a potential green solution to this looming dilemma, along with its close counterpart, the solid oxide electrolysis cell (SOEC). We review the recent research investigating the possibility of combining both cells into a single, reversible, and adaptable power generation unit.

INTRODUCTION

As worldwide energy demand continues to rise at a rapid pace, forecasts from the World Bank and International Energy Agency indicate that the current power supply will need to double by 2050 if recent trends continue.[1] Accordingly, much attention is being paid to finding green solutions to this increasingly imminent problem. Within the realm of research, the term "green" easily lends itself to consideration of biomass-derived options such as biofuels; however, inorganic and solid-state chemistry present an alternate option in the form of the solid oxide fuel cell (SOFC). SOFC technology has powerful proponents: in 2000, John B. Goodenough, famed inventor of the lithium-ion battery, devoted an article in *Nature* to SOFC technology and its vast potential market share.[2] Since then, rapid improvements have been made to this technology, and both large- and small-scale pilot projects have been demonstrated, ranging from broad utility power generation to specialized residential, commercial, and military uses.[3] Recently, reversal of the function of the SOFC, in order for it to serve as an electrolysis cell (SOEC) to reconstitute hydrogen gas and other fuels from water, have also garnered increased interest from an energy storage perspective; according to the Scopus© database, the amount of SOEC publications per year has increased tenfold between 2000 and 2015.[4] In the state of the art, reversible SOFC (RSOFC) technology that allows hybrid consumption and production of fuel on demand possesses great potential and warrants a closer look from a green chemistry perspective. This review aims to introduce the reader to SOFC, SOEC, and RSOFC technology in the context of future solutions to green power production.

SOLID OXIDE FUEL CELLS: A PRIMER

Whereas a traditional hydrogen fuel cell functions by conducting hydrogen protons from a cathode to an anode through an often-times liquid-phase electrolyte, an SOFC functions by conducting oxide ions from an anode to a cathode through a solid oxide or ceramic electrolyte. Oxide ion conductivity is achieved via the presence of anion deficiencies in the crystal structure of the electrolyte, permitting cascading travel of oxide ions. It is crucial that these deficiencies, also known as 'defects,' are randomly distributed and energetically equivalent along the crystal structure; otherwise, conductivity would decrease as some anionic sites would be preferentially occupied or vacant and result in an activation energy well for the oxide ions. A common crystal structure archetype in electrolytes meeting this criterion is that of fluorite, CaF_2, shown in Figure 1.

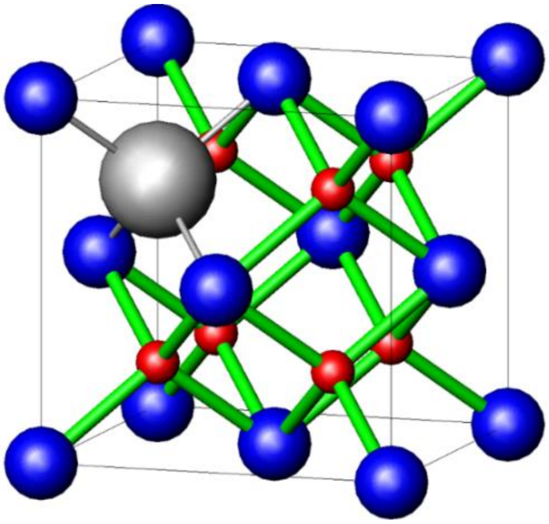


Figure 1. Crystal structure of a fluorite, CaF_2, with defects. Blue spheres represent Ca^{2+}, red spheres represent F^- and the grey sphere represents a 'defect' in the crystal structure.

The solid-state nature of the electrolyte confers many attractive properties to the fuel cell; particularly, high energy efficiencies exceeding 70% are readily achievable as a result.[5] Moreover, the durability of the solid-state electrolyte compared to liquid-phase electrolytes is quite remarkable, requiring little to no maintenance due to corrosion and allowing for many more design options from an engineering perspective.[6] Mobile oxide ions rather than protons also allow for fuel adaptability and tolerance when designing SOFCs; as they are procured from air and can oxidize natural and synthetic gas, the strict necessity of hydrogen gas to act as fuel at the anode no longer applies.[3]

Nonetheless, significant drawbacks are also accompanied by the use of the solid-state electrolyte. Yttria, zirconia, scandium and ceria are commonly used oxides in electrolyte components, often times doped with one another in various ratios to optimize conductivity, operating temperatures, and other technical properties.[4] Currently, yttrium-stabilized zirconia (YSZ) acts as the *de-facto* standard solid oxide electrolyte,[7] from a combined price and performance standpoint. While zirconia is a relatively common and available compound, yttrium is a rare earth element, posing a potential problem regarding its scarcity, as well as the extensive solvent extraction steps required to retrieve yttrium from xenotime, a prominent yttrium ore.[8] However, the United States Geological Survey notes that world yttrium reserves are likely "very large" nonetheless, albeit offering no guarantees of reasonable availability.[9] Scandium-stabilized zirconia (ScSZ) also performs very well as an oxide ion conductor, and in many cases better than YSZ, but rarity of scandium on earth sets a prohibitively high price point for applications beyond the laboratory [[10,11]]. Interestingly, Walther H. Nernst is credited for invention of YSZ in the late 1800s, which he then used to create the so-called Nernst glower, an early source of infrared radiation.[12] YSZ was subsequently used in the original SOFC developed by Baur and Preis in 1937;[13] soon after, the duo proposed plausible, albeit economically uncompetitive, plans to power the city of Berlin as a testament to the potential of their invention.

Another drawback is found in the high operating temperatures required for efficient conductivity and functionality of the SOFC, generally ranging from 400-1000 °C, depending on the solid electrolyte used.[14,15] Although these high temperatures prevent applications for some purposes, efforts to use the heat in tandem with other processes and cogeneration purposes, among which are solid oxide electrolysis cells (SOECs), have begun to shift the perception from drawback to feature.[14]

SOLID OXIDE ELECTROLYSIS CELL: THE OTHER SIDE OF THE COIN

Solid oxide electrolysis cells (SOECs) can be considered as simply the mirrored counterpart of the SOFC. The general model of an SOEC has water being fed to the cathode side (anode side of the SOFC), where it gets reduced to hydrogen gas and oxide ions; the latter travels across the solid electrolyte to the anode (cathode side of the SOFC) to then produce oxygen gas, affording the net hydrolysis of water in exchange for energy. Depending on the SOEC in question, atmospheric carbon dioxide can also be fed to the cell to obtain synthetic gas.[4] Given the shared need to conduct oxide ions, many of the electrolytes used in SOFCs are used in SOECs: YSZ, ScSZ and the like are popularly used, with YSZ continuing to be the most common.[16] Notably, Uchida et al. determined that ceria-containing electrolytes are unsuitable for electrolytic purposes as the high voltage applied between the electrodes invariably reduces Ce^{4+} to Ce^{3+}, decreasing the oxide ion conductivity significantly [[17]].

Hydrolysis of water becomes increasingly endothermic as temperatures increase.[16] Consequently, SOECs can attain extremely high efficiencies as the heat generated from the cell can be consumed in the electrolysis reaction and reduce electrical energy demand. Optimal operation of the SOEC at the thermoneutral potential – at which the generated heat is equal to the heat consumption of the electrolysis reaction – can reach a theoretical energy conversion efficiency of 100%.[16] As a result, SOECs are remarkably efficient when compared with low temperature electrolysers despite being less mature technologically.[16] In 2009, Wang et al. reported an SOEC efficiency of 98% at 650 °C using ScSZ as electrolyte,[18] whereas low temperature electrolysers such as alkaline and polymer electrolyte membrane (PEM) reach 80% and 83.4% respectively.[4] However, when the thermal source is taken into consideration as well, SOEC efficiency generally drops down to the whereabouts of 60%.[19] Nonetheless, increases in efficiency due to high operating temperatures inherent in SOECs effectively result in approximately two-thirds lower running costs when compared to low-temperature alternatives.[4]

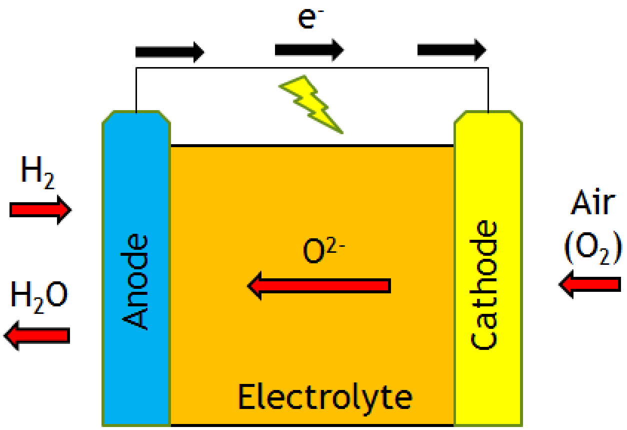


Figure 2. A simplified diagram of a Solid Oxide Fuel Cell (SOFC).

REVERSIBLE OXIDE FUEL CELLS: COMBINED ARMS

Potential combination of both SOFC and SOEC technology into a single, reversible unit (RSOFC) presents many advantageous properties for future energy production. Specifically, the ability to use biofuel to generate clean electricity while being able to also produce synthetic gas for long-term storage as the situation demands is greatly desirable.[4] Promisingly, work performed at the European Institute for Energy Research (EIfER) determined similar cell impedances for both SOFCs and SOECs, which spurred further probing into reversibility of one to afford the other.[4] Currently, however, RSOFC technology is in its infancy and is restricted mainly to laboratory scale. Advances in SOEC technology are currently seen as most important for further development of RSOFCs; challenges relating to SOECs are more pronounced and less addressed by the research community, compared to the more popular SOFCs.[4] Specifically, long-term degradation of the SOEC is a serious concern; Hauch et al. reported a 2% degradation of the Ni/YSZ oxygen electrode after 1300 hours of operation due to the high voltages required.[20] Additionally, there are roughly ten times more SOFC publications than SOEC per year between 2000 and 2015.[4] Unique to the RSOFC, however, are many challenges inherent to the combination at hand; functionality of the oxygen electrode (generally Ni/YSZ) in both forward and reverse modes and efficient design for the cell stand chiefly among them as of this writing.

ECONOMICS AND VIABILITY

In the context of green chemistry, it is important that real world concerns are considered. Fortunately in this regard, both SOFC and SOEC technologies have been examined in pilot projects of varying scales, from broad utility power generation to residential purposes.[3] As mentioned earlier, Baur and Preis quickly considered real world applications after having invented the SOFC in 1937. They proposed a plan for an SOFC power generation scheme for Berlin's "power station west" goal of 234 Marks/kWh; although they were only able to attain 1000 Marks/kWh, they concluded nonetheless that practical and space-efficient SOFC power generation was indeed possible, nearly a century ago.[21]

Recent years have been more promising in comparison. The University of Malaya in Kuala Lumpur completed a year-long economic analysis conducted at various regions around the world that considered an ideal RSOFC, working 2920 hours in SOEC mode and 2815.2 hours in SOFC mode for a hybrid photovoltaic system, and reported an electricity cost of 0.068 USD/kWh.[22] Competing renewable energy systems using solar-wind-diesel and diesel attained 0.438 and 0.510 USD/kWh respectively; in this case, the diesel was not noted as "biodiesel," but was used for price-comparison with renewable methods. The researchers also report that the geographical locations of these power generators were of large importance in harnessing solar energy efficiently and stressed the need for hybrid, adaptable systems.[22] In the same light, usage of SOECs to produce synthetic gasoline from atmospheric carbon dioxide via the Fischer-Tropsch synthesis can attain a market value of approximately $2 (USD)/gal.[4] In fact, it may already be economical to do so in countries with inexpensive renewable energy such as Iceland.[4] However, a large barrier to entry in current SOFC, SOEC, and RSOFC technology remains in the initial capital investment, largely due to expensive nature of the machinery involved in storing and using hydrogen. For a hybrid solar-SOFC system, a return on investment can be expected in up to 25 years.[1] Hybrid wind-diesel and solar-wind-diesel, on the other hand, require 3-4 and 6-7 years, respectively.[22]

CONCLUSION AND FINAL THOUGHTS

Summarily, SOFC and SOEC technology have been introduced in this review and discussed in terms of their advantageous and disadvantageous properties. Recent advances and trends were touched on, and economic viability was compared with renewable energy competitors in the solar, wind, and diesel domains. Although RSOFC technology seems quite promising and idealized models show it close to becoming profitable (and in some countries already is), it may be more effective to focus individually on SOFC and SOEC technology in the interim. RSOFC advancement is currently restricted by the latter for the time being in any case, and daunting challenges still exist in both SOFC and SOEC technology. That being said, there certainly exists intriguing economic potential for renewable energy production via SOFC technology that will surely bear fruit given continuation of current publication trends.

AUTHOR INFORMATION

Corresponding Author

* Pierre-Olivier Ferko; pierre-olivier.ferko@mail.mcgill.ca

ACKNOWLEDGMENT

We would like to thank Professors Robin Rogers and Audrey Moores for their guidance, along with the Fall 2016 class of CHEM 462 at McGill University for their support.

REFERENCES

(1) Türkay, B. E.; Telli, A. Y. *Renew. Energy* **2011**, *36*, 1931–1943.

(2) Goodenough, J. B. *Nature* **2000**, *404* (6780), 821–823.

(3) Stambouli, A. B.; Traversa, E. *Renew. Sustain. Energy Rev.* **2002**.

(4) Gómez, S. Y.; Hotza, D. *Renewable and Sustainable Energy Reviews*. **2016**.

(5) Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414* (6861), 345–352.

(6) Minh, N. Q. *J. Am. Ceram. Soc.* **1993**, *76* (3), 563–588.

(7) Tao, S.; Irvine, J. T. S. *Nat. Mater.* **2003**, *2* (5), 320–323.

(8) Reuter, M.; Oyj, O.; Hudson, C.; van Schaik, A.; Heiskanen, K.; Meskers, C.; Hagelüken, C. *Metal Recycling: Opportunities, Limits, Infrastructure, A Report of the Working Group on the Global Metal Flows to the Inter- national Resource Panel*; **2013**.

(9) National Minerals Information Center, U. Yttrium http://minerals.usgs.gov/minerals/pubs/commodity/rare_earths/mcs-2012-yttri.pdf (accessed Dec 2, 2016).

(10) Virbukas, D.; Laukaitis, G.; Dudonis, J.; Katkauskė, O.; Milčius, D. *Solid State Ionics* **2011**, *184* (1), 10–13.

(11) Wang, W.; Cheng, C. Y. *J. Chem. Technol. Biotechnol.* **2011**, *86* (10), 1237–1246.

(12) Kilner, J. A. *Nat. Mater.* **2008**, *7* (11), 838–839.

(13) Baur, E.; Preis, H. *Elektrochem* **1937**, *43*, 727–732.

(14) Singhal, S. . *Solid State Ionics* **2000**, *135* (1), 305–313.

(15) Meng, X.; Zhan, Z.; Liu, X.; Wu, H.; Wang, S.; Wen, T. *Low-temperature ceria-electrolyte solid oxide fuel cells for efficient methanol oxidation*; **2011**; Vol. 196.

(16) Laguna-Bercero, M. A. *Journal of Power Sources*. 2012.

(17) Uchida, H.; Osada, N.; Watanabe, M. *Electrochem. Solid-State Lett.* **2004**, *7* (12), A500.

(18) Wang, Z.; Mori, M.; Araki, T. *Int. J. Hydrogen Energy* **2010**.

(19) Holladay, J. D.; Hu, J.; King, D. L.; Wang, Y. *Catalysis Today*. **2009**.

(20) Hauch, A.; Ebbesen, S.; Jensen, S.; Mogensen, M. *J. Electrochem. Soc.* **2008**, *155* (11).

(21) Hoogers, G. *Fuel Cell Technology Handbook*; CRC Press, **2002**.

(22) Akikur, R. K.; Saidur, R.; Ping, H. W.; Ullah, K. R. *Renewable and Sustainable Energy Reviews*. **2013**.

Harnessing Renewable Energy from the Ocean as an Alternative Energy Source of Nuclear Energy

Alan An Jung Wei*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada, H3A 0B8.

KEYWORDS: Marine energy, nuclear energy, renewable, tidal power

ABSTRACT: Nuclear energy has been considered as the alternative energy source since the oil crisis took place in 1973[i]. Countries that relied heavily on fossil fuels switched their gear and invested more on the development of nuclear energy[ii]. As of 2015, there are 440 operating nuclear reactors generating a net capacity over 390,000 megawatts of electricity[iii]. It may seem to be a feasible alternative energy source to fossil fuels, but considering all the different aspects, nuclear energy is not a green energy source whatsoever. Aside from the threats it poses to the environment, recent accidents[iv] that contributed to nuclear leaks in the environment have the general public re-consider the safety of nuclear energy, as seven reactors have been permanently shut down since the year of 2015[v]. Marine energy that has incredible potential to be harnessed from the oceans, which covers up to seventy percent of the surface on Earth[vi], provides a future opportunity of being the optimal candidate of the renewable energy source. Methods to harness marine energy to apply it widely in terms of its usage will be discussed in this paper.

1. Introduction

Development of nuclear energy took the first step as one of the most well known physicists, Ernest Rutherford, discovered that an immense amount of energy could be released when atoms were split by protons from a proton accelerator[7]. In 1954, the Obninsk Nuclear Power Plant became the first nuclear power plant to generate electricity on a large scale where around five megawatts of power was produced[8]. Not long after, the oil crisis that took place in 1973 had also led countries like France and Japan to invest more on nuclear energy[9].

With the increasing dependence on nuclear energy, the voice of the opposition has also gone up in numbers, more and more by each year[10], as the public sees it from not being part of a solution[11] to being part of the problem[12]. Despite the proponents claim that nuclear energy produces less carbon dioxide emission and also an efficient energy source in terms of combating global warming, numbers of catastrophic accidents have proven it wrong. The 1979 accident at Three Mile Island, the 1986 Chernobyl disaster, and the most recent Fukushima accident in 2011 all acted as wake-up calls and indicators of how power generated by nuclear fission is not as green as it was originally thought[13], especially after the consequences it had cost and the concerning effects on human health and the environment.

The current storage of nuclear waste in Canada has claimed to be safe for interim storage[14]. However, leaked radiation and the harm it poses to the environment are also not considered green. This also has not taken into consideration of earthquakes and tsunamis caused by tectonic plate movement, as the frequency of occurrences and the harm can be quite unpredictable.

An alternative, renewable, and green energy source known as the marine energy has been greatly discussed by the general public[15]. The energy is stored in oceans partly as thermal energy and kinetic energy, and therefore harnessing renewable energy from the massive ocean that takes up to seventy percent of the total area on Earth has shown to be a promising and feasible technology that deserves more attention and applications[16].

2.1 Current Situation

Thirty-one countries currently operate nuclear energy as one of the energy sources. Out of all the countries on the list, four standouts, France, Hungary, Ukraine, and Slovakia have over half of their energy depended on nuclear energy[17]. This leads to another controversy, that is, the location and the method of waste storage. Proper handling of nuclear waste needs careful consideration and there is no guarantee of success, contrary to what the general population is told to believe. Despite the fact that nuclear energy engineers have claimed that more advanced and safer design of reactors has been implemented, it is difficult to observe what can possibly happen at larger time scales due to the long half-life of the radioisotopes, making it another safety issue of a long-term waste management[18].

2.2 Wake Up Call – An Urgent Call for an Alternative Source

A nuclear or radiation accident is an event that has led to significant consequences towards people, the environment or a facility according to International Atomic Energy Agency[19]. Fatal accidents that cause civilian casualty, damage to the living land, and damages to human health are clear evidences of the negative impact. A scale that takes measurement of the severity of a nuclear accident, International Nuclear and Radiological Event Scale (INES), have reported two level 7, the highest level of danger of nuclear accidents. Chernobyl and Fukushima are the two examples.

Uranium serves as one of the most important energy minerals, especially for energy powered by nuclear fission[20]. Mining for uranium however has brought up several controversies. The mining industry indicates an association between uranium mining and the chance of having lung cancer[21]. Not only does mining for uranium pose health threats to the workers, the negative and detrimental harm to the environment at the same time need to be taken into consideration. Contamination to the ground water can be detected at mining sites.[22] Heavy metals traces residuals in the soil also have a direct negative impact to the organisms, as soil macro-invertebrates have a three to thirty-seven lower abundance and biodiversity at the contaminated sites compared with an uncontaminated one[23].

Despite the fact that the safety and the operation of nuclear plants seem to be controllable by humans and the operating companies claim that nuclear waste is stored in very safe conditions and the radiation leaks have been minimized to not pose a threat, uncontrollable factors such as earthquakes and natural disasters that are caused by the tectonic plate movements can drastically initiate an uncontrollable disaster. Studies have been done on the concerns of the melting of the nuclear power plant core due to earthquakes in the late 1980s[24].

3.1 Marine Energy Now

Unlike nuclear energy where an immense amount of water required to cool of the nuclear reactors and where billions of microorganisms are being killed, generating electricity from the greatest body of water and not wasting the treasurable water resources is a possible method of energy generation provided by marine energy. Marine energy offers an applicable and feasible substitution to nuclear energy. The carbon dioxide emission is significantly reduced, as mining for energy minerals and extracting material is not required. The safety would increase exponentially due to the fact that there would not be nuclear waste in need to be stored and controlled. Marine energy has shown to be an alternative to nuclear power in both a socio-economical and environmental perspective.

The current energy demand worldwide is 17,500 Terawatts and the potential energy that can be harnessed from marine energy is 20,000 to 80,000 Terawatts by changes in ocean temperatures, salt content, movements of tides, currents, waves and swells[25]. With a non-negligible amount of energy, research to fully operate it to its full potential and allow it to be more feasible has been widely conducted.

3.2 Forms of Marine Energy

There are a great number of possible forms of marine energy. In this paper what will be focused on is the currently operating tidal power, and the potential large scale operating forms including ocean thermal power and wave power.

3.3.1 Tidal Power

Tides occur naturally in the oceans. As previously mentioned, seventy percent of Earth surface contributed by the oceans create massive number of possibilities and potential. Despite still being at the early stage of developing, there are currently seven operating tidal power stations in the world. Life cycle Impact Analysis has shown that tidal power has on average 115 times lower impact on climate change than electricity generated from coal power[26]. Two notable currently operating tidal power stations generate over two hundred Megawatts of electricity, one being Rance Tidal Power Station in France and the other one being Sihwa Lake Tidal Power Station in South Korea[27]. Upcoming constructions that would begin operating within the next five years are mainly located in Russia, the United Kingdom, and South Korea[28]. Penzhinskaya Tidal Power Plant even sets up a goal to generate over 87,000 Megawatts of power, making it the largest tidal power station once the operation begins[29].

3.3.2 Forms of Tidal Power

Methods of generation of tidal power are divided up to four different categories. There are Tidal stream generator, Tidal barrage, Dynamic tidal power, and Tidal Lagoon.

3.3.3 Tidal Stream Generator

Similar to the wind turbine that is responsible for wind power, tidal stream generator works in a way where the moving water to power turbines generate kinetic energy that can be harnessed[30]. A tidal stream generation needs a ring-cam diameter the same as the root, variable-displacement and the ability to take bearing loads[31].

Selecting optimal operating sites greatly increases the efficiency and the energy harnessed from the tides. Tidal stream systems work best at areas where fast currents and natural flows are concentrated[32].

3.3.4 Tidal Barrage

Generating electricity from the difference in water depth is the method used in tidal barrage. Between high and low tides, potential energy can be used to generate power. When the tide comes in, an increase in tidal power is held within a large basin behind the dam, and with receding tide the energy is converted into mechanical energy as the water is being released through the large turbines[33].

Tidal Barrage has shown promising results, as both of the largest operating tidal power stations, Sihwa Lake Tidal Power Station and Rance Tidal Power Station generate electricity of over two hundred Megawatts with this method.

3.3.5 Dynamic Tidal Power

Dynamic Tidal Power (DTP) generates power by the tidal difference between both sides of a hydraulic structure built perpendicular to a coastline[34]. Tidal phase differences are introduced across long dams, ranging from thirty to fifty kilometers in length, without an enclosed area. Power stations that follow this idea are proposed to be built at coasts where strong coast-parallel oscillating tidal currents can be found giving the most optimal outcome[35].

Benefit of Dynamic Tidal Power is that a single dam can accommodate over eight thousand Gigawatts of installed capacity, which equals to the electricity supply needed by 3.4 million Europeans per year[36]. This method does not require a very high natural tidal range, meaning that it is not a very limited method and the total availability would be high for countries with suitable conditions, like Korea, China, and the United Kingdom would have a potential to generate between eighty to one hundred and fifty Gigawatts[37].

3.3.6 Tidal Lagoon

In terms of generating power, tidal lagoon follows a similar concept as tidal barrage. By creating a head difference, water is allowed to pass through turbines when gates are open[38]. The difference from tidal barrage is the structure. Tidal lagoon harnesses its power from an artificial ecosystem, meaning without the preexisting naturally occurring conditions[39].

The first proposed to-be-built project using the Tidal Lagoon method is in Swansea Bay, Wales. Once the operation starts it would be the very first Tidal Lagoon Power Plant and it is expected to have a capacity of three hundred and twenty Megawatts[40].

3.4 Ocean Thermal Energy

Ocean thermal energy conversion utilizes the temperature difference between the surface water and the deep ocean, with a temperature difference of around twenty-degree Celsius and a height difference of a thousand meters.[41] A heat engine would work better with a greater temperature difference, and therefore the proposed ocean thermal energy conversion (OTEC) plant would yield better results at a tropic ocean[42].

OTEC is classified by three different cycles. A closed-cycle uses fluid with a relatively low boiling point to power a turbine to generate electricity. Warm surface seawater is pumped through a heat exchange to vaporize the fluid[43]. An open-cycle OTEC uses warm surface water to generate electricity directly. The warm water is first pumped into a low-pressure container that causes boiling, and then the vapour drives a low-pressure turbine attached to the electrical generator[44]. A hybrid cycle combines the two, where warm seawater enters a chamber and is instantly evaporated, and the steam then vaporizes the fluid with a low boiling point to generate electricity[45].

In 2015, a small but operational closed-cycle ocean thermal energy plant was inaugurated. At the early stage of development, the power plant yields an impressive result where one hundred and five kilowatts of power is produced, which supplies over one hundred homes in Hawaii.[46]The thermal efficiency of OTEC shows that it is at the early stage of development, however this shows a promising result and creates possibilities for the future.

3.5 Wave Power

The wind causes waves on the ocean surface[47]. The fluid dynamics it causes can be harnessed to generate electricity[48]. This is how the concept of wave power works. The idea of converting the energy of ocean surface waves into useful energy to humans is not a brand new concept. In fact it can be dated back to 1799 where the first patent can be found[49]. By 1980 there were more than a thousand registered patents regarding the various techniques of ocean wave energy generation[50]. The research and development has gained the support of the European Commission in 1986 where the evolution of wave energy field was observed[51]. Later on in 1999 the European Commission had even decided to include wave energy in their renewable energy program[52].

Hydrodynamics explain the physical concept behind wave energy conversion. The idea is to extract energy from a floating oscillating body from a regular sinusoidal wave[53]. With this fundamental idea, various methods were developed. Oscillating water column where an air turbine is installed, oscillating bodies where a hydraulic motor and a turbine generates electricity, and overtopping method where a low-head hydraulic turbine is used[54]. To ensure maximum power absorption, a wave power converter (WEC) should respond in resonance with the waves such that the exciting force and the response velocity are in phase[55].

There are currently four operating wave farms that harness energy from wave power, countries include United Kingdom, Spain, the United States, and Israel. Proposed projects of constructing wave farms can be seen in Denmark, Belgium, The Netherlands, Australia, Ireland, Finland, and Germany[56].

3.6 Challenges of Marine Power

Marine power shows a great number of advantages. In this paper, promising results from the current operating marine power plants and the beneficial effects the marine power introduces to the environment once again emphasizes the importance and the feasibility of replacing nuclear power.

However, a few drawbacks of marine power requires further discussion and more research on the solutions would need to be discovered. The possible contamination during the construction process of marine power plants requires further assessment to ensure no harm is done to the marine animals[57]. Furthermore, the current state of knowledge regarding the potential harms that the sound emission and the electromagnetic field generated by the power plants can do to the marine animals is still very limited[58]. In order to convince and implement this method to its full potential, more research has to be conducted.

4. Conclusion

Society needs a new energy source, one that is green, renewable, and generated from safe sources. Nuclear power indeed proves to not be a sustainable energy source due to all the threats it brings to humans and the environment. Lessons need to be learned, as catastrophic accidents were clearly illustrated in history, the urgency of replacing nuclear energy source with a more feasible and friendly technology needs to be implemented.

Marine energy, on the other hand, does offer a safer way of generating cleaner energy, without causing harms to humans and the environment. Using ocean to generate power guarantees a source that would not run out. Numerical data provided in this paper shows a steady growth and a promising pace of development, as more projects and investments are put into implementing the ideas and replacing the nonrenewable energy with new technologies simultaneously.

AUTHOR INFORMATION

*Alan An Jung Wei
an-jung.wei@mail.mcgill.ca

REFERENCES

(1) Verbong, G.Geels, F. The Ongoing Energy Transition: Lessons From A Socio-Technical, Multi-Level Analysis Of The Dutch Electricity System (1960–2004). *Energy Policy* **2007**, *35*, 1025-1037.

(2) Beder, S. Electricity Industry in Japan http://www.herinst.org/sbeder/privatisation/japan.html (accessed Nov 5, 2016).

(3) Nuclear Power Today | Nuclear Energy - World Nuclear Association http://www.world-nuclear.org/information-library/current-and-future-generation/nuclear-power-in-the-world-today.aspx (accessed Nov 5, 2016).

(4) Selimbegović, L.; Chatard, A.; Er-Rafiy, A.; Pyszczynski, T. Nuclear Accident Reminders And Support For Nuclear Energy: Paradoxical Effect. *Journal of Environmental Psychology* **2016**, *48*, 87-100.

(5) A Bunch of Nuclear Power Plants Are Closing, and It's Because of Fracking http://motherboard.vice.com/read/a-bunch-of-nuclear-power-plants-are-closing-and-its-because-of-fracking (accessed Nov 8, 2016).

(6) How much water is in the ocean? http://oceanservice.noaa.gov/facts/oceanwater.html (accessed Nov 8, 2016).

(7) Kumar, M. The man who went nuclear: How Ernest Rutherford ushered in the atomic http://www.independent.co.uk/news/science/the-man-who-went-nuclear-how-ernest-rutherford-ushered-in-the-atomic-age-2230533.html (accessed Nov 8, 2016).

(8) Hwang, I.; Jeong, S.; Park, B.; Yang, W.; Suh, K.; Kim, C. The Concept Of Proliferation-Resistant, Environment-Friendly, Accident-Tolerant, Continual And Economical Reactor (PEACER). *Progress in Nuclear Energy* **2000**, *37*, 217-222.

(9) Kohl, W. *After The Second Oil Crisis*; Lexington Books: Lexington, Mass., **1982**.

(10) For First Time, Majority in U.S. Oppose Nuclear Energy http://www.gallup.com/poll/190064/first-time-majority-oppose-nuclear-energy.aspx (accessed Nov 8, 2016).

(12) Costanza, R.; Cleveland, C.; Cooperstein, B.; Kubiszewski, I. Can Nuclear Power Be Part Of The Solution?. *The Solutions Journal* **2011**, *2*, 29-31.

(13) Selimbegović, L.; Chatard, A.; Er-Rafiy, A.; Pyszczynski, T. Nuclear Accident Reminders And Support For Nuclear Energy: Paradoxical Effect. *Journal of Environmental Psychology* **2016**, *48*, 87-100.

(14) Safe and Secure Transportation of Canada's Used Nuclear Fuel https://www.nwmo.ca/~/media/Site/Files/PDFs/2015/11/04/17/39/2620_safe_and_secure_transportation_of_canadas_used_nuc.ashx?la=en (accessed Nov 8, 2016).

(15) How the UK public feels about renewable energy http://www.climatexchange.org.uk/files/9913/7655/7802/Shaping_our_Energy_Future_-_How_the_public_feels_about_renewable_energy.pdf (accessed Nov 8, 2016).

(16) Elghali, S.; Benbouzid, M.; Charpentier, J. Marine Tidal Current Electric Power Generation Technology: State Of The Art And Current Status. *Electric Machines & Drives Conference, **2007**. IEMDC '07. IEEE International* 2007, 1407-1412.

(17) Nuclear Share of Electricity Generation in 2015 https://www.iaea.org/PRIS/WorldStatistics/NuclearShareofElectricityGeneration.aspx (accessed Nov 7, 2016).

(18) Diaz-Maurin, F.Kovacic, Z. The Unresolved Controversy Over Nuclear Power: A New Approach From Complexity Theory. *Global Environmental Change* **2015**, *31*, 207-216.

(19) The International Nuclear and Radiological Event Scale https://web.archive.org/web/20110515164252/http://www-pub.iaea.org/MTCD/publications/PDF/INES-2009_web.pdf (accessed Nov 8, 2016).

(20) Uranium Mining Overview http://www.world-nuclear.org/information-library/nuclear-fuel-cycle/mining-of-uranium/uranium-mining-overview.aspx (accessed Nov 7, 2016).

(21) Samet, J.; Kutvirt, D.; Waxweiler, R.; Key, C. Uranium Mining And Lung Cancer In Navajo Men. *New England Journal of Medicine* **1984**, *310*, 1481-1484.

(22) Clausen, G.Archibald, J. Uranium Mill Tailings As Backfill In Underground Uranium Mines. *Mining Science and Technology* **1983**, *1*, 69-75.

(23) Gongalsky, K. Impact Of Pollution Caused By Uranium Production On Soil Macrofauna. *Environmental Monitoring and Assessment* **2016**, *89*, 197-219.

(24) Nosowitz, D. How Nuclear Reactors Work, And How They Fail http://www.popsci.com/science/article/2011-03/whats-happening-japans-nuclear-power-plants (accessed Nov 8, 2016).

(25) Energy Technology Initiatives http://web.archieve.org/techinitiatives/renewableenergy/ocean (accessed Nov 5, 2016).

(26) Douziech, M.; Hellweg, S.; Verones, F. Are Wave And Tidal Energy Plants New Green Technologies?. *Environmental Science & Technology* **2016**, *50*, 7870-7878.

(27) Tidal giants - the world's five biggest tidal power plants http://www.power-technology.com/features/featuretidal-giants--- the-worlds-five-biggest-tidal-power-plants-4211218/ (accessed Nov 8, 2016).

(28) Ragjor, G. Tidal developments power forward - Renewable Energy Focus http://www.renewableenergyfocus.com/view/43898/tidal-developments-power-forward/ (accessed Nov 8, 2016).

(29) Kowalik, Z. Tide Distribution And Tapping Into Tidal Energy. *OCEANOLOGIA* **2004**, *46*, 291-331.

(30) Orme, J.Masters, I. Analysis And Comparison Of Support Structure Concepts For Tidal Stream Turbines. *Proceedings of World Maritime Technology Conference* **2006**.

(31) Salter, S. Proposal For A Large, Vertical-Axis Tidal-Stream Generator With Ring-Cam Hydraulics. *Third European Wave Energy Conference* **1998**.

(32) Hardisty, J. *The Analysis Of Tidal Stream Power*; Wiley: Chichester, UK, **2009.**

(33) O Rourke, F.; Boyle, F.; Reynolds, A. Tidal Energy Update **2009**. *Applied Energy* 2010, *87*, 398-409.

(34) Park, Y. Analysis Of Characteristics Of Dynamic Tidal Power On The West Coast Of Korea. *Renewable and Sustainable Energy Reviews* **2016**, *68*, 461-474.

(35) Wave & Tidal Energy Technology | Renewable Northwest http://www.rnp.org/node/wave-tidal-energy-technology (accessed Nov 8, 2016).

(36) Tousif, S.Taslim, S. Tidal Power: An Effective Method Of Generating Power. *International Journal of Scientific & Engineering Research* **2011**, *2*, 1-5.

(37) Tousif, S.Taslim, S. Tidal Power: An Effective Method Of Generating Power. *International Journal of Scientific & Engineering Research* **2011**, *2*, 1-5.

(38) Waters, S.Aggidis, G. A World First: Swansea Bay Tidal Lagoon In Review. *Renewable and Sustainable Energy Reviews* **2016**, *56*, 916-921.

(39) Tidal: Capturing tidal fluctuations with turbines, reciprocating devices, kites, screws, barrages, or lagoons https://tethys.pnnl.gov/technology-type/tidal (accessed Nov 8, 2016).

(40) Swansea Bay - Tidal Lagoon http://www.tidallagoonpower.com/projects/swansea-bay/ (accessed Nov 8, 2016).

(41) Afgan, N.Carvalho, M. Multi-Criteria Assessment Of New And Renewable Energy Power Plants. *Energy* **2002**, *27*, 739-755.

(42) DiChristina, M. Ocean Planet: Popular Science - Sea Power http://seawifs.gsfc.nasa.gov/OCEAN_PLANET/HTML/ps_power.html (accessed Nov 8, 2016).

(43) Uehara, H.Ikegami, Y. Optimization Of A Closed-Cycle OTEC System. *Journal of Solar Energy Engineering* **1990**, *112*, 247.

(44) Ocean Thermal Energy Conversion using the Oceans Energy http://www.alternative-energy-tutorials.com/energy-articles/ocean-thermal-energy-conversion.html (accessed Nov 8, 2016).

(45) Ocean Thermal Energy Conversion Basics http://energy.gov/eere/energybasics/articles/ocean-thermal-energy-conversion-basics (accessed Nov 8, 2016).

(46) Vyawahare, M. Hawaii First to Harness Deep-Ocean Temperatures for Power https://www.scientificamerican.com/article/hawaii-first-to-harness-deep-ocean-temperatures-for-power/ (accessed Nov 8, 2016).

(47) NDBC - Science Education - What causes ocean surface waves? http://www.ndbc.noaa.gov/educate/pacwave.shtml (accessed Nov 8, 2016).

(48) Making waves: Turning ocean power into electricity http://engineering.berkeley.edu/2016/03/making-waves-turning-ocean-power-electricity (accessed Nov 8, 2016).

(49) Clément, A.; McCullen, P.; Falcão, A.; Fiorentino, A.; Gardner, F.; Hammarlund, K.; Lemonis, G.; Lewis, T.; Nielsen, K.; Petroncini, S. et al. Wave Energy In Europe: Current Status And Perspectives. *Renewable & Sustainable Energy Reviews* **2002,** 405-431.

(50) McCormick, M. A Modified Linear Analysis Of A Wave-Energy Conversion Buoy. *Ocean Engineering* **1976**, *3*, 133-144.

(51) Clément, A.; McCullen, P.; Falcão, A.; Fiorentino, A.; Gardner, F.; Hammarlund, K.; Lemonis, G.; Lewis, T.; Nielsen, K.; Petroncini, S. et al. Wave Energy In Europe: Current Status And Perspectives. *Renewable & Sustainable Energy Reviews* 2002, 405-431.

(52) Falcão, A. Wave Energy Utilization: A Review Of The Technologies. *Renewable and Sustainable Energy Reviews* **2010**, *14*, 899-918.

(53) Falcão, A. Wave Energy Utilization: A Review Of The Technologies. *Renewable and Sustainable Energy Reviews* **2010**, *14*, 899-918.

(54) Falcão, A. Wave Energy Utilization: A Review Of The Technologies. *Renewable and Sustainable Energy Reviews* **2010**, *14*, 899-918.

(55) Shim, J.; Park, C.; Wilding, M. Identifying Policy Frames Through Semantic Network Analysis: An Examination Of Nuclear Energy Policy Across Six Countries. *Policy Sciences* **2015**, *48*, 51-83.

(56) Pelamis, World's First Commercial Wave Energy Project, Agucadoura http://www.power-technology.com/projects/pelamis/ (accessed Nov 8, 2016).

(57) European Commission,. *Marven - Environmental Impacts Of Noise, Vibrations And Electromagnetic Emissions From Marine Renewable Energy*; DHI, **2015**.

(58) European Commission,. *Marven - Environmental Impacts Of Noise, Vibrations And Electromagnetic Emissions From Marine RenewableEnergy*;DHI,**2015**

Greener Methods of Rare Earth Element Extraction and Separation from NdFeB Permanent Magnets: a Critical Review

Dongcang Zhou*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada, H3A 0B8

KEYWORDS: Rare Earth Element, NdFeB Magnet, Hydrometallurgy, Ionic Liquid, Pyrometallurgy, Hydrothermal

ABSTRACT: Rare earth elements (REEs), especially neodymium and dysprosium in NdFeB permanent magnets, currently play an invaluable role in industries ranging from fluorescent lamps to electric vehicles, with demand set to increase in the future. Current extraction and separation of REEs from NdFeB permanent magnets by hydrometallurgical processes require the use of hazardous and toxic mineral acids, as well as organic solvents, and generate large amounts of wastewater. Increased mining is neither environmentally friendly nor economically viable in the short-term. Therefore, greener methods to recycle, extract, and separate these REEs from each other and other transition metal elements in NdFeB magnets that improve upon conventional hydrometallurgical methods must be found. In this review, the uses of ionic liquids and molecular recognition technology are explored, as are other methods using pyrometallurgy and hydrothermal approaches.

INTRODUCTION

Known as 'rare' due to the difficulty in separation and extraction of the pure metals, the rare earth elements (REEs) are widely regarded to consist of the lanthanide series of elements, plus yttrium and scandium. REEs are considered highly valuable due to their unique physiochemical properties giving them uses in a wide range of significant applications including petroleum catalysis, hybrid engines, and permanent magnets.[1] In particular, NdFeB permanent magnets are invaluable to renewable, sustainable energy technologies, being used in electric vehicles, wind turbines and generators, with neodymium and dysprosium being the main two REEs used in these magnets.[1] Dysprosium is often alloyed with NdFeB magnets to raise the magnets' Curie temperature, increasing the magnets coercivity at higher temperatures. Neodymium and dysprosium have both been outlined as critical in terms of "importance to clean energy" by the U.S. Department of Energy in 2011.[2] Though research has been done in looking for substitutes for neodymium in NdFeB magnets such as cerium,[3] the strength of CeFeB magnets has been shown to be inferior. Both neodymium and dysprosium have been concluded to be irreplaceable in most applications, especially those requiring particularly strong permanent magnets.[2, 3]

China is currently the dominant leader in world REE production with various studies quoting their global market share to be between 80-95%.[1,4] Though it has been predicted that in the foreseeable future that world production of REEs *would* be able to keep up with demand, it is likely that *current* demand will soon exceed production,[4] with a study by Hoenderdaal *et al.* proposing dysprosium demand may well exceed global short-term supply by as early as 2020.[5] As also the world's largest consumer of REEs, the Chinese government now continuously seeks to limit the export of REEs resulting in large market price fluctuations.[6] Consequences of market price spikes may especially be felt in research, where many promising renewable-energy technologies, like underwater wave power and geothermal drilling,[1] rely heavily on NdFeB magnets to function. The obvious risks can be seen in relying on one primary exporter of REEs and so it is of upmost importance that much of the rest of the world, especially REE import-only areas such as Europe and Japan,[1] find alternative sources.

The supply risk, therefore, is not a consequence of low elemental abundance in the earth's crust, but rather due to the fact that only China has a fully developed supply chain: from the mining of REE ores all the way to the manufacturing of consumer goods. Though it could be argued that simply an increase in the mining of REEs around the world would be enough to solve this imbalance, the development of new mining infrastructure is expensive and long. Not including supply chain development, it is estimated to take 12-13 years for a mine to actually start production.[7] As well as this, the mining of REEs has been shown to not only pose health risks to workers, but to also have significant negative impacts on the environment via generation of large amounts of wastewater and radioactive waste from processing and refinement streams.[8] Previous reviews and life-cycle assessment of the current situation in the mining, supply, and demand of REEs are in agreement that advancement in recycling methods of REEs is crucial.[1, 4, 9, 10]

Due to the high current and future predicted demand of the elements neodymium and dysprosium for use in NdFeB magnets in particular, this review focuses on several recent developments in methods to recycle these metals back from NdFeB permanent magnets in two key areas that are: the extraction of the metals from their permanent magnets, and the separation of these rare metals from transition metals, i.e. iron and cobalt, as well as each other. The various methods are compared and evaluated in terms of relevant qualitative criteria for greenness such as their relative energy and chemical consumptions.

1. THE PROBLEM WITH HYDROMETALLURGY

Currently the most widely cited methods of recycling REEs from magnets and magnetic scrap are hydrometallurgical processes[11] that often involve a number of the following steps shown in figure **1**, below.[12, 13, 14]

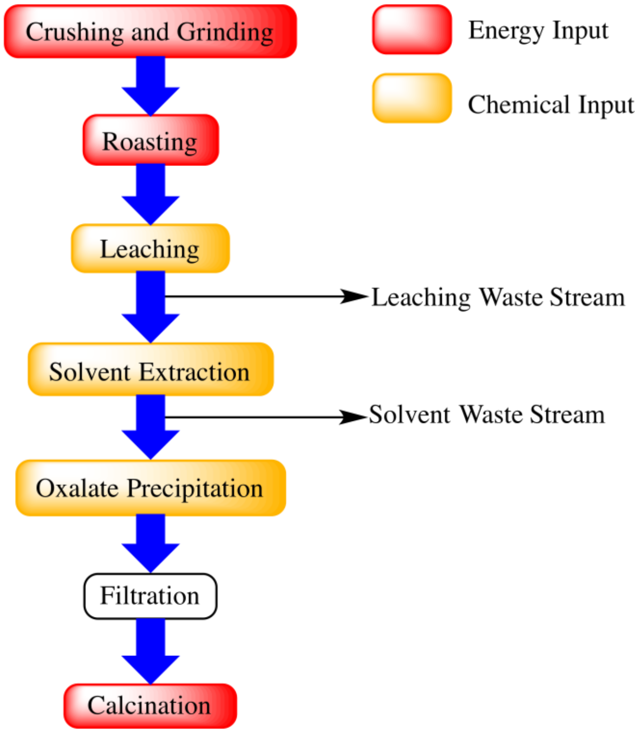


Figure 1. Steps often involved in hydrometallurgical methods of REE extraction and separation from NdFeB permanent magnets. Red boxes indicate large energy input while orange boxes indicate large chemical input.

Crushing and grinding mechanically pulverizes magnets and production scrap into powder, increasing the surface area for successive steps. Roasting demagnetizes the permanent magnet at high temperature and converts the metals to their respective oxides. Leaching involves the use of mineral acids i.e. hydrochloric acid, sulfuric acid, nitric acid, to selectively capture REE ions in the aqueous phase leaving iron behind as a precipitate. Solvent extraction separates REEs from each other (and other transition metal impurities like Co, Fe) by employing organic solvents i.e. kerosene, toluene, diethyl ether, to complex REE ions based on their affinity for the organic phase and solubility in the aqueous phase. Addition of oxalic acid precipitates REEs as their respective oxalates and after filtration the oxalates are finally calcined to obtain the useful rare earth oxides (REOs). Chemical waste streams are a result of the leaching and solvent extraction steps.

It can be easily seen that due to the complexity of the multi-step process combined with reliance on hazardous and toxic organic solvents and harsh mineral acids that standard hydrometallurgical methods are far from ideal green chemical processes. As a result, much research has been carried out to try and improve the greenness of hydrometallurgical processes.

2. IONIC LIQUIDS

The most extensively studied area in greener hydrometallurgical extraction and separation of REEs is in the application of ionic liquids (ILs). The origins of their implementation history in this field have already been covered comprehensively in a previous review paper,[15] Therefore this review will aim to evaluate only the most recent developments in this field.

ILs are most widely accepted to be defined as molten salts with melting temperatures generally under 100 °C. ILs are especially useful due to their synthetic nature, that is, due to their flexible definition, can easily be designed and created for specific applications. Often regarded as 'green solvents,'[16, 17] in the recycling of NdFeB magnets, they have been studied mostly commonly as a replacement for the volatile organic compounds (VOCs) used in the solvent extraction stage in order to separate REEs from solvated transition metal impurities and each other. Here, ILs replace the organic phase. Depending on various metal in solutions affinity for different ILs, transition metal impurities are extracted into the IL phase, while REE ions remain in the aqueous phase. Following separation, the procedure followed can be the same as in figure **1**, shown previously: addition of oxalic acid to yield REE oxalates, and so on.

Since ILs allow for creative versatility in their designs, various ILs have been created and shown to be able to separate REEs from transition metals and each other in different conditions such as pH[18] and temperature.[19] Riaño *et al*. have demonstrated the ability for the IL trihexyl(tetradecyl)phosphonium nitrate (TTPN) to successfully separate cobalt ion impurities from REE ions in solution,[20] while Hoogerstraete *et al*. showed similar results with trihexyl(tetradecyl)phosphonium chloride (TTPC) which was additionally tested and showed selectivity in separation with other elements such as zinc, and iron- the main component element in NdFeB magnets.[14] In Hoogerstraete's experiments, iron separation was achieved at 99.98% or above with separation factors of around 5.0 x 10^6. The experiments were all carried out in made-up leaching solution as to show how these ILs could easily be implemented in current industrial processes in the replacing of VOCs.

The previously mentioned research by Riaño and Hoogerstraete, whilst important in solving immediate issues with hydrometallurgical processes, their significance in improving the overall greenness of the existing hydrometallurgical process is limited. While the use of VOCs can be shown to be replaceable with ILs in solvent extraction, the use of hazardous mineral acids for the leaching process remains. Though in the research paper, Hoogerstraete argued that in the case of TTPC, strongly acidic conditions were necessary for efficient hydrometallurgy, the use of alternative, fluorinated ionic liquids could present alternative solutions. Even more recent, novel applications for using ILs in hydrometallurgy come from bi-functional ionic liquids, especially acid-base coupling bi-functional ionic liquids (ABC-BILs) that are often comprised of an ammonium cation and carboxylic anion.[21] Dupont and Binnemans have used an IL previously having shown success in recycling fluorescent lamp phosphor waste[22] to both extract and separate REEs present in NdFeB magnets in a single step: a combined leaching/extraction system using the IL betanium bis(trifluoro)methylsulfonyl imide (BFMSI). BFMSI is interesting in this method for two reasons. Firstly, BMFSI readily dissolves metal oxides. Secondly, BFMSI shows interesting thermomorphic properties in water: over 55 °C, the mixture will become one homogenous phase while at lower temperatures, the mixture will separate out into two phases. In this way, BFMSI is used both as the aqueous and organic phase in solvent extraction. Therefore by simply changing the temperature of the IL, both mineral acid use and VOCs are replaced in a single step.

As a result of the ion exchange process during the IL's metal extraction, some ionic liquid will dissolve into the aqueous phase in order to form new ILs with metal anions causing loss of ionic liquid.[14] Dupont solves this problem by using fluorinated ILs to increase the IL's hydrophobicity. However, fluorinated ILs present their own problems. Prices of fluorinated compounds are high and also, fluorinated ILs must be carefully controlled so that they do not mix with the aqueous phase, which would produce hazardous HF as a result of hydrolysis.[23] Hoogerstraete has successfully demonstrated using longer alkyl chain lengths as an alternative way to increase hydrophobicity of ILs[14] but so far research has not yet been combined to find a both non-fluorinated bi-functional IL capable of dissolving metal oxides like BFMSI.

Ignoring energy consumption, since all hydrometallurgical methods require heat for magnet oxidation and disintegration before leaching steps, the difference in these IL methods lies in either using a potentially hazardous fluorinated IL and eliminate the use of both mineral acids and VOCs, or use less hazardous non-fluorinated ionic liquids but still require a separate leaching step. Until non-fluorinated bi-functional ILs with REE separation abilities are discovered, in terms of health risks at the industrial scale, using TTPN or TTPC is likely better than using fluorinated BFMSI. This is because they present no constant risk of producing HF. However even so, though ILs have been around for a long time, there is still uncertainty regarding the toxicity of ionic liquids and their long term impacts on human health and the environment.[24, 25] In addition, the use of ILs in REE extraction has not yet been implemented in industry. Though research shows promise, further investigation must be done in scale-up. Finally, difficultly has also been found in stripping transition metals like iron from the ILs after use, so good recyclability of ILs must still be looked into.

3. MOLECULAR RECOGNITION TECHNOLOGY

Another approach to improve the greenness of existing hydrometallurgical processes that can be applied to the REE recycling of NdFeB magnets is known as molecular recognition technology (MRT). MRT works in the separation of metals from solution by using pre-designed ligands such as crown ethers, bonded to a support material such as a silica-gel or polymer surface. Requiring no organic solvents or other additional chemicals, feed solutions (like leaching waste streams) containing desired metals are run though a column containing the ligands. The sizes and affinities of different metal ions to different ligands traps out ions from solution and successfully separates different metal ions from each other. These ligand-support products are known as SuperLig®.

In experiments carried out by Izatt *et al*. using prepared leach solution containing 16 different REEs, MRT was shown to successfully separate REEs from non-REE elements at over 99% separation and to further separate the individual REE elements (including neodymium and dysprosium) at over 99% separation.[26] Their drawn conclusion, that a novel process for recycling REEs with green design principles is certainly sound. Presenting economical, operational and environmental benefits over solvent extraction methods, MRT will likely be a critical technology in near-future applications in REE, and therefore also in NdFeB magnet recycling industries.

The usefulness and significance of research in improving and building upon hydrometallurgical processes is that it is relevant to industries of today. These methods often show feasibility in terms of scale-up. They build upon existing infrastructure, making these developments undoubtedly important for immediate and near-future applications. That being said, from the directions that research appears to be going in, these methods are ultimately unsuitable for creating a future green economy. While the synthesis of new ionic liquids may be novel in their own right, their application to improving hydrometallurgy is not. Future research in green chemistry would be significant by seeking alternative options to hydrometallurgy rather than trying to remedy its existing problems.

4. PYROMETALLURGICAL PROCESSES

Pyrometallurgical recycling methods of REEs from NdFeB involve using thermal techniques to achieve separation and extraction of the useful products. Pyrometallurgical processes are in some ways considered more environmentally friendly and 'greener' than hydrometallurgical processes as they avoid the chemical intensive steps, namely leaching and solvent extraction steps that generate the primary waste streams in hydrometallurgical extraction. Pyrometallurgical techniques involve primarily heating at high temperatures.

Bian *et al.* have conducted pyrometallurgical experiments using a new, novel method they have called the vacuum induction melting followed by hydrolysis and magnetic separation strategy (VIM-HMS) for recovery of REEs from NdFeB magnet scrap. VIM-HMS obtains REEs as their respective rare earth hydroxides (REOH).[27] After heating in a graphite crucible to be converted into carbides, REOHs are obtained simply by soaking in water, with no additional chemicals necessary, and finally isolated from iron by magnetic separation (over 99.7% separation was achieved). The 3 main reactions in the VIM-HMS method are shown in equations (1), (2), and (3), below. These show VIM, hydrolysis of carbides and magnetic separation, respectively.

$$\mathrm{NdFeB\ Alloy} + \mathrm{C} \rightarrow \mathrm{NdFeBC_{sat}\ Alloy} \qquad (1)$$

$$\mathrm{NdC_2} + \mathrm{H_2O} \rightarrow \mathrm{Nd(OH)_3} + \mathrm{gas} \qquad (2)$$

$$\mathrm{Nd(OH)_3Fe\ (mixture)} \rightarrow \mathrm{Nd(OH)_3} + \mathrm{Fe} \qquad (3)$$

While the process is simple and efficient, and chemically green, the obvious drawbacks lie in the large energy input, with initial heating at 1400 ^{o}C, as well as the waste gas stream. According to Bian, there are 3 main components of the waste generated from the vacuum induction melting: hydrogen, ethane and ethyne. While fairly innocuous, future research could be conducted in retrieval and separation of these gases, since hydrogen is useful in renewable energy solutions[28] and ethene and ethyne both are valuable synthetic materials.

Another pyrometallurgical method of REE extraction from NdFeB magnets is molten salt extraction,[29] where REEs in the magnetic scrap react with molten salts such as NH_4Cl to extract their respective rare earth oxides (REOs) with the disadvantage of consuming much energy in obtaining the REOs. A method explored by Hua *et al*. uses molten $MgCl_2$-KCl as an extractant for formation of rare-earth chlorides, specifically, neodymium chloride, $NdCl_3$, with successful transition metal separation leaving behind Fe-B alloy.[30] In a second step, the molten neodymium chloride undergoes electrolysis to yield Nd-Mg alloys. This is also the shortfall of this method since currently, rare-earth chlorides have limited applications.[31] Whilst rare-earth alloys like Nd-Mg are being investigated,[32] REOs are much more valuable as they are used to create new NdFeB permanent magnets.[33] While Hua also states that pure metal can be obtained by evaporating off magnesium, this would surely defeat the purpose of this method seeking to find a greener, less energy consuming method of REE extraction in the first place.

5. A HYDROTHERMAL APPROACH

Currently at the forefront of NdFeB magnet recycling research, Maât *et al*. have developed a hydrothermal approach to recycling NdFeB magnets with easy scale-up potential.[34] This method employs green chemistry design principles and is both low in energy consumption and environmentally friendly from the use of limited amounts of innocuous solvent and chemicals: essentially only involving heating in water and sodium chloride at very low concentrations. NaCl was used as catalyst to improve water's oxidative power, and was shown to be replaceable with other oxidative salts such as $Na_2S_2O_6$ or $Na_2S_2O_4$. Complete pulverization of a magnet sample was observed in the reaction vessel after 18 h at 250 ^{o}. The Nd-Fe-B matrix was shown to be broken with neodymium and iron in distinct environments at room temperature, based on their different crystals formed: hexagonal $Nd(OH)_3$ (needle-like crystals) and cubic Fe_3O_4 (octahedral crystals). These geometries were determined after correlation with scanning electron microscope (SEM) images and REOHs were confirmed with X-ray diffraction (XRD). Finally, REOHs were magnetically separated from iron oxide on the basis of their different magnetization values.

In this particular experiment, magnetic separation was quite imperfect (using only a vial and magnet) with 5% iron impurity.[34] However, Bian *et al* have previously demonstrated separation with more thorough methods to obtain REOHs at 99.7%, showing better separations can be achieved.[27] Another current disadvantage, as with previous pyrometallurgical methods, is the lack of selectivity between the different rare earth elements themselves. While this hydrothermal approach has shown to be simple and efficient: far less energy and chemical consuming than previous methods, the research is still in its infancy. Though showing much promise, its separation and selectivity must still be further developed.

CONCLUSIONS

In summary this review has highlighted some recent trends and developments in the field of rare earth recycling from NdFeB permanent magnets and evaluated and compared their qualitative 'greenness' in terms of chemistry and energy consumption. Standard, common hydrometallurgical procedures may be improved by the use of ionic liquids in solvent extraction and leaching steps. This was concluded to be significant in terms of current industrial application today. Evaluation of MRT also showed its own significance and contribution to near future application. Neither solution was determined as suitable to replace the need for mineral acid leaching in current hydrometallurgical process. Since there has already been much contribution in the study of ionic liquids as a replacement to solvent extraction, now effort should be made in the search for a replacement to hydrometallurgical processes for rare earth extraction altogether. While pyrometallurgical and hydrothermal techniques look promising, it is still too soon to employ them industrially. Especially the hydrothermal approach, where research is still in its infancy. The future of greener rare earth recycling industry lies in the development of greener technologies designed from the ground up, with green chemistry principles in mind. Not in improvement of existing hydrometallurgical processes. This is a crucial challenge to overcome in the development of a greener economy.

AUTHOR INFORMATION

*Dongcang Zhou

dongcang.zhou@mail.mcgill.ca

ABBREVIATIONS

REE, Rare earth element; REO, rare earth oxide, MRT, Molecular recognition technology; IL, Ionic liquid; VOC, Volatile organic compound; TTPN, trihexyl(tetradecyl)phosphonium nitrate, TTPC, trihexyl(tetradecyl)phosphonium chloride; ABC-BIL, Acid-base coupling bi-functional ionic liquid; BFMSI, bis(trifluoro)methylsulfonyl imide; VIM-HMS, Vacuum induction heating – hydrolysis and magnetic separation; REOH, Rare earth hydroxide; REO, Rare earth oxide; SEM, scanning electron microscope; XRD, X-Ray Diffraction.

ACKNOWLEDGMENT

Acknowledgements go to Profs. Robin D. Rogers and Audrey H Moores, editor and assistant editors of the McGill Green Chemistry Journal: Arnold Downey, Pierre-Olivier Ferko, Joseph Marrett and Jill Bachelder.

REFERENCES

(1) Stegen, K. S. Heavy rare earths, permanent magnets, and renewable energies: An imminent crisis. *Energy Policy*. **2015**, *79*, 1–8.

(2) US Department of Energy. Critical Materials Strategy. **2011**, U.S. Department of Energy, Washington D. C. December.

(3) Pathak, A. K.; Khan, M.; Gschneidner Jr, K. A., McCallum, R. W., Zhou, L., Sun, K.; Dennis, K. W.; Zhou, C.; Pinkerton, F. E.; Kramer, M. J.; Pecharsky, V. K. Cerium: An unlikely replacement of dysprosium in high performance Nd-Fe-B permanent magnets. *Advanced Materials*. **2015**, *27*(16), 2663–2667.

(4) Haque, N.; Hughes, A.; Lim, S.; Vernon, C. Rare Earth Elements: Overview of Mining, Mineralogy, Uses, Sustainability and Environmental Impact. *Resources*. **2014**, *3*(4), 614–635.

(5) Hoenderdaal, S.; Tercero Espinoza, L.; Marscheider-Weidemann, F.; Graus, W. Can a dysprosium shortage threaten green energy technologies? *Energy*. **2013**, *49*(1), 344–355.

(6) Looney, R. Recent Developments on the Rare Earth Front Evidence of a new technocratic mercantilism emerging in China. *World Economics.* **2010**, *12*(1), 47–79.

(7) US Environmental Protection Agency. Rare earth elements: A review of production, processing, recycling, and associated environmental issues. **2012**, Office of Research and Development, Washington, DC, December.

(8) Rim, K. T.; Koo, K. H.; Park, J. S. Toxicological evaluations of rare earths and their health impacts to workers: a literature review. *Safety and Health at Work*. **2013**, *4*(1), 12–26.

(9) Machacek, E.; Kalvig, P. Assessing advanced rare earth element-bearing deposits for industrial demand in the EU. *Resources Policy*. **2016**, *49*, 186–203.

(10) Koltun, P.; Tharumarajah, A. Life Cycle Impact of Rare Earth Elements. *ISRN Metallurgy*, **2014**, 907536.

(11) Rabatho, J. P.; Tongamp, W.; Takasaki, Y.; Haga, K.; Shibayama, A. Recovery of Nd and Dy from rare earth magnetic waste sludge by hydrometallurgical process. *J. Mater. Cycles Waste Manage.* **2015**, 15, 171−178.

(12) Xie, F.; Zhang, T. A.; Dreisinger, D.; Doyle, F. A critical review on solvent extraction of rare earths from aqueous solutions. *Minerals Engineering*. **2014**, *56*, 10–28.

(13) Mochizuki, Y.; Tsubouchi, N.; Sugawara, K. Selective recovery of rare earth elements from Dy containing NdFeB magnets by chlorination. *ACS Sustainable Chem. Eng.* **2013**, *1*(6), 655–662.

(14) Vander Hoogerstraete, T.; Wellens, S.; Verachtert, K.; Binnemans, K. Removal of transition metals from rare earths by solvent extraction with an undiluted phosphonium ionic liquid: separations relevant to rare-earth magnet recycling. *Green Chemistry*. **2013**, *15*(4), 919.

(15) Liu, Y.; Chen, J.; Li, D. Application and Perspective of Ionic Liquids on Rare Earths Green Separation. *Separation Science and Technology*. **2012**, *47*(2), 223–232.

(16) Zhao, H.; Xia, S.; Ma, P. Use of ionic liquids as " green " solvents for extractions. *J. Chem. Technol. Biotechnol.* **2005**, *1096*, 1089–1096.

(17) Earle, J. M.; Seddon, K. R. Clean Solvents, ACS Symposium Series. **2002**, ch. 2, vol. 819, pp. 10–25.

(18) Chen, Y.; Wang, H.; Pei, Y.; Ren, J.; Wang, J. PH-Controlled Selective Separation of Neodymium (III) and Samarium (III) from Transition Metals with Carboxyl-Functionalized Ionic Liquids. *ACS Sustainable Chem. Eng.* **2015**, *3*(12), 3167–3174.

(19) Dupont, D.; Binnemans, K. Recycling of rare earths from NdFeB magnets using a combined leaching/extraction system based on the acidity and thermomorphism of the ionic liquid [Hbet][Tf2N]. *Green Chemistry*. **2015**, *17*(4), 2150–2163.

(20) Riano, S.; Binnemans, K. Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets. *Green Chemistry*. **2015**, *17*(5), 2931–2942.

(21) Sun, X.; Waters, K. E. Development of Industrial Extractants into Functional Ionic Liquids for Environmentally-friendly Rare Earth Separation. *ACS Sustainable Chemistry & Engineering*. **2014**, 2, 1910–1917.

(22) Dupont, D.; Binnemans, K. Rare-earth recycling using a functionalized ionic liquid for the selective dissolution and revalorization of Y 2 O 3 :Eu 3+ from lamp phosphor waste. *Green Chem.* **2015**, *17*(2), 856–868.

(23) Freire, M. G.; Neves, C. M. S. S.; Marrucho, I. M.; Coutinho, J. A. P.; Fernandes, A. M. Hydrolysis of Tetrafluoroborate and Hexafluorophosphate Counter Ions in Imidazolium-Based Ionic Liquids. *J. Phys. Chem. A.* **2009**, 114, 3744–3749.

(24) Ranke, J.; Müller, A.; Bottin-Weber, U.; Stock, F.; Stolte, S.; Arning, J.; Störmann, R.; Jastorff, B. (**2007**) Lipophilicity parameters for ionic liquid cations and their correlation to in vitro cytotoxicity. *Ecotoxicol. Environ. Saf*. **2007**, 67, 430–438.

(25) Laus, G.; Bentivoglio, G.; Schottenberger, H.; Kahlenberg, V.; Kopacka, H.; Roder, T.; Sixta, H. Ionic liquids: current developments, potential and drawbacks for industrial applications. *Lenzinger Berichte*. **2005**, 84 71–85.

(26) Izatt, S. R.; McKenzie, J. S.; Izatt, N. E.; Bruening, R. L.; Krakowiak, K. E.; & Izatt, R. M. Molecular Recognition Technology: a Green Chemistry Process for Separation of Individual Rare Earth Metals. *White Paper on Separation of Rare Earth Elements*. **2016**

(27) Bian, Y.; Guo, S.; Jiang, L.; Liu, J.; Tang, K.; Ding, W. Recovery of Rare Earth Elements from NdFeB Magnet by VIM-HMS Method. *ACS Sustainable Chem Eng*. **2016**, *4*(3), 810–818.

(28) Dunn, S. Hydrogen futures : toward a sustainable energy system. *International Journal of Hydrogen Energy*. **2002**, *27*, 235–264.

(29) Itoh, M.; Miura, K.; Machida, K. Extraction of rare earth elements from Nd−Fe−B magnet scraps by NH4Cl. *Chem. Lett*. **2008**, 37, 372−373.

(30) Hua, Z.; Wang, J.; Wang, L.; Zhao, Z.; Li, X.; Xiao, Y.; Yang, Y. Selective extraction of rare earth elements from NdFeB scrap by molten chlorides. *ACS Sustainable Chem. Eng.* **2014**, *2*(11), 2536–2543.

(31) Mochizuki, Y.; Mori, H.; Sugawara, K. Recovery of rare earth from Nd-Fe-B magnets by chlorination. *J. Soc. Chem. Eng. Jpn*. **2011** 1(8), 70−77.

(32) Han, W.; Wang, F.; Tian, Y.; Zhang, M.; Yan, Y. Electrochemical formation of Mg−Li−Sm alloys by codeposition from LiCl−KCl−MgCl2−SmCl3 molten salts. *Metall. Trans. B*. **2011**, 42, 1376−1382.

(33) Vander Hoogerstraete, T.; Blanpain, B.; Van Gerven, T.; Binnemans, K. From NdFeB magnets towards the rare-earth oxides: a recycling process consuming only oxalic acid. *RSC Advances*. **2014** *4*(109), 64099–64111.

(34) Maât, N.; Nachbaur, V.; Lardé, R., Juraszek, J.; Le Breton, J.-M. An Innovative Process Using Only Water and Sodium Chloride for Recovering Rare Earth Elements from Nd–Fe–B Permanent Magnets Found in the Waste of Electrical and Electronic Equipment. *ACS Sustainable Chem. Eng.* **2016**

Everybody P's: Investigating the Viability of Phosphorus Recycling from Human and Animal Waste

Arnold R. Downey*

Department of Chemistry. McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 0B8.

KEYWORDS phosphorus, food security, eutrophication, biosolids, struvite,

ABSTRACT: Global Phosphorus supplies are dwindling and posing a threat towards food supply, due to Phosphorus' crucial role in the fertilization of crops. Meanwhile, Phosphorus is thrown away in landfills and waterways, causing further issues of eutrophication and groundwater contamination. Promising methods to recycle Phosphorus are investigated; namely production of biosolids and precipitation of struvite from wastewater for use as fertilizer.

PHOSPHORUS SUPPLY AND DAMAGE

Did you eat this week? If you did, you should probably tip your hat to the element just below Nitrogen on the periodic table, Phosphorus. Phosphorus makes up one thousandth of earth's crust[1] and it plays a huge role in global food production, due to its essential role in the fertilization of crops. Phosphorus is so far suspected to be irreplaceable in this role.[2] Phosphorus that is taken up by plants is partly responsible for cell division, and thus the growth and maturity of the plant. Phosphate rock was initially used to accommodate the elevated need of food to feed an increasing world population, because it was a cheap and plentiful means of procuring synthetic fertilizer. It is clear now, however, that there are issues with this approach. The size of global Phosphorus reserves and how long they will last has been a topic of debate among researchers. In 2012, the United States Geological Survey (USGS) estimated that worldwide Phosphorus supplies amount to 71 billion tons, while mining production in 2011 was 0.19 billion tons.[3] While this would follow to suggest that reserves could last for another 370 years or longer, other estimates are not so optimistic. Some researchers estimate that reserves could be depleted in 50-100 years and that peak Phosphorus could occur by 2030.[4] With such a large variation in estimates, it is difficult to assert that there is or is not a shortage; however, given the vitality of this unique element, it would not be wise to gamble. Regardless of how much we may have left, one factor to consider is the decrease in the quality of mined Phosphate rock. The richness of mined phosphate rock has apparently decrease over decades, from just above 15% in the 1970s to below 13% in 1996.[5] To make matters worse, the bulk of this potentially dwindling supply is possessed by just a few of countries. Morocco and China control respectively 5750 and 3750 Mt of the world's remaining phosphate reserves, amounting to almost 60% of total reserves[6]. This could be a recipe for international political disaster, as it would for any resource as essential as Phosphorus.

Another important reason to move away from phosphate mining would be the toxic and deathly effects it has on ecosystems and human health. In order for phosphate rock to be useful in fertilizers, it must be treated with sulfuric and nitric acid to produce diammonium phosphate, fertilizer.[7] This process produces a waste product, phosphogypsum. Phosphogypsum contains a number of serious contaminants; including, fluoride, sulfates, and radionuclides from the U-238 decay series, all of which may contaminate groundwater.[8] The radionuclides are perhaps of the most concern. Ingested radionuclides from groundwater are known to accumulate in body tissues and have been linked to increased rates of leukemia, as well as various types of cancer.[9] Higher rates of lung cancer have also been reported in those that have worked in phosphate mines.[10]

Our current mismanagement of Phosphorus does not only spell danger for human health, but also has deathly effects on ecosystems; especially aquatic ecosystems. When humans and livestock eat food, they also eat the phosphorus contained in said food. Most of this Phosphorus leaves the body in the form of excreta and flows back to water bodies by way of streams and sewers. When too much nutrient collects in a water body, eutrophication occurs, which results in accelerated algae growth.[11] These algae plumes lay wreckage to aquatic habitat. Sunlight is attenuated and may no longer reach the flora and fauna that depend on it. Similarly, Oxygen concentrations are severely reduced, effectively suffocating wildlife.[12] These issues should be addressed as the threats they are. A more sustainable approach in which we recycle the plentitude of Phosphorus we currently have would address these concerns.

MAJOR LEAKS IN THE PHOSPHORUS CYCLE

In order to supply food for an increasing world population without polluting the environment, or possibly starting a Morocco-China take-all world war, a sustainable source of Phosphorus is needed. Meanwhile, we throw the stuff away by the tons in sewage systems, landfills and farm runoff.

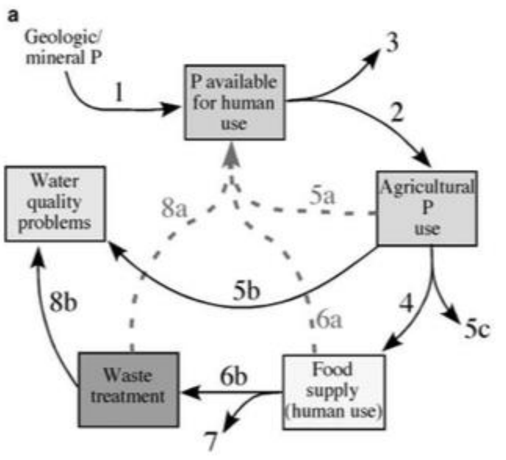


Figure 1. A conceptualization of the human phosphorus (P) cycle. (a Solid arrows represent key P flows and dashed arrows represent flows that close the human P cycle through sustainable solutions: (1) P mining and refining, (2) agricultural P use and efficiency, (3) nonagricultural P uses, (4) P in food, (5a) P recycled to agricultural production at the farm, (5b) P lost from farm fields, (5c) P lost in food processing and transportation inefficiencies, (6a) P in composted food waste, (6b) P in human excreta, (7) P in food waste lost to landfills, (8a) P from sewage treatment that is recycled to agricultural production, and (8b) P discharged from ineffectively treated sewage. *DL Childers, Sustainability Challenges of Phosphorus and Food: Solutions from Closing the Human Phosphorus Cycle, with permission*

About 2 Gt of dry matter animal waste is produced worldwide, with Phosphorus making up 16-20 Mt of this. Indeed, animal manures contain nearly a quarter of the Phosphorus available in the United States. However, manures are bulky, unevenly distributed and transport beyond a limited distance is not economical.[vi] As a result, only 6-8 Mt of this are reapplied to fields.[13] This represents a large leak in the Phosphorus cycle, illustrated by arrows 5b and 5c in figure 1. Much of this excess intrudes waterways as rain dissolves and carries the excess Phosphorus and as mentioned above, causes eutrophication.[14]

Regarding humans, estimates report that 3 Mt of Phosphorus are released in human waste annually.[vi] Much of this does not return to fields where it would be agriculturally useful, for it is estimated that nearly half of the Phosphorus released by humans ends up in waterways via urban wastewater, or as sludge in landfills.[vi] The direct application of this waste to fields is not good practice, as many would expect. Aside from the perceived foulness many have towards such a practice, high heavy metal content in the waste, as well as a tendency to spread disease, make this approach a nonstarter.[15] Nonetheless, removal of Phosphorus from waste water is commonly not done in completeness, if at all.[16] This represents another large leak in the Phosphorus cycle, arrow 6a, figure 1. However, these leaks also represent promising opportunities to recycle wasted Phosphorus. Human waste that enters a sewer system gets centralized in urban treatment systems, putting a bulk of the Phosphorus we lack in concentrated, accessible locations. It is estimated that if all of the Phosphorus from human waste were recycled, it would account for 22% of the world's current demand.[17] Tapping into this potential could be key in ensuring a stable food supply for decades to come.

BIOSOLIDS

The issue is clear. We have a depleting resource that is crucial for food production. We also have copious amounts of this resource being thrown away and simultaneously causing damage to the environment. One way that communities have already begun closing the broken Phosphorus cycle is the production of biosolids. Biosolids are nutrient-rich materials produced by special treatment of sewage. Sewage undergoes a number of different treatments so as to be suitable for application to land as fertilizer. Primary treatment involves sedimentation of wastewater to remove settled solids. The residing material is treated so as to control pathogen and contaminant levels, as well as water content. To achieve this, microorganisms are added to anaerobically digest the material rendering it usable for crop growth. Chemical treatments are necessary to remove pathogens. The most common chemical stabilization procedure is to elevate the pH of the solids using lime or other alkaline materials. The solids are then dried and stabilized and are then ready for field application.[18] The use of this method is ideal when the waste water is that of municipalities only, or when industrial waste is pretreated before release into the sewer system. If industries do not properly dispose of their waste however, the biosolids produced are not suitable for field application and are incinerated instead.

Biosolids have shown to perform very well as fertilizer and possess some advantages over conventional fertilizers. Application of biosolids increased total extractable Phosphorus content in soils, as well as increased Nitrogen concentration.[19] Further, biosolids contain a number of micronutrients which most conventional fertilizers do not, including Boron, Copper, and Iron among others.[20] This allows biosolids to remediate soil that may be lacking in these low-concentration components. Studies have shown that application of biosolids resulted in similar or greater yields than inorganic fertilizers.[21] Despite the apparent benefits in producing and using biosolids for fertilizer, US EPA estimates that biosolids are applied to approximately 0.1% of available agricultural land on annual basis.[22] An increased use of biosolids would help address issues of Phosphorus depletion and eutrophication by municipal waste water.

STRUVITE PRECIPITATION AS A METHOD TO PRODUCE HIGH-QUALITY FERTILIZER

Another technology that appears promising in closing the Phosphorus cycle is the precipitation of Struvite.

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2 \rightarrow MgNH_4PO_4 \cdot 6H_2O$$

Struvite, or magnesium ammonium phosphate ($MgNH_4PO_4$) occurs naturally upon breakdown of urea into urine by bacteria. It is perhaps better-known in its villainous role as kidney stones. Struvite is quite insoluble, with an approximate Ksp of 14[23] which is a reason for it residing in urinary tracks for so long. This low solubility also plays a devilish role in pipe blockage in wastewater treatment plants, which greatly increases pumping and maintenance costs.[24] This low solubility, however, also allows struvite to act as a rich, slow-release fertilizer. It even tends to outperform Diammonium Phosphate,[25] which is the most widely used fertilizer today. Technologies have been developed to make good use of this reaction. One example is the Pearl® process developed by Ostara Nutrient Recovery Technologies Inc. Ostara implements controlled precipitation of struvite in a cone-shaped reaction chamber, figure 2. Nutrient-rich waste water is introduced and mixed with Magnesium Chloride and Sodium Hydroxide to control the pH. Struvite crystals undergo significant growth until they are removed when they reach the desired size.[26]

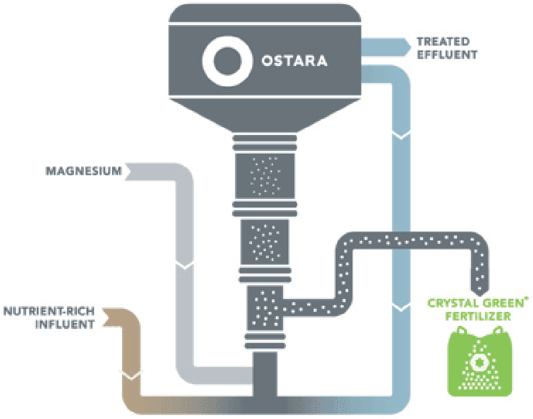


Figure 2. Schematic of Ostra's Pearl® Process for Precipitating Struvite from Waste

Not only does this technique produce high-quality fertilizer, it also helps remedy the issues of eutrophication and pipe blockage, as the problem components are removed in the precipitation. Up to 85% of Phosphorus can be removed in this process from municipal waste water, and the product is then sold as fertilizer. Ostara estimates that 200 wastewater plants in North America are candidates for this technology, as well as hundreds of others worldwide. This technology may also be used on farms where manure flows through a waste stream. Manure may run from a storage pit through a solid-liquid separator, after which it is sent to the struvite recovery system.[27]

The feasibility to implement this sort of technology is fair. It would involve the redirection of current waste streams to pass through a system like the one described. Investing in this technology would produce an additional revenue stream from materials that are otherwise considered waste. This technology has already been implemented, with one notable example being the Metropolitan Water Reclamation District of Greater Chicago's Stickney Water Reclamation Plant.

CONCLUSION

Despite the enormous issue being presented to humans regarding our current addiction to Phosphate mining, opportunities exist to allow for the closing of the currently open Phosphorus cycle. Major leaks exist in this cycle, including farm runoff and waste disposal, but these leaks can be redirected to terminals where they are agriculturally useful. Increased production and use of biosolids, as well as struvite precipitation from wastewater show to be promising technologies currently being implemented which may achieve this. To secure a sufficient supply of food for the future, sustainable approaches such as these should be taken for the betterment of humans and the environment.

AUTHOR INFORMATION

*Arnold Downey

arnold.downey@mail.mcgill.ca

ACKNOWLEDGEMENTS

I would like to acknowledge Dr. Audrey Moores and Dr. Robin Rogers for their support and guidance, as well as the other authors and editors who worked on this journal.

REFERENCES

(1) Ronov, A. B. and Yaroshevsky, A. A. **(1969)** Chemical Composition of the Earth's Crust, in The Earth's Crust and Upper Mantle (ed P. J. Hart), *American Geophysical Union*, Washington, D. C

(2) Junfa, T. **(2008).** Present status and development prospect of yellow phosphorus industry in China [J]. *Inorganic Chemicals Industry*, 6, 002.

(3) Jasinski, S. M. **(2002).** Phosphate rock.

(4) Buckingham, D. A., & Jasinski, S. M. **(2006).** Phosphate rock statistics, historical statistics for mineral and material commodities in the United States, Data series 140. *US Geological Survey*. Available: min-erals. usgs. gov/ds/2005/140.

(5) *Int. Fertil. Ind. Assoc*. **1998**. Mineral Fertilizer Use and the Environ-ment. Paris: IFA

(6) Smil, V. **(2000).** Phosphorus in the environment: natural flows and human interferences. Annual review of energy and the environment, 25(1), 53-88.

(7) Habashi, F. **(1985).** Trends in fertilizer technology and its impact on the environment. *Mater. Soc.*;(United States), 9(3).

(8) Rutherford, P. M., Dudas, M. J., & Samek, R. A. **(1994).** Environmental impacts of phosphogypsum. *Science of the total environment*, 149(1), 1-38.

(9) Canu, I. G., Laurent, O., Pires, N., Laurier, D., & Dublineau, I. **(2011).** Health Effects of Naturally Radioactive Water Ingestion: The Need for Enhanced Studies. *Environmental Health Perspectives*, 119(12), 1676–1680. http://doi.org/10.1289/ehp.1003224

(10) Block, G., Matanoski, G. M., Seltser, R., & Mitchell, T. **(1988).** Cancer morbidity and mortality in phosphate workers. *Cancer research*, 48(24 Part 1), 7298-7303.

(11) Smith, V. H., Tilman, G. D., & Nekola, J. C. **(1999).** Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental pollution*, 100(1), 179-196.

(12) Chislock, M. F., Doster, E., Zitomer, R. A., & Wilson, A. E. **(2013).** Eutrophication: causes, consequences, and controls in aquatic ecosys-tems. *Nature Education Knowledge*, 4(4), 10.

(13) Bouwman, A. F., Lee, D. S., Asman, W. A. H., Dentener, F. J., Van Der Hoek, K. W., & Olivier, J. G. J. **(1997).** A global high-resolution emission inventory for ammonia. *Global biogeochemical cycles*, 11(4), 561-587.

(14) Smith, V. H., Tilman, G. D., & Nekola, J. C. **(1999).** Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. *Environmental pollution*, 100(1), 179-196.

(15) Burge, W. D., & Marsh, P. B. **(1978).** Infectious disease hazards of landspreading sewage wastes. *Journal of Environmental Quality*, 7(1), 1-9.

(16) Sedlak, R. I. **(1991).** Phosphorus and nitrogen removal from munici-pal wastewater: principles and practice. *CRC press.*

(17) Mihelcic, J. R., Fry, L. M., & Shaw, R. **(2011).** Global potential of phos-phorus recovery from human urine and feces. *Chemosphere*, 84(6), 832-839.

(18) Tchobanoglous, G., & Burton, F. L. **(1991).** Wastewater engineering. *Management*, 7, 1-4.

(19) Brown, S., Kurtz, K., Bary, A., & Cogger, C. **(2011).** Quantifying benefits associated with land application of organic residuals in Washington State. *Environmental science & technology*, 45(17), 7451-7458.

(20) Warman, P. R., & Termeer, W. C. **(2005).** Evaluation of sewage sludge, septic waste and sludge compost applications to corn and forage: Ca, Mg, S, Fe, Mn, Cu, Zn and B content of crops and soils. *Bioresource technology*, 96(9), 1029-1038.

(21) Jaber, F. H., Shukla, S., Stoffella, P. J., Obreza, T. A., & Hanlon, E. A. **(2005).** Impact of organic amendments on groundwater nitrogen concentrations for sandy and calcareous soils. *Compost science & utilization*, 13(3), 194-202.

(22) Board on Environmental Studies and Toxicology Staff, Division on Earth and Life Sciences Staff, & National Research Council Staff. **(2002).** Biosolids applied to land: Advancing standards and practices. *National Academies Press.*

(23) Bhuiyan, M. I. H., Mavinic, D. S., & Beckie, R. D. **(2007).** A solubility and thermodynamic study of struvite. *Environmental technology*, 28(9), 1015-1026.

(24) Fattah, K. P. **(2012).** Assessing struvite formation potential at wastewater treatment plants. *International Journal of Environmental Science and Development*, 3(6), 548.

(25) Barak, P., & Stafford, A. **(2006, January).** Struvite: a recovered and recycled phosphorus fertilizer. In Proceedings of the 2006 Wisconsin Fertilizer, *Aglime & Pest Management Conference* (Vol. 45, p. 199).

(26) Britton, A. T., Sacluti, F., Oldham, W. K., Mohammed, A., Mavinic, D. S., & Koch, F. A. **(2007, June).** Value from waste–struvite recovery at the city of Edmonton's gold bar WWTP. In Proceedings of *the IWA Specialist Conference*,(SC'07), Moncton, New Brunswick, Canada.

(27) Jordaan, E. M., Ackerman, J., & Cicek, N. **(2010).** Phosphorus re-moval from anaerobically digested swine wastewater through struvite precipitation. *Water Science and Technology*, 61(12), 3228-3234.

5-hydroxymethylfurfural (HMF) as direct product of cellulose in ionic liquids

Joseph Marrett*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada, H3A 0B8

KEYWORDS. HMF, Biomass, lignocellulose, ionic liquids, alternative fuels

---

ABSTRACT: Platform molecules derived from biomass sources are attractive options as industrial 'nodes' for the replacement of fossil products. Fine chemicals, polymers, and fuels can be made through simple chemical transformations of these species. The platform molecule 5-hydroxymethyfurfural (HMF), a precursor to various fine chemicals and liquid fuels, can be produced in one-pot syntheses from cellulose in ionic liquids, often catalyzed by transition metal salts. Continuing work on these types of processes has produced promising results, but research into the logistics of scale-up and studies of the environmental impacts of the involved species are lacking. Additional research into the consequences of large scale production is required before industrialization would be prudent and reasonable. This review aims to introduce the chemical principles behind HMF production *via* ionic liquids, and to critically asses the feasibility of industrial application by considering logistical, economic, environmental, and toxicological issues associated with the process.

INTRODUCTION

Fossil and petroleum resources are currently the core feedstocks that supply energy and materials to consumers and industry. 86% of consumed energy and 96% of organic compounds are of fossil origin, but a dwindling supply of oil is pushing production prices skyward and prompting the search for renewable alternatives.[1] Already, the use of biomass has proven to be a promising tactic, and a wide range of relevant chemical precursors and high-quality transportation fuels have been derived from renewable sources by the utilization of certain platform molecules.[2]

One such platform molecule is 5-hydroxymethylfurfural (HMF), a product of the three-fold dehydration of hexose monosaccharides - usually fructose and glucose.[3] HMF is posed as promising platform molecule, in part, because of the diversity and significance of its derivatives.[4] Through facile chemical transformations, an array of simple organic compounds can be produced for fine chemical, pharmaceutical, and fuel purposes.[5,6] Notably, HMF can be easily derivatized to 2,5-dimethylfuran (DMF), a liquid biofuel with energy density similar to that of gasoline and 40% larger than that of ethanol.[7,8]

Since the discovery of HMF in 1895 by Dull and his colleagues, the bulk of synthetic methodologies have made use of pure monosaccharides.[3,9] Currently, HMF formation by the dehydration of pure fructose is the most thoroughly studied process. Increasingly, the formation of HMF from pure glucose by its natural isomerization to fructose is being studied.[3,4,10]

To date, countless novel methods have been explored for these processes. Inspired by Van Bekkum's original studies of the acid-catalyzed dehydration of fructose to HMF, processes involving aqueous, organic, and ionic liquid solvents in single and multi-phasic arrangements have been performed.[3,10] In these experiments, according to Cottier, homogenous and heterogeneous catalysis has been achieved using organic, inorganic, and Lewis acids.[11] Afonso *et al.,* in their exhaustive review of HMF formation by carbohydrate dehydration, pose chromium and other metal-based catalysts pioneered by Raines and Binder as promising agents for HMF formation from glucose and fructose.[3,4]

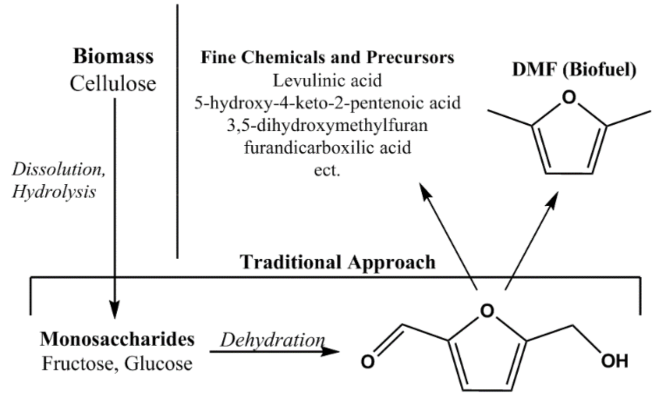


Figure 1: HMF Synthetic Route and Applications. Using information from Afonso 2011[3] and Chan 2009[12]

Unfortunately, this chemistry alone fails to address all of the problems associated with HMF production by only considering transformations that occur on purified monosaccharides, generally of an unspecified source. Any effort to develop HMF as a greener alternative to petrochemicals must consider not only the conversion of monosaccharides to HMF, but also the source of these sugar precursors. Recent and ongoing work has done this by demonstrating the possibility of integrated, cradle to gate production of HMF from biomass polymers dissolved in ionic liquids.[3,4,12] The general form of this conversion can be seen in Figure 1.

These technologies promise to offer considerable benefits to traditional methods. The advantage of cellulose use is two-fold. Cellulose, and thus the glucose it affords, are significantly less expensive than fructose. Cellulose is the most abundant polymer on earth, so this is not surprising.[12] Additionally, the production of cellulose is often natural and/or incidental, growing in the form of trees or agricultural byproduct, and consequently does not compete for resources with food production. Zhao *et al.* demonstrated the hydrolysis of cellulose to carbohydrates from corn stover, proving that value-added products can be derived from biomass that, by definition, does not compete with food.[13]

It is important to note that it is unlikely that these processes for HMF production, despite their use of inexpensive biomass, cannot yet compete in price with their petrochemical competitors. As the primary hurdle for any renewable source seeking to supplant oil, lowering the price of these methods is crucial to enabling a meaningful shift away from oil. Reducing the complexity of processing by streamlining to one-pot or integrated approaches may reduce processing time and cost.

HMF FROM BIOMASS: THE CHEMICAL PRINCIPLES

The complete conversion of cellulosic biomass to HMF requires three distinct steps: the dissolution of cellulose, the hydrolysis of the 1 → 4 glycosidic linkages of the biopolymer to form glucose, and the previously mentioned three-fold dehydration of isomerized fructose to HMF.[3,12] Each step presents its own challenges and is often performed separately. Each step is discussed below, and fully integrated approaches are discussed last.

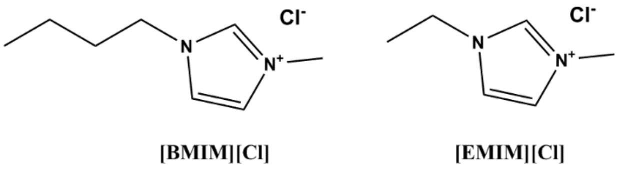


Figure 2: General form of [BMIM] and [EMIM] chlorides

Dissolution of Cellulose. The dissolution of cellulosic biomass in traditional solvents is not straightforward because of the nature of the robust hydrogen-bonded structure of cellulose.[14] Procedures using traditional solvents exist[15], but are generally considered impractical and often require harsh chemical and thermal conditions.[12] First reported in detail by Rogers[14] *et al.* in 2002, cellulose can be dissolved readily by 1-butyl-3-methylimidazolium chloride ([BMIM][Cl]) in its liquid form, with a solubility of 10 w/w% under gentle heating, and 25w/w% under microwave irradiation. This unique effect is likely due to the hydrogen bond accepting effect of the chloride ion; non-hydrogen bonding anions prevented cellulose dissolution.[14] The ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIM][Cl]) has also found use in dissolving cellulose and is central to Raines'[4] integrated approach to HMF production directly from cellulose, which is discussed later. It should be noted that the choice of chain length in the [RMIM][Cl] systems is considered a balancing act. Shorter chains yield higher effective chloride concentrations, thus improving cellulose dissolution. Longer chains feature reduced melting points and viscosities, making their application easier and less energy-consuming.[14] [BMIM][Cl] and [EMIM][Cl] are shown in their general form in Figure 2.

Hydrolysis of Cellulose to form Glucose. Traditional cellulose hydrolysis typically requires high temperatures and pressures in the presence of a Brønsted acid, and often results in monosaccharide yields which are well below 50%.[16] Many new methods rely on imidazolium ionic liquids, including the 1-allyl, ethyl and butyl methylimidazolium halides, in the presence of homogenous or solid acid catalysts.[12] Zhao and Li demonstrated the hydrolysis of cellulose to glucose in imidazolium halide ionic liquids using dissolved inorganic mineral acid catalysts.[13] Shuth and Zhang used Amberlyst and Zeolites, respectively, in ionic liquids as solid acid catalysts for cellulose hydrolysis.[17,18] While the bulk of cellulose dehydration methods focus on acid catalysis in imidazolium ionic liquids, Sheldrake[19] *et el.* have reported the generation of a mixture of sugars by pyrolysis of cellulose in dicationic imdazolium salts without the presence of acid. It is important to note that the *only* stoichiometric product of cellulose dehydration is water.

Dehydration of Glucose to form HMF. The historical approaches of monosaccharide dehydration to HMF rely on strong acid catalysis and generally only utilize pure fructose as feedstock.[3,12] These methods tend to be problematic due to the unavoidable formation of side-products by the rehydration of HMF during the reaction. Ionic liquids have presented themselves as useful alternatives to traditional methods due to high HMF selectivity and the ability to efficiently dehydrate glucose.[12] In 2007, H. Zhao[20] *et al.* showed that dehydration of glucose to form HMF was possible in ionic liquids, with favorable yields. Moreau[21] reported a 92% yield of HMF from monosaccharides with 1-H-3-methylimidazolium chloride, and HMF was proven to be stable in this system. The ionic liquid was determined to be recoverable and recyclable.[21]

Crucially, high conversions of glucose to HMF in imadolium ionic liquids has been achieved using chromium(III) chloride through a proposed mechanism involving catalytic isomerization of glucose to fructose prior to dehydration.[12] This is seen in Figure 3. Various other chromium(III) salts have proven highly successful in this endeavor by allowing the gradual reduction in severity of conditions and energy intensity involved in glucose dehydration to HMF.[3]

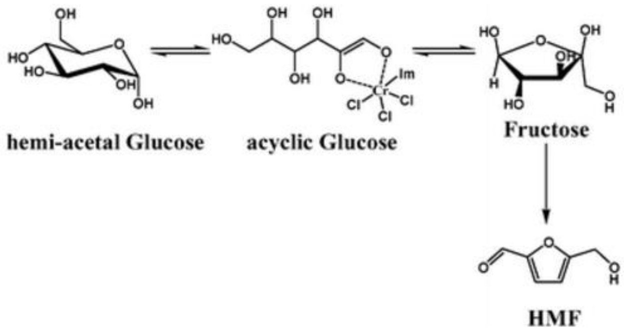


Figure 3: Chromium Catalyzed Isomerization of Glucose to Fructose: Reproduced from reference 12 with permission from the Royal Society of Chemistry

Integrated, One-Pot Approaches. The three methods explained above, by and large, have been studied as individual entities without consideration of the other steps involved in a complete conversion of cellulose to HMF. However, a number of promising tactics exist for this conversion in one-pot form. It should be noted that, at the current time, 50% yield of glucose from cellulose is the standard for these integrated methods; any more is considered exceptional while significantly less is considered sub-optimal.[12]

In 2009, Raines and Binder[4] achieved a total yield of 54% HMF from pure cellulose using mixture of lithium chloride dissolved in dimethylacetamide (DMA-LiCl) and [EMIM][Cl] with the addition of sub-stoichiometric quantities of chromium(II) and chromium(III) chlorides. Temperatures of 140C° were required, and the addition of the traditional cellulose solvent DMA-LiCl was rationalized as a way to reduce the usage of expensive ionic liquids. Using untreated corn stover and pine dust, they were able to achieve similar yields from raw biomass.[4] In the same year, Su and Zhang[22], *et al*. used pure [EMIM][Cl] and a mixture of copper(II) chloride and chromium(II) chloride catalysts to dissolve and convert cellulose to HMF in yields up to 65% at temperatures of 80 -120C° in 1 hour and 30 minutes. Interestingly, they found maximum yields of 10% when only one metal chloride was used, and unexpectedly noted that the strength of the catalyst as a Lewis acid was uncorrelated to yield.[22]

In 2012, Wu, Zhou, *et al*.[23] used [BMIM][Cl] and an acid-functionalized ionic liquid catalyst, Cr([PSMIM]HSO_4 , at 120C° to achieve HMF yields of up to 53% after 5 hours. Notably, the presence of the Brønsted acid did not serve to push yields higher than in acid-free methods.[23] Also in 2013, Zhao and Liu[24] used catalytic zirconium(IV) chloride in [BMIM][Cl] to convert cellulose to HMF in yields up to 51.4% in 3.5 minutes under 400W of microwave irradiation.

Quite notably, Peng, Wu, *et al.* achieved an exceptionally high yield of 80% HMF directly from cellulose in [EMIM][Cl] using mesoporous silica nanoparticles functionalized with both basic amines and acidic sulfonates.[25] This work represents a critical advance in HMF production in ionic liquids by exceeding the typical 50% yield. This provides a pathway for industrial application by reducing the costs associated with low yields in manufacturing. The use of solid acid/base catalysts also provides the opportunity for easy catalyst extraction and reuse.

HMF FROM CELLULOSIC BIOMASS: IN PRACTICE

Sourcing of Biomass and Economic Viability. The ability to use cellulosic biomass is perhaps the greatest and most obvious virtue of HMF as a direct product of cellulose. Lignocelluloses, the material which makes up the bulk of trees, often has cellulose compositions of up to 50% -- cellulose, by all estimations, is the most abundant biopolymer on earth.[12,26] According to Klein-Marcuschamer[27], there are 600-800 million tons of cellulosic biomass available for use in the United States at any given time. Besides trees, cellulose can be found in agricultural byproducts like corn stalks, leaves, and hay.[15] Naturally, byproducts like sawdust and woodchips from manufacture can also be used, offering low prices and avoiding competition for resources with food. In short, the sourcing of cellulose is not limited to purpose-cut trees. In fact, a huge variety of plant matter, by-product or purpose-grown, is suitable for cellulose production. By virtue of abundance and the ability to use waste products of manufacture, sourcing cellulose for HMF should not pose any significant hurdles in terms of price, availability, or logistics.

Ionic liquids feature negligible vapor pressures, preventing evaporation and conferring a certain *greenness*, and their demonstrated ability to be recycled by means like ionic exchange and salting out enable potential recycling of the solvent, stifling the need for continual production.[28,29] In many cases, especially for imidazolium ionic liquids, water reverses the ability of the solvents to dissolve cellulose.[14] This fact has been exploited to selectively extract and precipitate cellulose from lignocellulosic biomass, leaving lignin dissolved in the ionic liquid.[30]

The procurement and use of ionic liquids on an industrial scale, however, is not extensively documented. To date, no studies have been published that explicitly asses the viability of industrial scale conversion of cellulose to HMF using ionic liquids. However, Klein-Marcushamer[27] *et al.* assessed the financial viability of an ethanol bio refinery based on cellulosic biomass and ionic liquids. In their estimation, the production and use of ionic liquids would account for 30-60% of all costs involved in the endeavor. The most critical factor for lowering costs was determined to be the price of new ionic liquids; discussions with ionic liquid manufacturers yielded a range of prices from $2.5 USD / kg to $50 USD / kg, and profitability was shown to be highly dependent on this cost.[27]

George[31] *et al.* have demonstrated the feasibility for design of lower-cost ionic liquids which retain their ability to dissolve lignocellulosic materials. The existing ionic liquid [EMIM][OAc] was determined to fit favorable criteria already, and a number of new ionic liquids featuring protic cations were shown to be inexpensive, effective, and easy to produce.[31] It would be essential for potential manufacturers of HMF from cellulose to find and utilize low-cost ionic liquids that dissolve cellulose efficiently. Fortunately, research to lower the costs of ionic liquids is ongoing. It should also be noted that the use of ionic liquids which dissolve large weight percentages of cellulose is crucial for viability, reducing costs by lowering the physical scale required to produce a given quantity of HMF. Ease of recycling is also essential, as quantity of newly synthesized ionic liquids needed initially and over time is completely dependent of the speed and completeness of recycling processes.[27]

The production of valuable coproducts has proven, in many cases, to be crucial to ensuring economic viability of various bio refinery processes. Klein-Marcushamer[27] identified the production of value-added lignin as a crucial factor for the offset of high ionic liquid prices in a cellulose based bio refinery. Currently, separation of lignin and cellulose in ionic liquids is possible, and may offer a promising way to boost profitability by utilizing waste streams from HMF production. Despite lignin's notorious stubbornness as a material imparted by its irregular and branched structure, a number of resins and plastics have been developed based on the polymer, setting it up as a potential value-added byproduct of the production of HMF from raw lignocellulose.[27] Unfortunately, no numerical analysis has been performed to determine exactly how advantageous this tactic could be.

Toxicity and Production Waste Streams. In theory, the only byproduct of conversion of cellulose to HMF is water – a result of the multiple dehydration steps involved in the conversion of glucose to HMF. The dissolution of cellulose involves no chemical transformations, and thus has no stoichiometric byproduct. Hydrolysis of cellulose to glucose requires the addition of one equivalent of water per glucose, and the conversion of glucose to HMF produces three equivalent of water. Not only does this mean that the processes is of high atom-economy, but that the byproduct is, ideally, benign. Unfortunately, water is likely not to be the only byproduct of HMF manufacture from cellulose. The fate and environmental effect of the ionic liquids and catalysts used *must* be considered, as release of any chemical used in an industrial processes is, if not inevitable, highly likely.

It is clear that ionic liquids *should* be recycled if used in a refinery process. The cost of continued production and replacement is immense, and disposal of ionic liquids is certainly not a trivial problem. However, ionic liquids will inevitably have an end-of-life and require replacement during the continued operation of a plant.[27] For this reason, an assessment of the environmental and human toxicity is required to assess the viability of disposal and associated costs. Of course, the relevant metal catalysts and possibly HMF would be present in any wastes, so the effects of these must also be considered.

The toxicity of HMF itself has been shown to be quite low, and the molecule has been determined to be practically non-mutagenic in human by the Ames test, which involves exposure of bacteria to a test compound and subsequent determination of the degree of resultant DNA mutation. Additionally, human HepG2 liver cells showed little to no change when exposed to the compound.[32] In Pham's[33] comprehensive review on the toxicity and environmental impact of ionic liquids, it was found that many ionic liquids are toxic and pose extra risk to aquatic species due to their frequent water-miscibility. Also problematic was the tendency of ionic liquids, and [BMIM][Cl] specifically, to partake in soil sorption.[34] Most ionic liquids were also found to be non-biodegradable and only significantly chemically degradable under UV irradiation in the presence of chemical oxidants. Generally, it was concluded that the toxicity of ionic liquids was fairly unpredictable and under-studied.[33]

Latal *et al.*[35] have shown the particular vulnerability of freshwater algae to imidazolium ionic liquids by exhibiting the protective effects of salt-water. High chloride concentrations were postulated to prevent absorption by algal cell of imidazolium cations, preventing toxicity.[35] Freshwater plants receive no such benefits. Additionally, various carboxylate ionic liquids have been shown to react with the aldehyde moiety on open chain glucose, to produce adducts of unknown toxicity alongside formaldehyde.[36] While [EMIM][Cl] and [BMIM][Cl] have not been shown to do this, it is essential that side reactions and relevant products be considered. In most processes for HMF production from cellulose in [BMIM][Cl] and [EMIM][Cl], conversion is significantly higher than HMF yield. This mean that a number of yet unstudied byproducts are being produced. Identification of these and an analysis of associated risks is essential to an eventual scale up of HMF production.

Finally, the metal catalysts must be considered. Chromium(II) and chromium(III) chlorides have been the most utilized, and show the most promise for future application of this work. Chromium(III) chloride has been shown to be relatively nontoxic in rats, as high oral doses yielded no adverse effects after 24 weeks of study.[37] Dayan *et al*.[38] assert, however, that chromium(III) is indeed toxic on the cellular level due to its redox reactivity. In general, very little to no data exists on the toxicity of chromium(II), as its use is generally limited to the laboratory. Clearly, toxicity studies on ionic liquids and these chromium compounds have a long way to go before their industrial application is realized. Logistics for the recycling of the ionic liquids alongside the chromium catalysts may also prove difficult.

CONCLUSION

While the prospect of producing HMF as a value-added target molecule directly from cellulose is an attractive one, the time is clearly not ripe for the large-scale industrial application of the process. A number of promising methods have been explored, but yields for most processes still hover around 50%, and side products are generally not known. These methods have hardly been scaled up, and toxicities and environmental dynamics of the reagents and products are only partially understood. Certain logistical dynamics are not well studied, including how to effectively separate value-added byproducts like lignin from cellulose while preserving the activity and recyclability of the ionic liquids. Before industrialization, definite and explicit studies must be performed to elucidate a method for large scale production which includes effective solvent and catalyst recycling, and full analyses must be performed to determine the effects of the ionic liquids and relevant transition metal catalysts on the environment.

AUTHOR INFORMATION

Corresponding Author

*Joseph Marrett

joseph.marrett@mail.mcgill.ca

ACKNOWLEDGMENT

The author thanks Prof. Robin Rogers and Prof. Audrey Moores for guidance in this project. Help from the editors is also appreciated.

ABBREVIATIONS

HMF, 5-hydroxymethylfurfural; [XMIM][Cl], 1-x-3-methylimadolium chloride

REFERENCES

(1) Facing the Hard Truths About Energy. Council, U. N. P., Ed.; US National Petrolium Council: Washington, DC, 2007.

(2) Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chemical Reviews* **2007**, *107*, 2411-2502.

(3) Rosatella, A. A.; Simeonov, S. P.; Frade, R. F. M.; Afonso, C. A. M. 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chemistry* **2011**, *13*, 754-793.

(4) Binder, J. B.; Raines, R. T. Simple Chemical Transformation of Lignocellulosic Biomass into Furans for Fuels and Chemicals. *Journal of the American Chemical Society* **2009**, *131*, 1979-1985.

(5) Lewkowski, J. Synthesis, chemistry and applications of 5-hydroxymethylfurfural and its derivatives. *Arkivoc* **2001**, 17-54.

(6) Lichtenthaler, F. W. Unsaturated O- and N-heterocycles from carbohydrate feedstocks. *Accounts of Chemical Research* **2002**, *35*, 728-737.

(7) Nisbet, H. B. *J. Inst. Petrol.* **1946**, *32*, 162-166.

(8) Roman-Leshkov, Y.; Barrett, C. J.; Liu, Z. Y.; Dumesic, J. A. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* **2007**, *447*, 982-U985.

(9) Düll, G. Action of oxalic acid on inulin. *Chem. Ztg* **1895**, *19*, 216-220.

(10) Halliday, G. A.; Young, R. J.; Grushin, V. V. One-pot, two-step, practical catalytic synthesis of 2, 5-diformylfuran from fructose. *Organic letters* **2003**, *5*, 2003-2005.

(11) Cottier, L.; Descotes, G. *Trends Heterocycl. Chem* **1991**, *2*, 233.

(12) Zhang, Y. G.; Chan, J. Y. G. Sustainable chemistry: imidazolium salts in biomass conversion and CO2 fixation. *Energy & Environmental Science* **2010**, *3*, 408-417.

(13) Li, C. Z.; Zhao, Z. K. B. Efficient acid-catalyzed hydrolysis of cellulose in ionic liquid. *Advanced Synthesis & Catalysis* **2007**, *349*, 1847-1850.

(14) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Dissolution of cellose with ionic liquids. *Journal of the American Chemical Society* **2002**, *124*, 4974-4975.

(15) Wyman, C. E.; Dale, B. E.; Elander, R. T.; Holtzapple, M.; Ladisch, M. R.; Lee, Y. Comparative sugar recovery data from laboratory scale application of leading pretreatment technologies to corn stover. *Bioresource technology* **2005**, *96*, 2026-2032.

(16) Kono, T.; Matsuhisa, H.; Maehara, H.; Horie, H.; Matsuda, K. Chemical transformation of lignocellulosic biomass into fuels and chemicals. *Jpn Pat Appl* **2005**, *2005232116*.

(17) Rinaldi, R.; Palkovits, R.; Schüth, F. Depolymerization of cellulose using solid catalysts in ionic liquids. *Angewandte Chemie International Edition* **2008**, *47*, 8047-8050.

(18) Tan, M.; Zhao, L.; Zhang, Y. Production of 5-hydroxymethyl furfural from cellulose in CrCl 2/Zeolite/BMIMCl system. *Biomass and bioenergy* **2011**, *35*, 1367-1370.

(19) Sheldrake, G. N.; Schleck, D. Dicationic molten salts (ionic liquids) as re-usable media for the controlled pyrolysis of cellulose to anhydrosugars. *Green Chemistry* **2007**, *9*, 1044-1046.

(20) Zhao, H.; Holladay, J. E.; Brown, H.; Zhang, Z. C. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. *Science* **2007**, *316*, 1597-1600.

(21) Moreau, C.; Finiels, A.; Vanoye, L. Dehydration of fructose and sucrose into 5-hydroxymethylfurfural in the presence of 1-H-3-methyl imidazolium chloride acting both as solvent and catalyst. *Journal of Molecular Catalysis A: Chemical* **2006**, *253*, 165-169.

(22) Su, Y.; Brown, H. M.; Huang, X.; Zhou, X.-d.; Amonette, J. E.; Zhang, Z. C. Single-step conversion of cellulose to 5-hydroxymethylfurfural (HMF), a versatile platform chemical. *Applied Catalysis A: General* **2009**, *361*, 117-122.

(23) Zhou, L. L.; Liang, R. J.; Ma, Z. W.; Wu, T. H.; Wu, Y. Conversion of cellulose to HMF in ionic liquid catalyzed by bifunctional ionic liquids. *Bioresource Technology* **2013**, *129*, 450-455.

(24) Liu, B.; Zhang, Z.; Zhao, Z. K. Microwave-assisted catalytic conversion of cellulose into 5-hydroxymethylfurfural in ionic liquids. *Chemical engineering journal* **2013**, *215*, 517-521.

(25) Peng, W.-H.; Lee, Y.-Y.; Wu, C.; Wu, K. C. W. Acid-base bi-functionalized, large-pored mesoporous silica nanoparticles for cooperative catalysis of one-pot cellulose-to-HMF conversion. *Journal of Materials Chemistry* **2012**, *22*, 23181-23185.

(26) Horton, D. Preface. The two most abundant organic substances on Earth, cellulose and starch. *Advances in carbohydrate chemistry and biochemistry* **2010**, *64*, xi.

(27) Klein- Marcuschamer, D.; Simmons, B. A.; Blanch, H. W. Techno- economic analysis of a lignocellulosic ethanol biorefinery with ionic liquid pre- treatment. *Biofuels, Bioproducts and Biorefining* **2011**, *5*, 562-569.

(28) Gutowski, K. E.; Broker, G. A.; Willauer, H. D.; Huddleston, J. G.; Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. Controlling the aqueous miscibility of ionic liquids: aqueous biphasic systems of water-miscible ionic liquids and water-structuring salts for recycle, metathesis, and separations. *Journal of the American Chemical Society* **2003**, *125*, 6632-6633.

(29) Zhu, S.; Wu, Y.; Chen, Q.; Yu, Z.; Wang, C.; Jin, S.; Ding, Y.; Wu, G. Dissolution of cellulose with ionic liquids and its application: a mini-review. *Green Chemistry* **2006**, *8*, 325-327.

(30) MYLLYMÄKI, V.; Aksela, R.: Dissolution method for lignocellulosic materials. Google Patents, 2005.

(31) George, A.; Brandt, A.; Tran, K.; Zahari, S. M. N. S.; Klein-Marcuschamer, D.; Sun, N.; Sathitsuksanoh, N.; Shi, J.; Stavila, V.; Parthasarathi, R. Design of low-cost ionic liquids for lignocellulosic biomass pretreatment. *Green Chemistry* **2015**, *17*, 1728-1734.

(32) Severin, I.; Dumont, C.; Jondeau-Cabaton, A.; Graillot, V.; Chagnon, M.-C. Genotoxic activities of the food contaminant 5-hydroxymethylfurfural using different in vitro bioassays. *Toxicology letters* **2010**, *192*, 189-194.

(33) Pham, T. P. T.; Cho, C.-W.; Yun, Y.-S. Environmental fate and toxicity of ionic liquids: a review. *Water research* **2010**, *44*, 352-372.

(34) Stepnowski, P. Preliminary assessment of the sorption of some alkyl imidazolium cations as used in ionic liquids to soils and sediments. *Australian journal of chemistry* **2005**, *58*, 170-173.

(35) Latała, A.; Nędzi, M.; Stepnowski, P. Toxicity of imidazolium ionic liquids towards algae. Influence of salinity variations. *Green Chemistry* **2010**, *12*, 60-64.

(36) Clough, M. T.; Geyer, K.; Hunt, P. A.; Son, S.; Vagt, U.; Welton, T. Ionic liquids: not always innocent solvents for cellulose. *Green Chemistry* **2015**, *17*, 231-243.

(37) Anderson, R. A.; Bryden, N. A.; Polansky, M. M. Lack of toxicity of chromium chloride and chromium picolinate in rats. *Journal of the American College of Nutrition* **1997**, *16*, 273-279.

(38) Dayan, A.; Paine, A. Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000. *Human & Experimental Toxicology* **2001**, *20*, 439-451.

Visible Light Photoredox Catalysis as a Greener Mode of Synthesis

Oliver P. Williams*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 0B8

KEYWORDS Visible Light Photoredox Catalysis, Sunlight, Energy, Sustainability

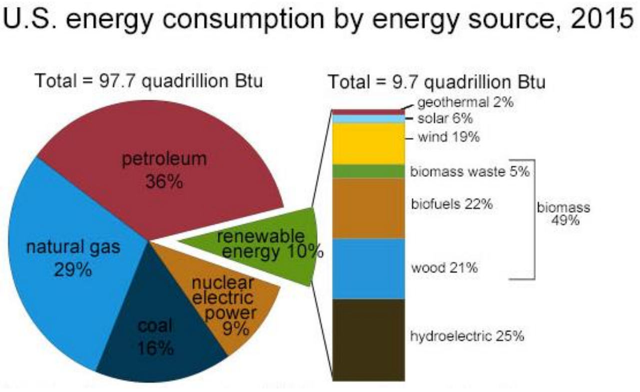
ABSTRACT: Visible light photoredox catalysis is a synthetic chemical method that has recently garnered much attention. This novel type of homogeneous catalysis uses light as a source of activation energy for chemical transformations. It has the potential to directly use energy from the sun in the form of ambient sunlight, thus potentially eliminating the need for energy derived from fossil fuel. While exciting and promising, this method of synthesis is not without flaws. The photocatalysts used are derived from precious metals and petrochemicals, and with regard to the chemistry, activated reagents are still needed. However, as visible light photoredox catalysis holds promise to increase independence from fossil fuels and is able to directly convert visible light energy into chemical energy, these intriguing reactions have a bright future.

THE PROBLEM

It is now evident and without doubt that human industry has had a definite and damaging impact on the environment.[4] Climate change and pollution are now two of the major problems that society faces. The root cause of many of these problems is how natural resources are used, which is largely determined by chemists. The role of a synthetic chemist is to discover ways to manipulate natural resources, including petroleum, minerals, and plant and animal materials into useful entities. These entities include pharmaceuticals, pesticides, paints, plastics, fuels, and so on. Currently, the chemical industry heavily relies on the petroleum industry, as the vast majority of chemical building blocks are petrochemicals.[5] It is well known that synthetic chemical products – for example, pesticides – can be harmful to the environment.[6] Less obvious is that the actual processes of making them can have equally harmful effects. At the end of a chemical process the desired product is obtained, but at the expense of waste in the form of side products, byproducts, unreacted reagents, additives, or solvent. These wastes need to be disposed of, which poses a problem if they are environmentally hazardous.[7]

ENERGY

Another aspect of chemical reactions is that energy is a necessary input for chemical transformations. Not only are many chemical building blocks sourced from the petroleum industry, as much of the energy used to perform reactions also comes from fossil fuels. Burning fossil fuels is a process that emits copious amounts of greenhouse gases, which in turn contribute to climate change. Furthermore, petroleum is a nonrenewable resource because it is being consumed faster than it is produced. In the U.S., 27% of the energy used by industry was consumed by chemical production; moreover, 81% of the total industrial energy consumption in the U.S. comes from the burning of fossil fuels (Figure 1).[1, 3]



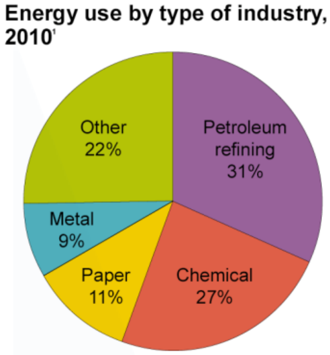


Figure 1. Breakdown of U.S. industrial energy consumption by sector and source. (*Top*) Data from the April 2016 "Monthly Energy Review;" due to independent rounding, components may not sum to 100%.[1] Source: U.S. Energy Information Administration, June 2016. (*Right*) Data from Table 1.2 of "Manufacturing Energy Consumption Survey 2010;" any consumption of energy and fuels is included, but the data excludes onsite produced energy shipments.[3] Source: U.S. Energy Information Administration, Dec 2014.

Clearly, the strong dependence on petroleum is not a sustainable way to interact with the environment. Due to chemists' strong influence on how the compounds and materials we use and consume daily are made, they have a striking opportunity to help our society and planet. Efforts have been made to address waste problems.[8-11] Alternatively, chemists may address environmental issues by altering the quantity, source, and way in which energy is used for chemical reactions. One way this can be achieved is by inventing novel and environmentally friendly chemical processes. Much effort has been geared toward catalysis, which, by definition, lowers the activation energy of a reaction. However, fossil fuels are still required as a source of energy, albeit in lower quantities. A more impactful approach would be to find a new source of energy entirely.

PHOTOCHEMISTRY

As defined by the International Union of Pure and Applied Chemistry, photochemical reactions are chemical reactions that are caused by the absorption of light energy. Light can play a dual role as both a catalyst and a source of activation energy. Photochemical reactions are interesting because light is an efficient source of energy, as it only targets chemical bonds; very little energy is wasted heating the surroundings. Also, novel reactivities can be achieved via chemical excitation with light. For example, [2+2] cycloadditions are thermally forbidden, but will proceed via irradiation with light. Typical photochemical reactions are not a solution to the environmental problem, however, because they rely on ultraviolet (UV) light, and many organic molecules absorb in this range. And because the range of UV light is not abundant in the solar spectrum, UV light for these reactions needs to come from eclectically powered lamps, whose energy is usually sourced form fossil fuels.[12]

VISIBLE LIGHT

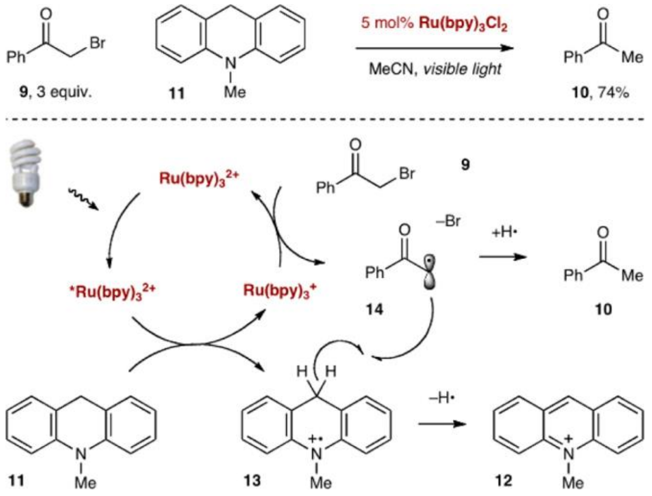
Ideally, chemical reactions could be carried out with no dependence on energy derived from the combustion of fossil fuels. It would also be advantageous to skip multiple steps of energy conversion, such as the formation of electricity.[13] This is possible and can be done by directly harvesting the energy of the sun for chemical transformations. Sunlight is a renewable and practically unlimited source of energy in the form of visible light, and is the ideal reagent because it is environmentally friendly and nontoxic. The notion of harvesting sunlight to carry out chemical reactions is not a novel one; plants have already mastered this technique in the form of photosynthesis.

Visible light photoredox catalysis mimics photosynthesis in the sense that light energy is collected to enable single electron transfer events. In considering energy demands for chemical reactions, the ultimate goal would be to efficiently harvest and convert solar energy into chemical energy and functionality.[14-15] Visible light photoredox catalysis represents a mode of synthesis that can potentially eliminate the need for fossil fuel-derived energy to carry out chemical reactions. Instead, it can use ambient sunlight as the sole source of energy for a chemical reaction.[16]

An example of a visible light photoredox catalytic reaction is presented in Scheme 1. First, the absorption of a visible light photon causes the photocatalyst, Ru(bipy)$_3^{2+}$ in this case, to enter an excited state. To reach this state, a single electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The photocatalyst is now a potent reductant due to the high-energy electron that now occupies the LUMO, as well as a powerful oxidant due to the now empty low-lying HOMO (Scheme 2).

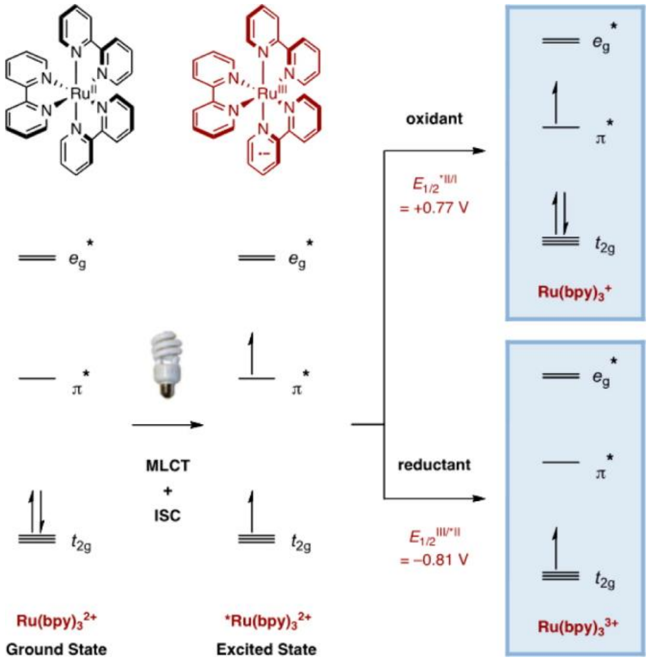
In this particular situation, the photocatalyst first acts as an oxidant and accepts an electron from a tertiary amine. The photocatalyst now becomes a potent reductant, and donates an electron to a carbon-bromine bond, causing the loss of bromide and formation of a radical. This transiently formed radical is able to abstract a proton from the oxidized amine, thus forming the final dehalogenated product. A common characteristic of these types of reactions is the ability of the photocatalyst to act as both an electron donor and acceptor, as well as the formation of highly reactive, but short lived, radicals.

Scheme 1. Example of Visible Light Photoredox Catalytic Reaction: Reductive Dehalogenation of Phenacyl Bromides



Reprinted with permission from Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C., Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chemical Reviews* **2013,** *113* (7), 5322-5363. Copyright 2013 American Chemical Society.

Scheme 2. Simplified Molecular Orbital Depiction of Ru(bipy)$_3^{2+}$ Photochemistry[2]



Reprinted with permission from Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C., Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chemical Reviews* **2013,** *113* (7), 5322-5363. Copyright 2013 American Chemical Society.

Table 1. Adherence of Visible Light Photoredox Catalysis to the principles of green chemistry.

Green Chemistry Principles[17]	Visible Light Photoredox Catalysis
Employ renewable energy sources (6)	Examples of reactions solely powered by sunlight
Increase energy efficiency (6)	Visible light is selectively absorbed, energy is directed to bonds
Reduce use of auxiliaries (5)	Ability to access previously difficult reactivities may reduce number of synthetic steps
Use benign reagents (3)	Reaction mixture and reagents are unreactive until exposure to light
Produce minimal and benign waste (1, 3)	Examples of coupling reactions, unreactive reagents and waste
Maximize atom economy (2)	Examples of coupling reactions
Reduce derivitization (8)	Examples of C-H functionalization
Employ mild reaction conditions (6)	Many benchtop reactions, performed at room temperature and pressure
Minimize accident potential (12)	Visible light is used instead of heating, high pressure, etc.
Utilize catalytic processes (9)	Use of a photocatalyst, examples of cooperative catalysis

PROS OF VISIBLE LIGHT PHOTOREDOX CATALYSIS

Many aspects of visible light photoredox catalysis adhere to the principles of green chemistry, as summarized by Table 1.

The ability of visible light photoredox catalysis to bypass the use of fossil fuel-derived electricity is astounding. These types of processes are characteristically more energy efficient than traditional solvothermal methods because the heating of solvent and surroundings is eliminated. The use of relatively low-energy visible light imparts yet another advantage. Most organic molecules found in reaction mixtures only absorb in the UV range. The use of visible light thus limits adverse side reactions. This also increases the applicability to late-stage functionalization, particularly of delicate and high value compounds, such as natural products.[18]

Another benefit is that new or previously difficult reactivities can be accessed, for example α-alkylation of aldehydes.[19] The ability to easily synthesize previously difficult products has a direct link to greener chemical synthesis. Decreasing the number of synthetic steps also decreases the total amount of reagents, solvents, and energy required for a certain transformation. Many C-C bond forming reactions are available, previously performed with poor atom economy and harsh, highly controlled conditions that required additives.[20] The facile formation of C-C bonds has the potential to further streamline chemical synthesis.

Compared to traditional synthetic methods, the reagents used in these types of reactions are relatively unreactive and benign. Instead of mixing a reactive species into a reaction, the reactive species are generated transiently, simply by irradiation with visible light. Interestingly, the catalyst is only a potent redox active species when light is shined upon it. The reactive intermediates generated from light exposure are usually radicals, which are highly reactive, and short-lived because they are quickly consumed to form products. This illustrates a way in which reactive species can be generated in a green manner. The short lifetimes of the reactive species means that the waste is generally not hazardous, as all of the reactive species are no longer present.

There are many examples of coupling reactions and C-H functinalizations.[21-23] C-H and C-X bonds can be transformed into C-C and H-X bonds, producing only mineral acid as waste, in an atomically economical form of synthesis. The use of visible light photoredox catalyzed reactions can replace current methods that rely on toxic reagents and harsh conditions, or that only get low yields and poor chemo- and regioselectivities.[24]

These reactions are operationally simple and mild. They can be performed at room temperature and atmospheric pressure. Furthermore, they do not require any specialized equipment, such as the photoreactors required when using UV light. They also offer high yields and selectivities of important synthetic intermediates.[25]

Although in its infancy, this area of research already covers a broad range of reactions using simple starting materials.[26] As Shaw et al. noted, "Recent advances in photoredox catalysis have demonstrated that a broad array of radical intermediates can be accessed from readily available chemicals such as carboxylic acids, halides and, in some cases, direct homolysis of C-H bonds, thereby expanding the range of methodologies for native functionalization."[27]

CONS OF VISIBLE LIGHT PHOTOREDOX CATALYSIS

Despite their extraordinary ability to use visible light as a source of energy for a chemical reaction, visible light photoredox reactions still have their environmental faults, particularly in the catalysts themselves. The photocatalysts used for these types of reactions are usually precious metal-based organometallic complexes, typically Ru or Ir polypyridal complexes (Figure 2). Ru and Ir are precious metals that need to be mined, and in its current state, the mining industry is by no means an environmentally friendly one.[28] As the name implies, precious metals are both rare and expensive. This is mostly due to their low concentrations in nature: as Ru is present in 100 ppt and Ir in 1000 ppt, they two of the nine least abundant elements in Earth's crust.[29] Furthermore, these are hardly renewable resources; 12 tonnes of Ru is mined each year with only 5000 tonnes in world reserves, and the processes required to purify the mined materials are highly energy intensive and require harsh chemicals.[30,31] Precious metal catalysts continue to be used due to their desirable characteristics, namely long excited state lifetimes, high quantum efficiency of photoexcited state formation, chemical stability of the ground state, favorable redox potentials, and ability to tune ligands for reaction optimization.[26]

Organic dyes have also been shown to work and have been increasingly utilized due to their environmental advantages over precious metal based catalysts.[32-33] According to Hari et al., "for several applications Eosin Y serves as an attractive alternative to redox active metal complexes and even outperforms them in some cases."[34] Organic dyes are commercially available and readily accessible. The precious metal based catalysts are also commercially available, but less accessible due to their high price: Eosin Y costs $0.54/mmol while Ir catalysts cost more than $1200/mmol.[35] Organic dyes may be favored because they are cheaper, easy to modify, and less toxic than the metal catalysts.

A majority of the reactions are limited to activated substrates, such as C-H bonds adjacent to tertiary amines and at benzylic positions. Also, there are few examples of intramolecular reactions, which are important for the synthesis of cyclic compounds.[36] This demonstrates that more reactions are needed with a larger substrate scope.[37]

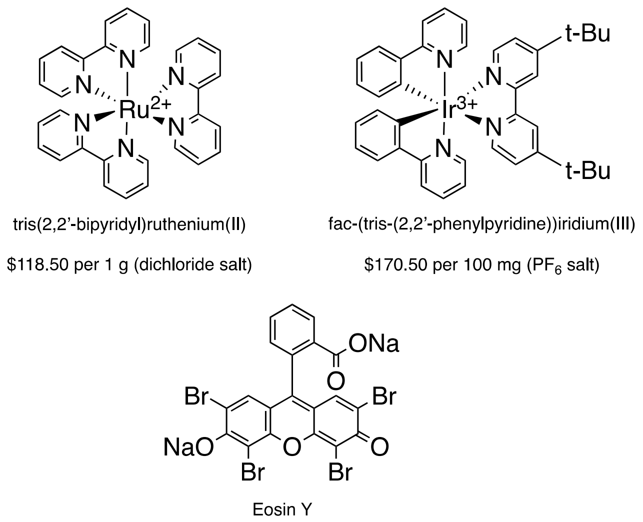


Figure 2. Structures of selected photocatalysts. Prices are listed in CAD for Sigma-Aldrich products (accessed November 2016). The price of Eosin Y is based on the Eosin Y disodium salt, Dye content ≥85 %.

Organic dyes may not be very environmentally friendly though, as they are synthesized from petrochemical feedstock, which, like precious metals, are another nonrenewable resource. According to the U.S. Energy Information Administration, the main reasons why the petroleum industry is detrimental are because it is based on a nonrenewable resource and because most of its products are burned as fuels, which emit greenhouse gases. Thus, it would not be so environmentally harmful if petroleum were to be used as a chemical feedstock only, and not as a fuel. In this sense, petroleum-based organic dyes are greener compared to rare earth metal based complexes, even without considering that the metal complexes rely on supporting ligands derived from petrochemicals. Organic dyes simply eliminate the reliance on metals, and therefore the mining industry. However, metals may not be that bad after all. Plants and animals use metals, such as iron used by cytochrome enzymes in redox reactions, and magnesium in light harvesting chlorophyll pigments. The key is to switch to earth abundant metals, of which examples in visible light photoredox catalysis already exist.[38]

It should also be noted that in the literature most reactions are performed under irradiation by light-emitting diodes (LEDs). No matter how efficient LEDs can be, they still rely on electricity. Fortunately, reactions can proceed under ambient sunlight; for example, DiRocco et al. noted it is possible to maintain both yield and diastereoselectivity in a photocatalytic cycloaddition performed on the gram scale, using solely ambient sunlight as a light source.[16] The use of these reactions with sunlight will inherently be limited to its availability. Solar intensity varies with altitude, latitude, and weather, and a cloudy day can dramatically affect yield. Furthermore, these reactions would not be possible during the night.[12]

ADDRESSING THE CONS

Some visible light photoredox reactions require stoichiometric reagents, such as terminal oxidants, thus decreasing the appeal of these catalytic reactions. However, there are reports of using molecular oxygen as the terminal oxidant, as well as completely oxidant free reactions.[39] Instead of being used as sacrificial electron donors or substrates, amines can be used as both.[36] These reactions also offer an alternative to accessing carbon-centered radicals from toxic tin reagents.

On another note, there are examples of using photoexcited aliphatic ketones as low cost radical initiators.[40] These can be molecules such as acetone, which is widely used, safe, and incredibly cheap, that would replace dangerous peroxides. Thiyl radical catalyzed reactions have also been reported.[41] These reactions use visible light and require neither a photocatalyst nor a photosensitizer.

Limitations of visible light photoredox catalysis can be addressed by employing cooperative techniques.[42,43] Coupling with earth abundant metal catalysis, organocatalysis, and others have delivered considerable and promising results.[44,45]

CONCLUSIONS

Society faces a serious environmental problem, which the chemical industry is partially responsible for. To address this problem the chemical industry can decrease its energy dependence on burning fossil fuels. Ideally, all energy required for a chemical reaction would be directly derived from the sun – a free, unlimited, and completely clean source of energy. This vision may be possible with visible light photoredox catalysis. Along with these catalysts' ability to directly derive all activation energy from sunlight, the reactions involved offer novel reactivates and routes of synthesis, and adhere to many of the 12 Principles of Green Chemistry. Modes of production are more likely to be industrially employed if they are smarter, more efficient, and resultantly greener. By reducing reliance on hazardous and reactive starting materials and longer syntheses, the chemical industry will potentially increase profits, making these types of reactions more probable to be embraced. Further savings are predicted because sunlight is free, and industry will have fewer safety concerns, such as worker exposure to hazardous materials, cleanup of hazardous waste spills, and high temperature or high-pressure reactors. The methods discussed herein are by no means perfect, due to their reliance on the petroleum and mining industries and currently limited applicability. Nonetheless, visible light photoredox catalysis offers itself is a step forward for greener synthetic chemical production because sunlight can be the only form of energy input.

FUTURE PERSPECTIVES

It should be noted that visible light photoredox catalysis is still an immature area of research and does not entirely eliminate the use of fossil fuels as energy input. In some ways this is exciting because there is still so much to learn form this promising and quickly growing field.[46] Recently, the Journal of Organic Chemistry released a special issue dedicated to photochemistry (August 2016 vol. 81 issue 16 pg. 6895-7341).

In other ways it is disappointing because it is not quite ready for industrial scale up. Milligram to kilogram scale syntheses of key industrial intermediates have been accomplished using cheap and commercially available starting materials.[47] However, specialized equipment to concentrate direct sunlight was used. Current research is focused on utilizing flow reactors, with promising results being reported (Figure 3).[48] According to Shaw, “the pharmaceutical industry has chosen to adopt these technologies at an unprecedented rate. Early work on their part has demonstrated that these catalytic platforms can be readily scaled up using flow technology.”[27] Visible light photoredox catalysis is particularly well-suited for flow chemistry, as this would alleviate the problem of light penetration into the reaction mixture. Despite its downsides, visible light photoredox catalysis will most certainly be a fascinating technique in a fossil fuel-free era.

Figure 3. Process-scale photoredox flow reactor at Merck. Photo courtesy of Merck and Co. Inc. Copyright 2016 American Chemical Society.[27,49]

AUTHOR INFORMATION

Corresponding Author

*Oliver Williams
oliver.williams@mail.mcgill.ca

REFERENCES

(1) U.S. Energy Facts Explained. http://www.eia.gov/energyexplained/?page=us_energy_home (accessed Nov 17, 2016).

(2) Kalyanasundaram, K., Photophysics, photochemistry and solar energy conversion with tris (bipyridyl) ruthenium (II) and its analogues. *Coordination Chemistry Reviews* **1982,** *46*, 159-244.

(3) Energy Use in Industry. http://www.eia.gov/energyexplained/index.cfm/data/index.cfm?page=us_energy_industry (accessed Nov 17).

(4) Goudie, A., *The human impact on the natural environment*. MIT press: 2000.

(5) Diercks, R.; Arndt, J. D.; Freyer, S.; Geier, R.; Machhammer, O.; Schwartze, J.; Volland, M., Raw material changes in the chemical industry. *Chemical engineering & technology* **2008,** *31* (5), 631-637.

(6) Damalas, C. A.; Eleftherohorinos, I. G., Pesticide exposure, safety issues, and risk assessment indicators. *International journal of environmental research and public health* **2011,** *8* (5), 1402-1419.

(7) Maczulak, A. E., *Pollution: treating environmental toxins*. Infobase Publishing: 2010.

(8) Krause, T.; Baader, S.; Erb, B.; Gooßen, L., Atom-economic catalytic amide synthesis from amines and carboxylic acids activated in situ with acetylenes. *Nature communications* **2016,** *7*, 11732.

(9) Trost, B. M., On inventing reactions for atom economy. *Accounts of chemical research* **2002,** *35* (9), 695-705.

(10) Kaupp, G.; Herrmann, A.; Schmeyers, J., Waste-Free Chemistry of Diazonium Salts and Benign Separation of Coupling Products in Solid Salt Reactions. *Chemistry–A European Journal* **2002,** *8* (6), 1395-1406.

(11) Su, N.; Fang, H.-Y.; Chen, Z.-H.; Liu, F.-S., Reuse of waste catalysts from petrochemical industries for cement substitution. *Cement and Concrete Research* **2000,** *30* (11), 1773-1783.

(12) Esser, P.; Pohlmann, B.; Scharf, H. D., The photochemical synthesis of fine chemicals with sunlight. *Angewandte Chemie International Edition in English* **1994,** *33* (20), 2009-2023.

(13) Protti, S.; Fagnoni, M., The sunny side of chemistry: green synthesis by solar light. *Photochemical & Photobiological Sciences* **2009,** *8* (11), 1499-1516.

(14) Lewis, N. S.; Nocera, D. G., Powering the planet: Chemical challenges in solar energy utilization. *Proceedings of the National Academy of Sciences* **2006,** *103* (43), 15729-15735.

(15) Balzani, V.; Credi, A.; Venturi, M., Photochemical conversion of solar energy. *ChemSusChem* **2008,** *1* (1-2), 26-58.

(16) Yoon, T. P.; Ischay, M. A.; Du, J., Visible light photocatalysis as a greener approach to photochemical synthesis. *Nature Chemistry* **2010,** *2* (7), 527-532.

(17) Anastas, P. T.; Warner, J. C., Principles of green chemistry. *Green chemistry: Theory and practice* **1998**, 29-56.

(18) DiRocco, D. A.; Dykstra, K.; Krska, S.; Vachal, P.; Conway, D. V.; Tudge, M., Late-Stage Functionalization of Biologically Active Heterocycles Through Photoredox Catalysis. *Angewandte Chemie International Edition* **2014,** *53* (19), 4802-4806.

(19) Nicewicz, D. A.; MacMillan, D. W., Merging photoredox catalysis with organocatalysis: The direct asymmetric alkylation of aldehydes. *Science* **2008,** *322* (5898), 77-80.

(20) Fagnoni, M.; Dondi, D.; Ravelli, D.; Albini, A., Photocatalysis for the formation of the CC bond. *Chemical Reviews* **2007,** *107* (6), 2725-2756.

(21) Condie, A. G.; González-Gómez, J. C.; Stephenson, C. R., Visible-light photoredox catalysis: Aza-Henry reactions via C− H functionalization. *Journal of the American Chemical Society* **2010,** *132* (5), 1464-1465.

(22) Zuo, Z.; Ahneman, D. T.; Chu, L.; Terrett, J. A.; Doyle, A. G.; MacMillan, D. W., Merging photoredox with nickel catalysis: Coupling of α-carboxyl sp3-carbons with aryl halides. *Science* **2014,** *345* (6195), 437-440.

(23) Hager, D.; MacMillan, D. W., Activation of C–H bonds via the merger of photoredox and organocatalysis: a coupling of benzylic ethers with Schiff bases. *Journal of the American Chemical Society* **2014,** *136* (49), 16986-16989.

(24) Fukuzumi, S.; Ohkubo, K., Selective photocatalytic reactions with organic photocatalysts. *Chemical Science* **2013,** *4* (2), 561-574.

(25) Zhao, Y.; Li, Z.; Yang, C.; Lin, R.; Xia, W., Visible-light photoredox catalysis enabled bromination of phenols and alkenes. *Beilstein journal of organic chemistry* **2014,** *10* (1), 622-627.

(26) Prier, C. K.; Rankic, D. A.; MacMillan, D. W., Visible light photoredox catalysis with transition metal complexes: Applications in organic synthesis. *Chemical reviews* **2013,** *113* (7), 5322-5363.

(27) Shaw, M. H.; Twilton, J.; MacMillan, D. W., Photoredox catalysis in organic chemistry. *J. Org. Chem* **2016,** *81* (16), 6898-6926.

(28) Nuss, P.; Eckelman, M. J., Life cycle assessment of metals: A scientific synthesis. PLoS One 2014.

(29) Earshaw, N. G. A., *Chemistry of the elements*. Butterworth-Heinemann: Oxford: Boston, 2006.

(30) Emsley, J., *Nature's Building Blocks: An A-Z Guide to the Elements*. Oxford University Press: 2001.

(31) Renner, H. S., G.; Kleinwächter, I.; Drost, E.; Lüschow, H. M.; Tews, P.; Panster, P.; Diehl, M.; Lang, J.; Kreuzer, T.; Knödler, A.; Starz, K. A.; Dermann, K.; Rothaut, J.; Drieselmann, R.; Peter, C.; Schiele, R., *Platinum Group Metals and Compounds. In Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA: 2000.

(32) Neumann, M.; Füldner, S.; König, B.; Zeitler, K., Metal-Free, Cooperative Asymmetric Organophotoredox Catalysis with Visible Light. *Angewandte Chemie International Edition* **2011,** *50* (4), 951-954.

(33) Fidaly, K.; Ceballos, C.; Falguières, A.; Veitia, M. S.-I.; Guy, A.; Ferroud, C., Visible light photoredox organocatalysis: a fully

transition metal-free direct asymmetric α-alkylation of aldehydes. *Green Chemistry* **2012,** *14* (5), 1293-1297.

(34) Hari, D. P.; König, B., Synthetic applications of eosin Y in photoredox catalysis. *Chemical Communications* **2014,** *50* (51), 6688-6699.

(35) Heitz, D. R.; Rizwan, K.; Molander, G. A., Visible-Light-Mediated Alkenylation, Allylation, and Cyanation of Potassium Alkyltrifluoroborates with Organic Photoredox Catalysts. *The Journal of Organic Chemistry* **2016,** *81* (16), 7308-7313.

(36) Maity, S.; Zhu, M.; Shinabery, R. S.; Zheng, N., Intermolecular [3+ 2] Cycloaddition of Cyclopropylamines with Olefins by Visible-Light Photocatalysis. *Angewandte Chemie International Edition* **2012,** *51* (1), 222-226.

(37) Xi, Y.; Yi, H.; Lei, A., Synthetic applications of photoredox catalysis with visible light. *Organic & biomolecular chemistry* **2013,** *11* (15), 2387-2403.

(38) Rawner, T.; Knorn, M.; Lutsker, E.; Hossain, A.; Reiser, O., Synthesis of Trifluoromethylated Sultones from Alkenols Using a Copper Photoredox Catalyst. *The Journal of Organic Chemistry* **2016,** *81* (16), 7139-7147.

(39) Pan, Y.; Wang, S.; Kee, C. W.; Dubuisson, E.; Yang, Y.; Loh, K. P.; Tan, C.-H., Graphene oxide and Rose Bengal: oxidative C–H functionalisation of tertiary amines using visible light. *Green chemistry* **2011,** *13* (12), 3341-3344.

(40) Li, L.; Mu, X.; Liu, W.; Wang, Y.; Mi, Z.; Li, C.-J., Simple and Clean Photoinduced Aromatic Trifluoromethylation Reaction. *Journal of the American Chemical Society* **2016**.

(41) Zhu, X.; Li, P.; Shi, Q.; Wang, L., Thiyl radical catalyzed oxidation of diarylalkynes to α-diketones by molecular oxygen under visible-light irradiation. *Green Chemistry* **2016,** *18* (23), 6373-6379.

(42) Skubi, K. L.; Blum, T. R.; Yoon, T. P., Dual Catalysis Strategies in Photochemical Synthesis. *Chemical reviews* **2016**.

(43) Lang, X.; Zhao, J.; Chen, X., Cooperative photoredox catalysis. *Chemical Society Reviews* **2016,** *45* (11), 3026-3038.

(44) Rabet, P. T.; Fumagalli, G.; Boyd, S.; Greaney, M. F., Benzylic C–H Azidation Using the Zhdankin Reagent and a Copper Photoredox Catalyst. *Organic letters* **2016,** *18* (7), 1646-1649.

(45) Terrett, J. A.; Clift, M. D.; MacMillan, D. W., Direct β-Alkylation of Aldehydes via Photoredox Organocatalysis. *Journal of the American Chemical Society* **2014,** *136* (19), 6858-6861.

(46) Narayanam, J. M.; Stephenson, C. R., Visible light photoredox catalysis: applications in organic synthesis. *Chemical Society Reviews* **2011,** *40* (1), 102-113.

(47) Oelgemöller, M.; Jung, C.; Mattay, J., Green photochemistry: Production of fine chemicals with sunlight. *Pure and Applied Chemistry* **2007,** *79* (11), 1939-1947.

(48) Cambié, D.; Bottecchia, C.; Straathof, N. J.; Hessel, V.; Noël, T., Applications of Continuous-Flow Photochemistry in Organic Synthesis, Material Science, and Water Treatment. *Chemical reviews* **2016**.

(49) 100% Organic. *Chemical & Engineering News Archive* **2015,** *93* (29), 33-34.

Introduction of green terminologies in organic synthesis and palladium-catalyzed cascade reactions for total synthesis of natural products

Yi Liu*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada, H3A 0B8

KEYWORDS: cascade reaction, palladium, total synthesis

ABSTRACT: Seeking for efficient and green synthetic methods has largely attracted scientists' attention because of the high demanding of cost saving and the increasing environmental issues. There are many terminologies defined to meet these green goals in synthesis, such as cascade reaction, domino reaction, and tandem reaction. There are also many concepts in terms of describing efficiency, such as atom economy, step economy and redox economy. This article first focuses on the explanations of these terms. Furthermore, it discusses several palladium-catalyzed cascade reactions for the total synthesis of natural products as case studies.

INTRODUCTION

Synthetic chemists are excited about transforming easily obtaining materials to molecular targets with large complexity. The design of organic reactions was mainly focused on the chemo-, region- and enantio-selectivity for a long time. A milestone work, which indicating the strength and arts of synthetic chemistry is the preparation of palytoxin amide that has 64 chiral carbon centers.[1] Scientists realized that, ideally, there shall not be any limitations of reaching complex molecules, but it come to the decision making point: is it worth the time, effort and cost we putting in? How can this process affect our environment? Can we reach the targeting molecule in an efficient and green way?

GREEN TERMINOLOGIES IN ORGANIC SYNTHESIS

1. Cascade reaction, domino reaction, and tandem reaction

Cascade reaction, where a sequence of reactions happens and the product of the former reaction is the starting material of the following reaction, was first applied by Robinson in 1917 for the synthesis of tropinone.[2] Cascade reaction can reduce the cost of synthesis by reducing the usage of reagents, solvents, and catalysts, etc. It can also save time and labor by avoiding unnecessary isolation and purification steps. More importantly, it enables reactions that occur through intermediates that are impractical for isolation. Unstable key intermediates can be trapped rapidly by the next step and transformed to the final stable product. The design of cascade reactions is crucial to reach the complexity of synthesis and it is also considered as the art of synthesis.

Domino reaction was first proposed by Tietze in 1996, which is a type of transformation where multiple bonds form without any modification of the reaction systems, such as reaction reagents and conditions, etc.[3]

Tandem reaction, where reactions happen one by one, was proposed by Denmark in 1996.[4] He further defined three types of tandem reactions when describe tandem cycloaddition, i.e. tandem cascade, tandem consecutive and tandem sequential reaction. Tandem cascade cycloaddition reactions occur under the same conditions and the reaction intermediates cannot be isolated. Tandem consecutive cycloaddtion: even though the second reaction does not require addition of reagents, it does not occur spontaneously because it needs an outer force to help overcome activation barrier, such as heating or light. The product of the first reaction in a tandem consecutive system is stable and can be isolated. Tandem sequential cycloaddition: the second process requires an addition of other reagents that will react with the product of the first step. The product of the first step may or may not be isolated.

Multi-component reaction is a type of reaction in which three or more starting materials are converged to form one product. The first example of multi-component reaction was reported by Laurent in 1838 for the synthesis of cyanohydrinimines.[5] Multi-component reaction can efficiently achieve high complexity in the construction of molecules and it can provide large diversity by simply change the functionality of each component.[6-7] Multi-component reactions are essential for drug discoveries because they allow the access to a library of molecules for the screening. There are many reviews or books available for this type of reaction.[8-11]

2. Atom economy, step economy, and redox economy

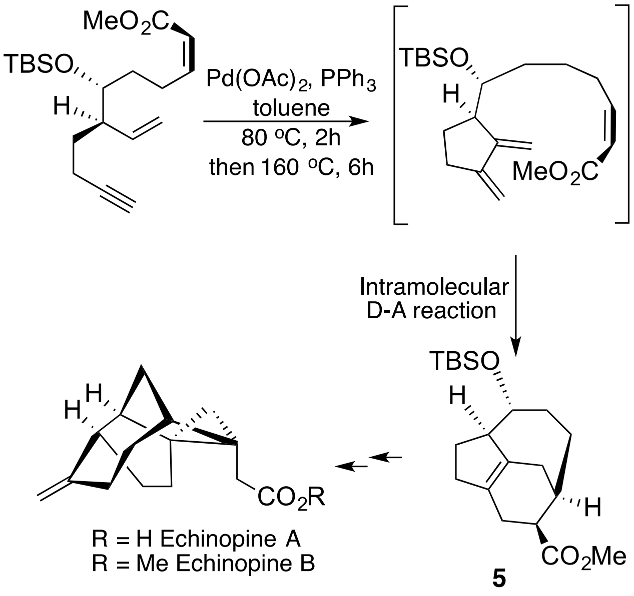
Atom economy was first brought up by Trost in 1991.[12] He opened a view of looking the efficiency of organic synthesis by counting the number of atoms that from the starting materials and end up in the desired product. An ideal atom economic reaction would be that all the mass of the reactants is incorporated to the targeting product.

Step economy, another goal in synthetic chemistry, is to minimize the number of reaction steps for the transformation of molecules.[13-14] The essential rationale to achieve step economy is to maximize the desired functionalities in each step by a careful selection of reaction type and reagents.

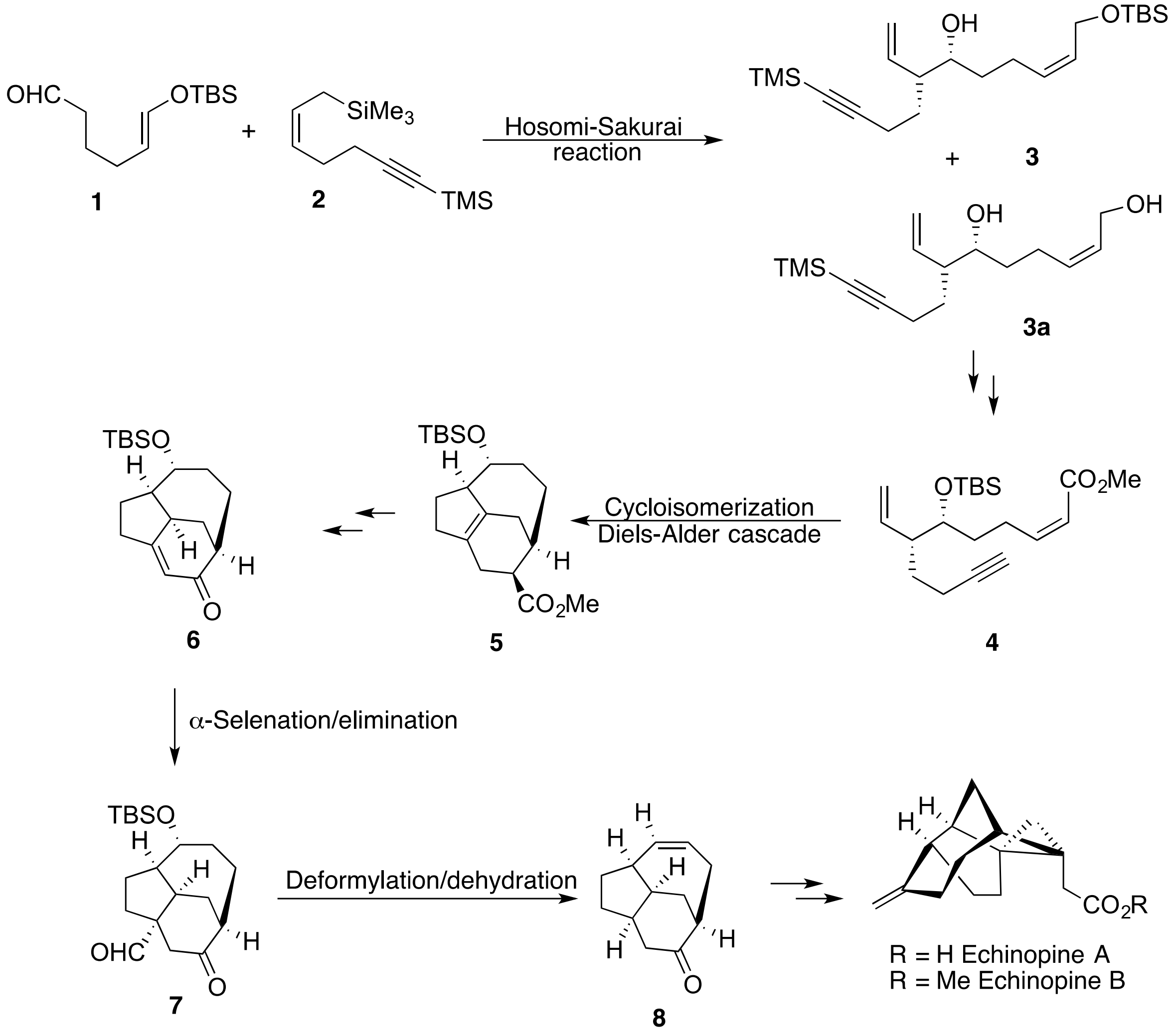
Redox economy is suggested by Baran and Hoffmann in 2009 to address specifically the importance of minimizing the use of redox steps in organic synthesis, not only in the perspective of step economy but also in the perspective of environmental benigh.[14-15] Redox reactions usually come along with toxic byproducts generation, which causes environmental issues and requires efforts for waste treatment.

PALLADIUM-CATALYZED CASCADE REACTIONS FOR THE TOTAL SYNTHESIS OF NATURAL PRODUCTS

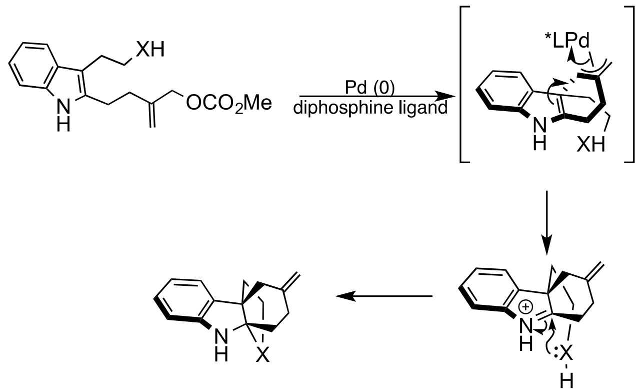
Transition-metal catalysis is ubiquitous in organic synthesis. Palladium-based catalysts are famous for their high catalytic reactivity and selectivity in the synthesis of organic molecules, which minimizes their drawback that they are relatively expensive.[16-17] Because of the large diversity of the catalytic reactions they provide, palladium-catalysts can be easily applied in cascade reactions, which acts as an important role in the total synthesis of natural products, for example cross-coupling reactions[18-21], Tsuji-Trost reaction[22-23], etc. The followings are two detailed cases of palladium-catalyzed cascade reactions in total synthesis.



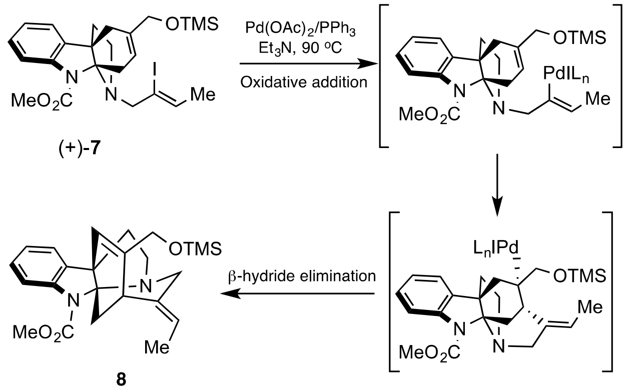
Scheme 1 Palladium-catalyzed cycloisomerization and intramolecular Diels-Alder cascade.[24]



Scheme 2 The total synthesis of (+)-echinopine A and B.[24]



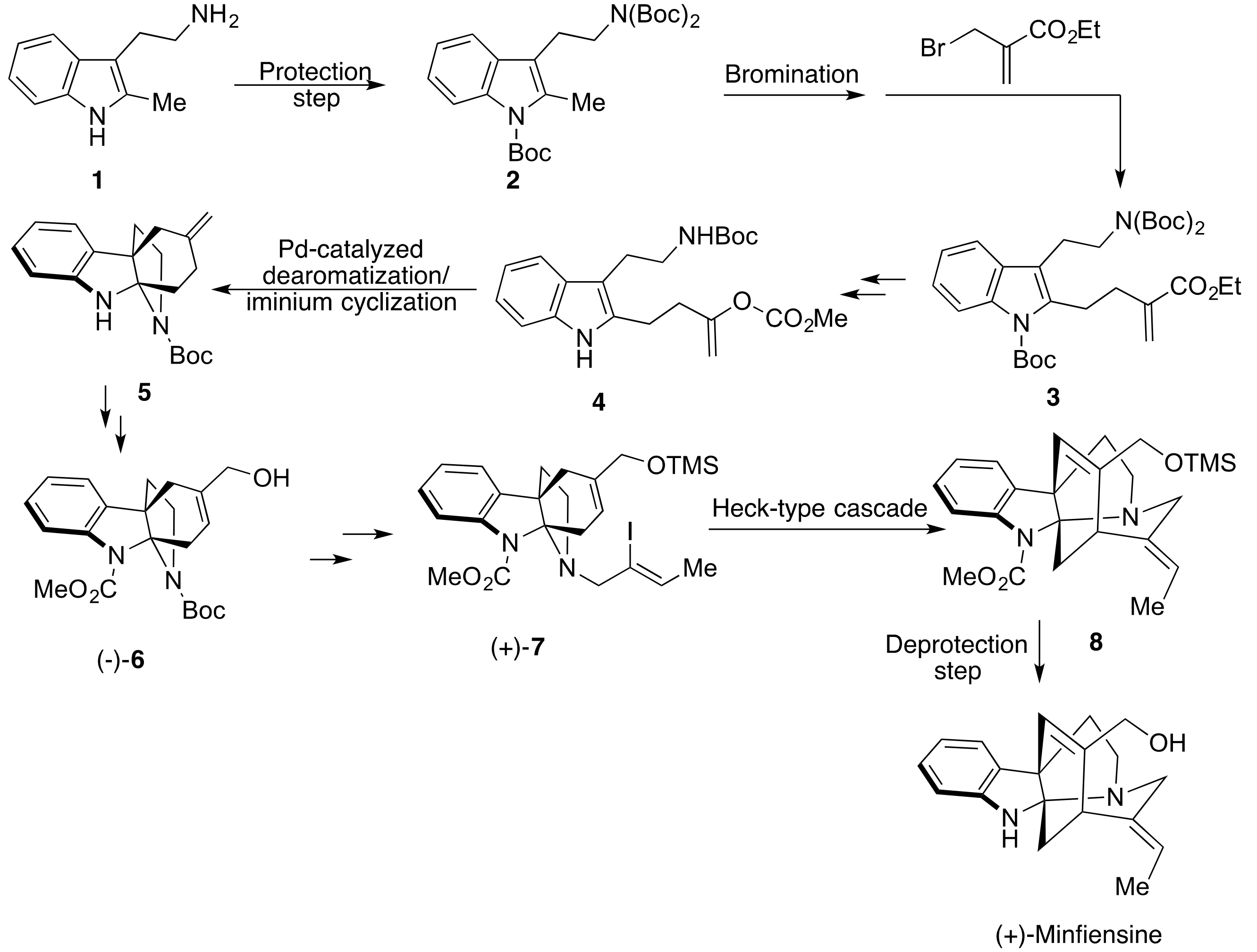
Scheme 3 Palladium-catalyzed asymmetric indole dearomatization/iminium cyclization cascade.[25]



Scheme 4 Heck-type cascade.[26]

Chen and coworkers synthesized (+)-echinopine **A** and **B** using a palladium-catalyzed cycloisomerization and intramolecular Diels-Alder cascade (Scheme 1).[24] The synthesis starts with the preparations of an alkenyl aldehyde **1** and an allyl silane **2** (Scheme 2). Reaction of **1** and **2** activated by $TiCl_4$ through a Hosomi-Sakurai reaction affords alcohol **3**, followed by a sequential change of the protecting groups and then oxidation to generate he key precursor **4**. Compound **4** is transferred to a [5,6,7] tricycle **5** in the presence of $Pd(OAc)_2/PPh_3$ at 80 °C and then at 160 °C for elongated time, where the cycloisomerization and intramolecular Diels-Alder cascade occur. Compound **5** undergoes reduction to give the alcohol, iodination/ elimination to give alkene, and oxidation to generate ketone **6**. Compound **6** further undergoes α-selenation/elimination to give α,β-unsaturated ketone and then followed by epoxidation and ring-opening to generate the ketoaldehyde **7**. Deformylation and dehydration of **7** deliver the tricyclic product **8**, which can be transformed to (+)-echinopine **A** and B using the method reported early by them.[27]

Minfiensine is a representative framework in monoterpene



Scheme 5 The total synthesis of (+)-minfiensine.[25]

indole alkaloids, which construct many natural products, such as akuammiline alkaloids. Akuammiline alkaloids have attracted large attention among scientific and pharmacological interests for over a century, since they have anticancer and analgesic effects.[28] Jiao and coworkers synthesized (+)-minfiensine using a palladium-catalyzed asymmetric indole dearomatization/iminium cyclization cascade and a Heck-type cascade.[25] As shown in Scheme 3, indole substrate generates an intermediate via intramolecular asymmetric allylic substitution, followed by the reaction with iminium ion to form the tetracyclic product. As shown in Scheme 4, the intermediate **9** was generated via oxidative addition of Pd to the C-I bond and the β-hydride elimination does not follow because of the lack of proper hydrogen, instead, a 1,2-insertion of the alkene occur to generate the tetracycle **10**, which then undergoes β-hydride elimination to give **8**.[26]

The total synthesis of (+)-minfiensine is shown in Scheme 5, which started with the commercially available 2-methyltryptamine to generate a Boc protected 2-methyltryptamine derivative **2**, followed by bromination to generate a bromomethylindole, and then coupling with a bromide using indium metal as catalyst to give **3**. Compound **3** undergoes reduction of the ester group, esterification, deprotection and reprotection of the amine group to generate the cyclic precursor **4**. Through the key palladium-catalyzed cascade, **4** is converted to the tetracycle **5**, which then is transformed to the hydroxymethyl moiety **6** by protection of the aniline NH, oxidation of the exocyclic C=C bond to an epoxide, regioselective ring-opening using bulky TMP-$AlMe_2$ (TMP: 2,2,6,6-tetramethylpiperdine). The deprotection of the amine group/converting of the hydroxyl group to –OTMS (TMS: trimethylsilyl), and then an N-alkylation step afford compound **7**, which undergoes Heck-type cascade reaction to afford **8**. (+)-Minfiensine was obtained by treatment of **8** with NaOH.

CONCLUSION

Green synthetic methods have being come up along with the rapid development of organic synthesis. The discovery of new reagents to selectively reach a targeting molecule is barely enough to satisfy the social and environmental demands, which promotes synthetic chemists to climb higher and gain new perspective through looking at the overall efficiency of the reactions and processes. There are many green terminologies that baring different focuses, but the overall goal is colored by “green”, i.e. to improve the efficiency of organic synthesis and make it environmental sustainable. Total synthesis of organic molecules opens a wide door, in terms of the amount and the diversity, for human beings for access to natural products. The discovery/design of cascade reactions is the real beauty of this molecular choreography.

AUTHOR INFORMATION

Corresponding Author

*Yi Liu
yi.liu3@mail.mcgill.ca

REFERENCES

(1) Armstrong, R. W.; Beau, J. M.; Cheon, S. H.; Christ, W. J.; Fujioka, H.; Ham, W. H.; Hawkins, L. D.; Jin, H.; Kang, S. H., Total synthesis of palytoxin carboxylic acid and palytoxin amide. *Journal of the American Chemical Society* **1989,** *111* (19), 7530-7533.

(2) Robinson, R., LXIII.-A synthesis of tropinone. *Journal of the Chemical Society, Transactions* **1917,** *111* (0), 762-768.

(3) Tietze, L. F., Domino Reactions in Organic Synthesis. *Chemical Reviews* **1996,** *96* (1), 115-136.

(4) Denmark, S. E.; Thorarensen, A., Tandem [4+2]/[3+2] Cycloadditions of Nitroalkenes. *Chemical Reviews* **1996,** *96* (1), 137-166.

(5) Laurent, A., Ueber das Oel der bituminösen Schiefer, das Eupion, die Ampelinsäure und das Ampelin. *Annalen der Pharmacie* **1838,** *25* (3), 283-290.

(6) Kayser, L. V.; Vollmer, M.; Welnhofer, M.; Krikcziokat, H.; Meerholz, K.; Arndtsen, B. A., Metal-Free, Multicomponent Synthesis of Pyrrole-Based π-Conjugated Polymers from Imines, Acid Chlorides, and Alkynes. *Journal of the American Chemical Society* **2016,** *138* (33), 10516-10521.

(7) Torres, G. M.; Quesnel, J. S.; Bijou, D.; Arndtsen, B. A., From Aryl Iodides to 1,3-Dipoles: Design and Mechanism of a Palladium Catalyzed Multicomponent Synthesis of Pyrroles. *Journal of the American Chemical Society* **2016,** *138* (23), 7315-7324.

(8) Dömling, A., Recent Developments in Isocyanide Based Multicomponent Reactions in Applied Chemistry. *Chemical Reviews* **2006,** *106* (1), 17-89.

(9) Zhu, J.; Bienaym, H., *Multicomponent Reactions*. Wiley: 2006.

(10) Brauch, S.; Van Berkel, S. S.; Westermann, B., Higher-order multicomponent reactions: beyond four reactants. *Chemical Society Reviews* **2013,** *42* (12), 4948-4962.

(11) Cioc, R. C.; Ruijter, E.; Orru, R. V., Multicomponent reactions: advanced tools for sustainable organic synthesis. *Green Chemistry* **2014,** *16* (6), 2958-2975.

(12) Trost, B. M., The atom economy--a search for synthetic efficiency. *Science* **1991,** *254* (5037), 1471.

(13) Wender, P. A.; Croatt, M. P.; Witulski, B., New reactions and step economy: the total synthesis of (±)-salsolene oxide based on the type II transition metal-catalyzed intramolecular [4+4] cycloaddition. *Tetrahedron* **2006,** *62* (32), 7505-7511.

(14) Wender, P. A.; Verma, V. A.; Paxton, T. J.; Pillow, T. H., Function-Oriented Synthesis, Step Economy, and Drug Design. *Accounts of Chemical Research* **2008,** *41* (1), 40-49.

(15) Burns, N. Z.; Baran, P. S.; Hoffmann, R. W., Redox economy in organic synthesis. *Angewandte Chemie International Edition* **2009,** *48* (16), 2854-2867.

(16) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D., Palladium-Catalyzed Cross-Coupling Reactions in Total Synthesis. *Angewandte Chemie International Edition* **2005,** *44* (29), 4442-4489.

(17) Tsuji, J., *Organic synthesis with palladium compounds*. Springer Science & Business Media: 2012; Vol. 10.

(18) Koseki, Y.; Sugimura, T.; Ogawa, K.; Suzuki, R.; Yamada, H.; Suzuki, N.; Masuyama, Y.; Lin, Y. Y.; Usuki, T., Total Synthesis of Isodesmosine by Stepwise, Regioselective Negishi and Sonogashira Cross- Coupling Reactions. *European Journal of Organic Chemistry* **2015,** *2015* (18), 4024-4032.

(19) Rossi, R.; Bellina, F.; Lessi, M.; Manzini, C.; Marianetti, G.; A Perego, L., Recent Applications of Phosphane-based Palladium Catalysts in Suzuki-Miyaura Reactions Involved in Total Syntheses of Natural Products. *Current Organic Chemistry* **2015,** *19* (14), 1302-1409.

(20) Rummelt, S. M.; Preindl, J.; Sommer, H.; Fürstner, A., Selective Formation of a Trisubstituted Alkene Motif by trans-Hydrostannation/Stille Coupling: Application to the Total Synthesis and Late- Stage Modification of 5, 6- Dihydrocineromycin B. *Angewandte Chemie International Edition* **2015,** *54* (21), 6241-6245.

(21) Yang, M.; Yang, X.; Sun, H.; Li, A., Total Synthesis of Ileabethoxazole, Pseudopteroxazole, and seco- Pseudopteroxazole. *Angewandte Chemie International Edition* **2016**.

(22) Tsuji, J.; Takahashi, H.; Morikawa, M., Organic syntheses by means of noble metal compounds XVII. Reaction of π-allylpalladium chloride with nucleophiles. *Tetrahedron Letters* **1965,** *6* (49), 4387-4388.

(23) Trost, B. M.; Fullerton, T. J., New synthetic reactions. Allylic alkylation. *Journal of the American Chemical Society* **1973,** *95* (1), 292-294.

(24) Peixoto, P. A.; Severin, R.; Tseng, C. C.; Chen, D. Y. K., Formal Asymmetric Synthesis of Echinopine A and B. *Angewandte Chemie* **2011,** *123* (13), 3069-3072.

(25) Zhang, Z. X.; Chen, S. C.; Jiao, L., Total Synthesis of (+)-Minfiensine: Construction of the Tetracyclic Core Structure by an Asymmetric Cascade Cyclization. *Angewandte Chemie International Edition* **2016,** *55* (28), 8090-8094.

(26) Xu, P.-F.; Wang, W., *Catalytic Cascade Reactions*. Wiley Online Library: 2014.

(27) Magauer, T.; Mulzer, J.; Tiefenbacher, K., Total Syntheses of (+)-Echinopine A and B: Determination of Absolute Stereochemistry. *Organic Letters* **2009,** *11* (22), 5306-5309.

(28) Smith, J. M.; Moreno, J.; Boal, B. W.; Garg, N. K., Cascade Reactions: A Driving Force in Akuammiline Alkaloid Total Synthesis. *Angewandte Chemie International Edition* **2015,** *54* (2), 400-412.

Lyocell: Exploring Greener Options in Today's Fiber Market

Qudsia Saadat*

Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada, H3A 0B8

KEYWORDS: lyocell, NMMO, fiber industry, fabric, cotton, synthetic fibers

ABSTRACT: The global fiber market is growing and as it continues to do so, implementing greener alternatives to existing fabrics is essential. Lyocell, a fiber derived from cellulose has the potential to replace cotton, rayon and other synthetics as the textile industry's mainstay. It is produced on a closed loop system that recovers over 99% of its solvent, rendering it minimally wasteful. Advantageous properties such as its durability, high tensile strength and absorbency make lyocell a simultaneously green and competitive fiber. This review will introduce the reader to lyocell, from the perspective of green chemistry and textile economics, as an alternative to petroleum synthetics and traditional fabrics such as cotton and rayon.

INTRODUCTION

Fiber and apparel industries are growing, with cotton, petroleum synthetics (nylon and polyester) and rayon forming the majority of the global fiber production [1]. Each of these fibers has its own unique disadvantages. Traditional fibers like cotton which account for 50% of the fibers used to make clothing and textiles require massive amounts of water, land and pesticides. Oil-based synthetic fibers, which hold 62.1% of global fiber shares, are energy intensive and non-biodegradable [2]. Rayon is primarily produced via the viscose process and its usage is declining as its manufacturing process is harmful to the environment [4].

Lyocell, also known by its trade name, Tencel, is an iteration of rayon that has more favorable implications for the environment along with competitive fabric properties. The key features of lyocell are due to a green overhaul of the manufacturing process typically involved for rayon; one that incorporates a closed-loop system that recuperates nearly all of its solvent as opposed to its predecessor [5]. Although still nascent in the global rayon market, lyocell is projected to grow in the coming years and potentially lessen dependence on petrochemical-based synthetics.

BACKGROUND

It was in the late 19th century when the first partially synthetic fibers came to be. Originally referred to as "regenerated cellulose fibers" because of the materials' origin in wood by-products, they are more commonly known today as "rayon" after having been renamed by the US Department of Commerce. Rayon went on to be widely adopted by the garments industry due to economies of scale afforded by cheaply-procurable raw materials and minimal processing requirements, particularly when compared to traditional fibers like cotton [5]. While still popular, rayon has largely been superseded by contemporary petrochemical synthetics such as polyester and nylon, maintaining less than 5% of artificial fiber market share in the recent years [1]. Aside from economic considerations, rayon production has historically been devastating for the environment; three of the U.S's largest Superfund cleanup sites are the location of former rayon production facilities [6].

While Lyocell only started to see commercial success in the late 90s at the hands of Lenzing AG, it owes its existence to various additional firms whose work dates all the way to mid 20th century, such as Eastman Kodak, American Enka, Courtaulds Fibers and Azko Nobel (which acquired Courtalds and American Enka). The primary drive to develop lyocell was brought about by the British firm Courtaulds in the 1950s. At the time, viscose rayon accounted for 80-90% of Courtaulds' revenue and they were experiencing stagnating profits due to the introduction of newer synthetic fibers [7].

It is only towards the 1980's that Courtaulds decided to double down on lyocell development, hoping to revitalize the dying rayon market after a drop in oil prices due to geopolitical issues involving OPEC [8]. Development was further made possible by the research of Kodak and American Enka. While employed at Kodak, Dee Lynn Johnson performed crucial research on the use of cyclic mono compounds, such as NMMO, triggering large slides in lyocell development. He discovered ways of dissolving difficult natural and synthetic compounds, namely cellulose through these saturated, cyclic, amine oxides (N-methylmorpholine-N-oxide, NMMO) (Figure 1). He then posited that this could be used to alter the properties of cellulose solutions to favor their use in various medical, culinary, industrial and textile applications [9].

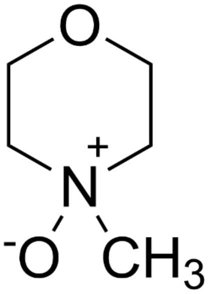


Figure 2. Chemical structure of NMMO (10)

American Enka built on this research by devising ways of concentrating the cellulose solutions produced with NNMO solvents. In the mid 70s, Enka researchers, Julianna Varga and Neal Franks, determined that maintaining the water content of the system at a certain level would keep the solution free of both solvent crystals and undissolved cellulose strands [5].

Despite pioneering these advancements, Enka didn't seriously invest in this new research; rather, it was Courtaulds that capitalized the opportunity. From 1979 to 1987, Courtaulds worked on the "Genesis" project to bring about what is now known as lyocell. While other researchers had demonstrated the theory behind the process of dissolving cellulose in amine oxides, it was Courtaulds' research team that developed the manufacturing process that avoided previously common explosive reactions, while remaining economically viable [11].

They soon launched their new lyocell following a heavy marketing campaign, but production did not last very long as other synthetic fibers were still more economical. Despite the projected long-term profitability, lyocell fashion never materialized in anywhere but Japan and Courtaulds had no choice but to sell itself to Azko Nobel, a casualty of early green chemistry endeavors [5]. Concurrently, Lenzing AG had also started developing their own version of lyocell and through a series of acquisitions and acrimonious patent disputes, by the turn of the century, eventually became the leading manufacturer of lyocell globally in the 90s, as it continues to be today [12].

CELLULOSE DISSOLUTION IN NMMO SOLVENT

Lyocell, as a subcategory of rayon fibers, is a macromolecular arrangement of cellulose (Figure 1) and is produced by a solvent spinning process that involves the dissolution of cellulose in the cyclic amine oxide solvent, NMMO.

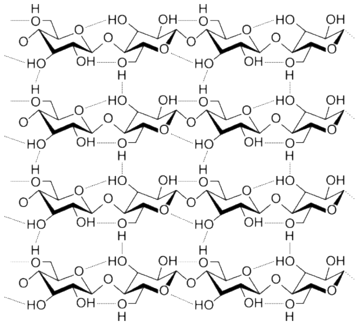


Figure 1. Cellulose, main component of lyocell (13)

NMMO is made by the oxidation of the ternary amine N-methylmorpholine with hydrogen peroxide, and it is cyclic and aliphatic. NMMO monohydrate, produced by hydrating NMMO with one water molecule, is often used as a solvent as it has a lower melting temperature and a higher solvation strength [4].

Although the dissolution of cellulose in NMMO has been investigated, the interaction process is still not fully understood. However, it is known that NMMO's highly polar N-O dipole allows it to dissolve cellulose very well in aqueous solution [14], without any derivatization (as normally occurs with rayon fibres [4]). NMMO has the ability to disrupt the hydrogen bonds of the cellulose structure and form new complexes with the macromolecules through interactions between its N-O dipole and hydroxyl groups on the cellulose [14].

Cellulose desolvation can also occur under the same hydrogen-bonding mechanisms when NMMO is in aqueous solution, as water is a polar liquid and is miscible with NMMO. Water interferes with the interaction between cellulose and NMMO and allows for the cellulose molecules to reform their hydrogen bonds. As such, the water content of the NMMO-water solution is limited, as high water content would precipitate, rather than dissolve the cellulose [4].

PROPERTIES AND APPLICATIONS

As a subcategory of rayon, lyocell encompasses many of the traits typically associated with other cellulosic fibers such as rayon. Accordingly, lyocell is known to possess high tensile strength, whether dry or wet. When dry, it is comparable to other forms of rayon and near that of polyester. When wet, it has a wet tensile strength exceeding that of cotton, unlike other forms of rayon [15].

Lyocell excels in functionality which is an important consideration of clothing design. Due to its ability to absorb moisture, lyocell can serve many applications that require contact with the skin. In addition to all varieties of clothing, this includes covers for beds, medical disposables such as bandages and swabs and other household items such as towels and diapers. Because lyocell allows for air circulation, less moisture collects and consequently, bacteria thrive less on the material. This makes lyocell clothing less conducive to the development of odors, ideal for applications in athletic clothing and footwear [16]. Conversely, petrochemical synthetics barely absorb moisture at all [17]. This and its non-use of abrasive chemicals normally found within petrochemical synthetics makes it an exceptionally hypoallergenic material. Lyocell is also softer than regular rayon and this makes it a better silk substitute. It has high dimensional stability; this is paramount in producing shrinkage averse clothing [16].

Many of lyocell's favorable properties are bestowed upon it by nanofibrils, fibers which have diameters of less than 0.5 microns that are longitudinally split. These fibers are hydrophilic and thus allow the material to absorb moisture. The nanofibrils are also the cause of lyocell's softness. They are finer and thus less abrasive against the skin [18].

Lyocell exhibits various desirable properties for the consumer, but it is also pleasant for garment producers to work with as well. It has excellent dye uptake capabilities, due to its cellulosic nature. Its fibrils can also be intentionally manipulated to create a variety of textures, such as suede, "peach skin", silk or denim. When properties of other fibers are desired, it will easily blend to produce hybrid fabrics. Because of its fibrillation properties, lyocell is also more vulnerable to enzymatic attack. The smaller fibril diameters provide a larger surface area for enzyme treatment. This makes the enzyme treatment a more efficient process for manufacturers to alter the aesthetic and functional properties of the fabric [19].

MANUFACTURING PROCESS

As mentioned earlier, the key distinguishing feature of lyocell among its alternatives is the waste efficiency of its manufacturing process. One of the most commonly used techniques in manufacturing synthetic and cellulosic fibers is the solvent spinning process. This method involves pumping a viscous solution through the tiny pores of a device called a spinneret to form strands of polymer. What separates the production of lyocell from the other fibers is that it involves the dissolution of cellulose in NMMO solutions. When Courtaulds' research team was investigating possible solvents to directly dissolve cellulose, NMMO was determined as the most viable candidate: it dissolves cellulose completely without degrading it, it is non-toxic [20], it is not harmful to the environment when spilled, and it is almost entirely recyclable [21].

As detailed in White et al, the lyocell process itself is well-known for its closed loop system, which allows for nearly 99.8% recovery of the solvent. In the first step of the process, wood pulp is dissolved in a solution of hot NMMO in water. The solution is then heated under vacuum, using a thin film evaporator, to remove traces of water. As the solution flows down the center of the evaporator vessel, it gets heated from the surroundings of the inner shell. It is performed in a vacuum to maintain a controlled temperature as higher temperatures could degrade the NMMO solvent. The solution gets transported to undergo two filtrations in order to get rid of the remaining inorganic compounds and undissolved pulp fibers. Once filtered, the solution is ready for the spinning process; it is pumped through the thousands of microscopic holes of the spinneret. As the solution seeps out as filaments, cool air is circulated to ensure that the fibers maintain their aligned structure and strength. The fibers are then soaked into a dilute NMMO bath where they precipitate, followed by several washes with demineralized water [18]. During the bath and wash, the solvent is circulated for recovery and regenerated for reuse [21]. At this time, different treatments, such as bleaching and other enzymatic treatments can be applied to give the fiber its desired properties. The fiber is then dried, crimped, cut and baled to be sold as lyocell [18].

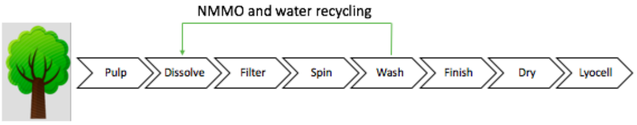


Figure 3. The lyocell process in general.

While the lyocell production process would ideally be solely physical, chemical side reactions that complicate the process can also occur. For example, NMMO and cellulose can degrade and the fibers can become discolored. NMMO is thermally unstable and a strong oxidant [22], and explosions, otherwise referred to as, 'runway thermal reactions' have occurred in the past in pilot-scale plants. All of these can negatively influence the percentage of recovery of NMMO, the quality of the fiber and can be hazardous to workers. Significant research is continually being conducted to counteract these reactions and to make these processes safe. Sufficient progress has been made and this is demonstrated by the large scale industrial production facilities of lyocell fibres [4]. Currently, the degradation of cellulose is being minimized by including degradation inhibitors in the solution. Before reaching filtration, the solution is transported under highly pressurized and cool pumps as NMMO has the potential to degrade exothermically. As the temperature increases, the pressure does as well. In order to avoid this, bursting discs are planted to diffuse the gas into the atmosphere and prevent explosions [18]. Additives are put into place, such as long-chain surfactants, which help increase the interaction between NMMO and cellulose. Stabilizers, such as antioxidants (e.g. gallic acid propylester) [8] are also added to reduce degradation of NNMO and cellulose, and to reduce the chances of thermal runaway reactions from occurring [4].

ENVIRONMENTAL IMPACT

When considering lyocell's life from cradle to grave, its environmental impact is minimal. Lyocell is made of nearly 100% cellulose, the most abundant renewable biopolymer in the world, and is thus fully biodegradable [18]. A wide variety of trees can be used to make lyocell, however, eucalyptus trees are the most commonly used. Eucalyptus trees grow quickly without the application of fertilizers, pesticides or genetic modifications, and they do not need to compete with food production as they can grow on non-arable land. The trees are grown in forests that are sustainably managed and constantly replanted [18]. In addition, the remaining polymers from wood can be extracted for other purposes. For example, lignin can be used to make biofuels, which can be used to generate energy for the facilities to operate [23]. The extracts from the leaves and barks of the trees can be made into natural coloring and used as a dye for the lyocell fabric as well [24].

The manufacturing process is remarkably waste efficient, as over 99% of the amine-oxide solvent is recycled. NMMO is not acidic nor toxic as such it is safe for the environment in cases of spillage [18]. In terms of quantity, only a few kilograms of solvent are required to develop one ton of fiber [21].

The manufacturing process of most fibers is energy- and water-intensive. The Stockholm Environment Institute reported that energy consumption for the production of polyester is 10 times higher than cotton, when comparing plants around the world. In contrast to it's energy consumption, polyester production requires little to almost no water. This is almost close to none when compared to cotton (one kg of cotton requires 8000 L of water) and other fibers [25]. Another study compared the "water footprint," or the total amount of freshwater used for the production and consumption of a material by humans, of a pair of jeans made out of either lyocell or cotton, by looking at the total amount of freshwater used for the production and consumption of a material. They found that lyocell compares favorably to cotton in this metric [26].

The lyocell process itself can be used with source materials other than lyocell, and Lenzing AG has been incorporating recycled materials as a first showing of this potential [27]. Studies have shown that using cotton waste as feedstock generates fibers that have similar qualities to cotton and lyocell, and mechanical properties that resemble those of lyocell [18]. In a very green manner, the process can be reinvented to work with materials that would otherwise go to waste.

At the consumer level, lyocell's energy expenditure is low. Lyocell has moisture absorptive properties that keep clothes odor- and bacteria-free for longer periods, allowing consumers fewer washings between wear. This reduces energy and water use consumption while conserving the product [16].

When lyocell reaches the end of its life, it can be used as feedstock and recycled to produce lyocell again. However, a concern regarding the recycling of lyocell is that the low fibrillation fibers don't degrade easily, making it less suitable for reuse. Over time, the quality of the fiber decreases as well. Nonetheless, its biodegradability makes it suitable for composting, incinerating, or landfill disposal [28].

ECONOMIC AND LONG-TERM OUTLOOK

Lyocell has gained traction in the market because of its versatility, biodegradability, and some attractive qualities in applications, such as home textiles and apparel. However, its environmentally responsible and efficient manufacturing process is what sets lyocell apart from natural fibers as a greener fiber. Cotton requires massive amounts of water, land, and pesticide use [3]. Synthetic materials also come with a plethora of problems, which include being energy intensive, non-biodegradable, and production from petroleum.

In recent years, there has been an increased awareness of the detrimental environmental impact fibers have had in the western world. As a result, industry and academia have been paying more attention to sustainable material replacements. This has translated into prime conditions for a fiber with properties similar to those of lyocell to thrive. The global lyocell fibers market is projected to be at 1.1 billion dollars in 2020, an increase from 700 million dollars in 2013, with apparel making up 50% of the lyocell fiber market [29]. Moreover, while lyocell is more expensive to produce than other fibers due to the price of the amine-oxide solvent, this has not necessarily transferred to shoppers. Major retailers like H&M, Gap and Patagonia have started incorporating lyocell into their clothing offerings, at price points that are on par with other items in the store, capitalizing on consumer desire for greener products. The introduction of lyocell to the general public, in addition to its properties, and environmentally responsible approach will only serve to increase demand.

NEW [PERHAPS EVEN GREENER] DIRECTIONS

One of the drawbacks to the lyocell process is that the amine-oxide solvent is relatively expensive [8]. However, the recycling rates of solvent in the lyocell process are near 100%, peaking at 99.8% industrially [18]. Despite the exceedingly high solvent recovery rate, research is being done to see how the lyocell process can be altered to make it even more efficient. It is known that ionic liquids (ILs), essentially liquid salts, directly dissolve cellulose [30], implying potential as replacement to NMMO. ILs are salts that are liquid at low temperatures [22]. They are chemically stable, have tunable properties [23], and low vapor pressure [31]. Using IL as the solvent, Ioncell was developed under the same processes of lyocell. Ioncell has stronger mechanical properties, and better quality than lyocell. With ILs, the operating temperatures can be reduced, thus, lowering the energy, expenses and the chance of cellulose degrading [32]. ILs also seem to be a promising avenue that could be incorporated with the lyocell process.

CONCLUSIONS

When materials are being decided upon for a specific application, they often fall short of one or more criteria. This can include, durability, texture, toxicity, environmental impact, and ease of working with the material. Lyocell has shown to exceed acceptable levels of performance and tolerance for all these properties and many more. Its primary downside to date is still its cost of manufacture. While it already sees extensive use in the consumer and medical industries, its continual development is being hampered by readily available cheaper substitutes. Still, with further advances in green chemistry and a reduction in dependence on petrochemical synthetics, lyocell has a bright future in ushering a future era where the environmental impact of textiles is minimal.

AUTHOR INFORMATION

Corresponding Author

Qudsia Saadat
qudsia.saadat@mail.mcgill.ca

ACKNOWLEDGMENT

I would like to thank Prof. Robin D. Rogers and Prof. Audrey Moores for their assistance and mentorship as well as the McGill Green Chemistry Journal Editorial Board for the editing and publishing of this article.

ABBREVIATIONS

NMMO, N-methylmorpholine-N-oxide; IL, ionic liquid

REFERENCES

(1) Vartest Laboratories. http://vartest.com/resources/technology-portal/polymers-in-textile-fibers/ (assessed November 22, 2016)

(2) Lenzing. The Global Fibre Market in 2015. http://www.lenzing.com/en/investors/equity-story/global-fiber-market.html (assessed November 22, 2016)

(3) Eichinger D., A vision of the world of cellulosic fibers in 2020. *Lenzinger Ber* **2012**, 90,1-7.

(4) Rosenau, T.; Potthast, A.; Sixta, H.; Kosma, P., The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (Lyocell process). *Progress in Polymer Science* **2001**, 26 (9), 1763-1837.

(5) Woodings, C. A brief history of regenerated cellulosic fibers; Woodhead Publishing Ltd, **2001**.

(6) United States Environmental Protection Agency. EPA Superfund Program. https://cumulis.epa.gov/supercpad/cursites/csitinfo.cfm?id=0302606 (assessed November 21, 2016)

(7) Tencel at Courtaulds: From Genesis to Exodus and Beyond.http://www.lyocell-development.com/2012/12/tencel-history-from-regenerated.html (assessed November 5, 2016)

(8) Gately, D. Lessons from the 1986 Oil Price Collapse. *Brookings Papers on Economic Activity* **1986**, 17 (2), 237-284.

(9) Tencel at Courtaulds: From Genesis to Exodus and Beyond. http://www.lyocell-development.com/2013/01/geoffrey-owens-tencel-lyocell-history.html (assessed November 5, 2016)

(10) By Edgar181 – Own work, Public Domain, via Wikipedia Commons. https://commons.wikimedia.org/w/index.php?curid=3009904 (assessed November 3, 2016)

(11) Tencel at Courtaulds: From Genesis to Exodus and Beyond. http://www.lyocell-development.com/2012/09/the-genesis-of-sustainable-fibres-2012.html (assessed November 5, 2016)

(12) The Lenzing Lyocell Story. http://75years.lenzing.com/en/75-years-of-innovation/lenzing-lyocell-story.html (assessed November 5, 2016)

(13) CC-BY-SA-3.0, via Wikimedia Commons http://creativecommons.org/licenses/by-sa/3.0/ (assessed November 25, 2016)

(14) Fink, H. P.; Weigel, P.; Purz, H. J.; Ganster, J. Structure formation of regenerated cellulose materials from NMMO-solutions. *Progress in Polymer Science*. **2001**, 26 (9), 1473.

(15) Kim, D. B.; Lee, W. S.; Jo, S. M.; Lee, Y. M.; Kim, B. C. Physical properties of lyocell fibers spun from different solution-dope phases. *J. Appl. Polym. Sci*. **2002**, 83 (5), 981.

(16) Borsa, J. Antimicrobial natural fibers; Woodhead Publishing Limited, **2012**; Vol. 2.

(17) Ramsden, E.N.. Chemistry; Nelson Thornes, **2001**

(18) P White; M Hayhurst; J Taylor; A Slater. Lyocell fibers. Regenerated Cellulose Fibers. **2005**, 157-190.

(19) Chen, J. Synthetic Textile Fibers: Regenerated Cellulose Fibers; Elsevier Ltd, **2014**; Vol. 2014.

(20) Haule, L. V.; Carr, C. M.; Rigout, M., Preparation and physical properties of regenerated cellulose fibers from cotton waste garments. *Journal of Cleaner Production* **2016**, 112, 4445-4451.

(21) Woodings, C. R., The development of advanced cellulosic fibers. International Journal of Biological Macromolecules **1995**, 17 (6), 305-309.

(22) Wendler, F.; Kolbe, A.; Kraft, J.; Einax, J. W.; Heinze, T., Thermal stability of lyocell solutions: Experimental results and modeling using cluster analysis and partial least squares regression. Macromolecular *Theory and Simulations* **2008**, 17 (1), 32-38.

(23) Fellows, C.M.; Brown, T.C.; Doherty, O.S.; Lignocellulosics as a Renewable Feedstock for Chemical Industry: Chemicals from Lignin. In Sanghi, R., and Singh, V; Green Chemistry for Environmental Remediation **2012**, 45-78

(24) Ellams, D. L.; Christie, R. M.; Robertson, S., An approach to sustainable coloration of lyocell fabrics by screen printing using extracts of leaves and bark from eucalyptus. *Coloration Technology* **2014**, 130 (1), 48-53.

(25) Cherrett, N.; Barret, J.; Clemett, A.; Chadwick, M.; Chadwick, M. J., Ecological Footprint and Water Analysis of Cotton Hemp and Polyester. Stockholm Environment Institute **2005**

(26) Hoekstra, A. Y. The water footprint of industry; Elsevier Inc., **2015**.

(27) Tencel at Courtaulds: From Genesis to Exodus and Beyond. http://www.lyocell-development.com/2016/08/lenzing-uses-post-consumer-recycled.html (assessed October 16, 2016)

(28) Uniform Reuse. http://www.uniformreuse.co.uk/alternative-fabric.php?textile=8 (assessed October 16, 2016)

(29) Transparency Market Research. http://www.transparencymarketresearch.com/lyocell-fibers-market.html (assessed October 23, 2016)

(30) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D., Dissolution of cellose with ionic liquids. *Journal of the American Chemical Society* **2002**, 124 (18), 4974-4975

(31) Sathitsuksanoh, N.; George, A.; Zhang, Y. H. P., New lignocellulose pretreatments using cellulose solvents: a review. *Journal of Chemical Technology and Biotechnology* **2013**, 88 (2), 169-180

(32) Michud, A.; Tanttu, M.; Asaadi, S.; Ma, Y. B.; Netti, E.; Kaariainen, P.; Persson, A.; Berntsson, A.; Hummel, M.; Sixta, H., Ioncell-F: ionic liquid-based cellulosic textile fibers as an alternative to viscose and Lyocell. *Textile Research Journal* **2016**, 86 (5), 543-552.

(33) Cover Photo: https://pixabay.com/en/rolls-of-fabric-factory-material-1767504/ (assessed November 25, 2016)

Greener Methods of Cadmium Removal from Industrial Effluent: A review

Jill Bachelder *

Department of Chemistry, McGill University, 801 Sherbrooke St West Montreal, QC H2A 0B8

KEYWORDS: Cadmium; Water Remediation; Heavy Metal Pollution; Greener Sorbent Materials

ABSTRACT: Cadmium removal from industrial effluent is vital in order to prevent contamination of local waters and eventual harm to the environment and human health. Industrial effluent can be highly contaminated with toxic levels of cadmium; however, standard removal processes are often costly in terms of money and energy, and may be metals to a level below the EPA accepted cadmium concentration limit of 5 ppb. Green chemistry can be used to devise methods of removing cadmium from industrial effluent that are more efficient in terms of energy, cost, and waste generation, with the added potential to improve the current cadmium removal rates. In this review, three overarching areas of research are highlighted – biomass adsorption, non-biomass waste, and nanomaterials – aimed at devising more sustainable strategies for removing cadmium from industrial effluent. It is concluded that while all areas do hold merit, the use of either chitin or nanoparticles has the most potential to provide a green replacement to current methods of cadmium removal from industrial waste.

INTRODUCTION. Cadmium contaminates industrial effluent due to its use in nuclear reactors, nickel-cadmium batteries, plating iron and steel to prevent rust, among other applications.[1] Furthermore, cadmium is highly toxic to both human health and the environment.[2] For these reasons, purification of industrial effluent is extremely important to mitigating the effects of cadmium pollution.

Methods currently employed to remove cadmium from wastewater include precipitation via increase of pH, adsorption onto activated carbon, reverse osmosis, ion exchange, and membrane filtration. These methods are often quite expensive, produce toxic byproducts in need of further treatment, and sometimes are even ineffective at low or high cadmium concentrations.[3] Many of these processes are particularly inaccessible to those in non-western countries.[4] Precipitation of the metals via increasing pH is one of the most widely used and cost-effective techniques available. However, this technique produces a toxic sludge that must be further treated, usually by removing the water and then dumping into landfills.[5] This is a barrier to implementation, as the process is costly and requires a large amount of land resources to allow great volumes of sludge to settle to then have water removed.[5] Ion exchange, in which a resin exchanges its own nontoxic ions with the metal ions contaminating the solution, is highly sensitive to pH and is easily fouled by solutions with high concentrations of metals. It is also very non-selective regarding the particular metal removed.[6] Furthermore, adsorption by activated carbon, an established technique for removal of heavy metals, is quite expensive, coal-based, and the activated carbon is energy intensive to produce.[7] While membrane filtration techniques have shown to be highly effective in heavy metal removal, these techniques can be energy-intensive due to high pressure pumping and membrane upkeep, and often require costly infrastructure.[7-8] Other techniques such as electrolytic recovery and solvent extraction are wasteful and unsustainable. In electrolytic recovery, the metal electrodes easily corrode and must be replaced frequently. In solvent extraction processes, much solvent must be added to the wastewater.[6, 9]

Currently, greener alternatives to these techniques focus on adsorption to a range of sorbents. Adsorption using biomass has been heavily studied for its potential use in cadmium removal, while processing of non-biomass waste has also been a focus of some investigation. Use of nanotechnology has emerged within the last decade as a viable candidate for cadmium removal as well. These techniques show promise over the currently used methods for a number of reasons. Firstly, it is arguable that a technique that is cheaper to perform is also greener, as this lowers the barrier that companies face in implementing these solutions, increasing the probability firms will remove the cadmium from their wastewater, and ultimately leading to a decreased emission of cadmium to the environment. Thus, removal techniques relying on cheap materials, such as waste products, or on materials that can be recycled, are green in that they are may be more cost effective that other products that are not reusable, require expensive infrastructure, or rely on materials manufactured and bought for the sole purpose of water remediation. A technique can also be considered greener if it is less energy intensive than currently used methods, as this decreases the amount of fossil fuel energy needed to sustain this removal. Finally, if the materials used are renewable, such as in the case of biomass, they may be more sustainable than materials that are non-renewable, as renewable materials may be less likely to be depleted. It is due to their relevance to these criteria, of material renewability, repurposing of waste products, and ability to be regenerated, that the green sorbents to be discussed are included in this review.

Furthermore, the kinetics behind sorption via the materials reviewed are not discussed in great depth – focus is placed on the factors affecting the implementation of these techniques in industry. One influential factor is pH. There are two driving forces behind the pH dependence of cadmium adsorption; the effects of pH on cadmium solubility, and its effect on the binding sites on the surface of the sorbent. Cadmium becomes more soluble in water as the pH of the water decreases, as is the case with most metal ions; with more ions in solution comes a greater chance that the sorbent will come into contact with these ions, theoretically increasing its sorption capacity.[10] However, sorbents are effective due to the existence of several functional groups on the surfaces that can form strong bonds with the solvated Cd^{2+} ion, either through complexation or ion exchange.[11-13] For example, in biomass these carbonyl sites might be present due to proteins, such as in cell walls, or carbonate groups as part of shells.[12-13] When the pH of the solution increases, the Cd^{2+} binding step finds itself competing with protonation, decreasing the adsorption capacity of the sorbent. It is the interplay between these two processes, the increased solubility of cadmium and increased competition with H^+ with increasing pH, that determine the optimal pH for sorption of cadmium in contaminated waters. The particle size of the sorbent is another factor that can influence its uptake properties.[3]

For the adsorption capacity, the unit mg/g will be used. This signifies the mass of cadmium adsorbed per each gram of sorbent. Furthermore, it is taken that, when discussing metal ions in water, the concentration of 1 mg/L is equivalent to the mixing ratio of 1 ppm; likewise, 1 μg/L will be taken as equivalent to 1 ppb. To note, the recovery rate is the mass of cadmium recovered over the initial mass in solution. The adsorption capacity and the recovery rate may be at odds with one another; sorbents may have an exceptionally high adsorption capacity while maintaining a low recovery rate, and vice versa, depending on the initial concentration of the cadmium in solution and the physical and chemical properties of the sorbent.

Here, we present and evaluate potentially greener methods for cadmium removal from industrial effluent. While the methods discussed may also be applicable to removal of solvated cadmium from other sources as well, they have been selected and will be evaluated only for their potential for use in treating industrial effluent in mind.

BIOMASS ADSORPTION. To start, it is important to note not all proposed biomass adsorption methods are feasible for use in water remediation – for example, one study explored the use of human hair as a potential agent for cadmium removal.[14] Though not inherently practical or "green," biomass adsorption has been studied for decades and has serious potential advantages over conventional methods for use in cadmium removal from wastewater. These include high adsorption capacities and ability to remove cadmium, as well as other heavy metals at low concentrations where conventional methods are often ineffective.[3]

Chitin provides a promising source of sorbent. Chitin flakes extracted from crab shells were shown to have an absorbance capacity of 16 mg/g when confronted with a 200 mg/L Cd^{2+} solution.[3] Jha et al. noted the sorption of chitosan significantly decreased with increasing particle size, that using acid the cadmium could be desorbed and the chitosan reused, and that the sorption rates of cadmium onto chitosan was intensely pH dependent.[15]

Peat has been tested in a variety of studies for its use in cadmium removal, generally with promising results. Chaney et al. found columns filled with 200 g of dried peat were able to remove the majority of cadmium in a 100 mg/L Cd^{2+} solution, leaving usually just 1 μL/L (1 ppb) of Cd^{2+} in solution.[16] However, peat is likely not a viable candidate for use in cadmium removal, as it is used in a variety of other purposes – mainly horticultural – and is at risk of becoming depleated.[17] Thus, while impossible to ignore due to the vast number of studies on the use of peat for removal of toxic metals, it is not recommended that peat be seen as a viable option for biomass adsorption of cadmium.

Table 1. Various biomass sorbents and their adsorption capacities in mg cadmium adsorbed per gram of sorbent. Values were obtained with initial cadmium concentrations of 200 mg/L, pH of 5–6, and 25 ºC.

Sorbent	*Adsorption Capacity (mg/g)*
Fungi	60 (alive), 80 (dead)
Chitin	14
Algae	53
Bacteria	24.61

In addition, algae have been explored for their use in cadmium removal. Marine brown algae, pre-treated with 0.2 M calcium chloride for 24 hours with slow stirring, was found to reach a recover rate of 90% after just 30 minutes of exposure, no matter the initial concentration of cadmium in solution. The calcium chloride pretreatment step is important, as the addition of calcium ions creates larger sites where cadmium can bind; the calcium coordinates with the amino acids in a way that orders the protein chains in the alginate – a component of the cell wall unique to brown algae – creating these larger cavities.[12] The algae *L. taylorii* were investigated for their use in adsorption of metal ions in a mixture of cadmium, zinc, nickel, and lead; the sorption rates for these metals were relatively consistent, with a slightly higher lead adsorption rate. (Figure 1).[18]

Fungi, bacteria, and several other biomass sources have been investigated for their potential use as sorbetbs.[19-20] This is just a small taste of the vast research that has been completed into biomass adsorption as a means of performing cadmium removal from wastewater.

Several of these processes required use of additional chemicals, solvent, and energy in the form of either heating or stirring, thus decreasing how green they are. The studies mentioned above were not unique in this; metal-resistant bacteria were pelleted at 10,000 rpm, and fungi samples were also agitated at 150 rpm at 30 ºC for five days before sorption studies were completed.[19-20] Drying steps played a major role in this. While no sample activation was performed, Gupta et al. sun dried their algae samples for four days, dried them at 70 ºC for 24 h, and finally ground their samples using a mortar and pestle.[21] Benguella et al. evacuated the crab shells they used for 12 hours at 200 °C to remove impurities.[3]

A major drawback of biomass adsorption is recovery of sorbents once used.[7] It is possible to use ionic liquids to dissolve chitin and, from the extract, create films and fibers that could be used as sorbents in the place of chitin powder.[22] Use of methods such as these may make removal of sorbents easier.

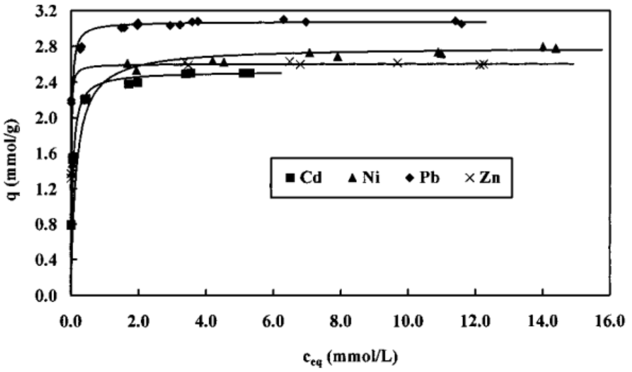


Figure 1. Sorption isotherms for adsorption by *L. taylorii* algae.[18]

NON-BIOMASS WASTE. The idea to use industry waste products has surfaced several times in the literature, with studies seeking sorbents in discarded electronic waste, byproducts of oil extraction, and more. This is an attractive option due to the large quantities of waste material generated, and added benefit of using materials which would otherwise be waste, non-biomass waste must be processed – at times, extensively – in order to be used, thus decreasing the ease and efficiency of its use as a sorbent for solvated cadmium.

Fly ash, a byproduct of oil shale processing, was converted into zeolite, a mineral with known sorption capacity for heavy metals.[23] This conversion was done by burning off the existing hydrocarbons in the collected sample at 950 °C for 8 hours, with subsequent activation with 8M NaOH for varied lengths and at varied temperatures. A maximum adsorption capacity of 95.6 mg/g was found when the activation was performed at 160 °C for 24 hours.[24] The processing of the fly ash is unsustainable as it was performed in this method. Further investigation into less energy-intensive methods of hydrocarbon removal and activation would be necessary to make this method a viable option for cadmium removal from wastewater. In addition, more information on the nature of resulting cadmium/zeolite sludge, such as toxicity and possibility for regeneration of zeolite, must be provided in order to make this method a more viable candidate for cadmium removal from industrial effluent.

Iron and chromium hydroxide from waste produced by the fertilizer industry was found to have an absorbance capacity of over 90% at a pH of 8. The waste was ground, washed, and heated at 60 °C overnight.[4] Non-metallic powder derived from printed circuit board waste has been used successfully to remove cadmium from wastewater; this also underwent significant processing, including 3 hours of stirring at room temperature, three hours of heating, and several washes with water. Once processed, the adsorption capacity was demonstrated to be 234 mg/g (or 2.1 mmol/g) when the initial pH was set to 4.[25] Both of these processes still result in sludge that requires similar treatment to that produced by precipitation.

NANOMATERIALS. The use of nanomaterials in water remediation is an attractive solution due to their high rate of metal ion recovery and potential for regeneration and subsequent reuse. In addition, the high surface area-to-volume ratio of nanomaterials and the ability to vary their shape results in a large number of sorption sites.[26] In the last decade, there has been a surge of new studies into using various nanoparticles and other nanotechnology – such as microbots – for removing metal ions from wastewater.[11, 27-29] While this technique does hold promise, it also possesses certain pitfalls that must be addressed.

Various studies have focused on using nanoparticles to retrieve cadmium from solution. Orange peel powder was attached to the surfaces of iron oxide nanoparticles (MNP-OPP) and demonstrated a cadmium removal rate of 82%, with a 98% cadmium desorption rate after use and a decrease in adsorption capacity from 76 mg/g to 72 mg/g after five cycles of use.[30] These particles are especially notable for the speed at which they reached their maximum adsorption capacities, with the MNP-OPP plateauing in less than 40 min. These studies were carried out in 50 mL batches; desorption was performed in a rotary shaker in 0.1 M HNO_3 (200 rpm, 30 min).[30]

Particles synthesized with a silicon core and aluminum shell (Si-Al) using the sol-gel method were shown to have a recovery rate of over 99.99%, reducing the concentration of cadmium in solution from 140 ppm to less than 5 ppb.[11] Many other studies have evaluated use of nanoparticles in removal of heavy metals, but neglected to include cadmium in their tests.[26-27, 29]

Hydroxyapatite ($Ca_{10}(PO_4)_6OH_2$), a molecule known for its biocompatibility,[31] was also tested for its effectiveness in cadmium removal. Hydroxyapatite nanorods (nHAp) and nano-hydroxyapatite-chitosan composites (nHApC) were synthesized using the sol-gel method from calcium nitrate, phosphoric acid, and, for nHApC, chitosan (a derivative of chitin). These nanomaterials were able to remove cadmium with adsorption capacities of 92 and 122 mg/g respectively, both demonstrating recover rates of 92% over the course of 90 minutes. However, upon regeneration, the efficiency of nHAp was quite low, at close to 60%. This indicates these particles may not be suitable for reuse. Nevertheless, the synthesis of these materials was performed with no heating was required – particles were stirred at 25 °C for 16 hours and allowed to age for 24 hours – demonstrating relatively low energy cost.[32]

DISCUSSION. The studies presented here are indicative of the current state of research into greener methods of cadmium removal from wastewater. Use of biomass, non-biomass waste, and nanomaterials as sorbents have all showed promise in the laboratory, having all successfully removed over 90% of cadmium from low-concentration solutions.

Biomass adsorption and the use of non-biomass waste are attractive solutions, as they have high sorption capacities and do not hold the potential to further pollute the waters treated, as is the case with nanomaterials. However, certain feasibility issues exist when considering biomass or non-biomass waste for use treating industrial effluent for cadmium. First of all, both sorbents do require heating and other processing in order to be used. Jha et al. heated the chitin they used for five hours at 80 °C during pretreatment and then applied further heating at 80 °C in order to dry the samples. Benguella et al. did not pre-treat the crab shells they used, but did evacuate the shells for 12 hours at 200 °C to remove impurities.[3, 15] Likewise, the processing used to prepare oil shale ash was incredibly energy intensive due to heating. The environmental and monetary costs of using these materials to remove cadmium from wastewater may be high due to the level of processing and heating they must undergo. Ultimately, this makes their use on the large scale less favorable.

The use of iron/chromium hydroxide from fertilizer waste comprises a toxic sludge; non-metallic printed circuit board waste required activation by concentrated KOH, which would be hazardous to workers, corrosive, and an additional solvent wasted by the process; and, as mentioned previously, the intense energy input required to pretreat oil shale ash renders this method completely unsustainable.[4, 24-25] Thus, these methods are not recommended green sorbents for cadmium removal. Moreover, if algae, bacteria, or fungi were used as sorbents, they would have to be grown specifically for this purpose. On the other hand, chitin can be obtained from crab and shrimp shell waste, which is sold in bulk online. It does not require activation before use, cutting down on solvent usage compared to other biomass sorbents. Thus, of the sorbents derived from biomass and non-biomass waste, chitin is the most reasonable and sustainable option for greener cadmium removal.

The nanoparticles evaluated so far for use in cadmium removal from wastewater are commercially available (or their starting materials are), inexpensive to purchase, and do not require hours of heating during their preparation for use. The majority of studies performed using nanomaterials to remove cadmium had highly favorable adsorption capacities and recovery rates, often achieved within an hour. Furthermore, the metals used to make the nanoparticles presented here are quite common and cheap – including iron oxide, silicon, and aluminum – meaning companies would not grapple with the issue of scarcity. Preparation of these nanoparticles often requires energy input only in the form of agitation. In addition, the nanoparticles can be regenerated and reused, which cuts down on the costs and waste generated by this technique. This process does require dilute acid and energy in the form of aggitation, which is a cost in terms of sustainability. Nevertheless, use of nanoparticles to remove cadmium from wastewater seems to be the most promising technique presented here, with real potential to be used on the large scale, particularly in countries where current methods of removal are not feasible.

However, more investigation into the use of nanoparticles for cadmium removal is necessary; while these particles may have demonstrated high rates of removal at low concentrations, their adsorption capacity at higher concentrations (i.e., 200 – 2000 mg/L) should also be observed to further evaluate their potential for use in cadmium removal from industrial effluent. This applies to chitin as well. In addition, the studies reviewed here were performed on a laboratory scale; more information is needed on the feasibility of using nanomaterials as sorbents on a larger, industry scale, as well as the feasibility of large-scale recovery, desorption, and subsequent regeneration.

As a side note, we must highlight the fact that use of nanomaterials, are highly pH dependent, as with most sorption methods. This means sorption rates differ for various toxic metals, as the optimal pH for sorption varies greatly between metal ions. Hu et al found that at a pH of 6.5, the rate of copper recovery was 96.2%, while only 5.1% of nickel was recovered.[27] This may either be a blessing or a curse; if one-pot remediation is desired, then this is not ideal, though if a sorbent is selective to one metal ion, this might make metal recycling a possibility.

For the studies reviewed, the pH was either demonstrated to have a large effect on the adsorption capacity, or it was ignored by the studies examined here. Thus, one area that should be explored in the quest to make nanoparticles an even more efficient – and by extension a slightly greener – agent for heavy metal removal would be to determine how to overcome the pH dependence of adsorption, in order to be able to remove multiple heavy metal contaminants simultaneously and decrease the time and number of steps needed for this process. This would increase the sustainability of processes to removal of heavy metals from industrial effluent as a whole, instead of solely those used for cadmium removal.

Addition of metal nanoparticles to wastewater may also be problematic, as it is inevitable that at least some fraction of the particles will remain in the water after treatment. If nanoparticles did contaminate the water, this could have detrimental effects on human health. For example, one study found increased exposure to particulate matter – including magnetite, an iron oxide nanoparticle common in pollution – increased risk of Alzheimer's disease.[33] More research is required into the levels of contamination of nanoparticles in water after cadmium removal, especially on a large scale, and the effect these levels might have on human health and the environment.

CONCLUSIONS. Techniques for cadmium removal for wastewater have been presented and evaluated for their potential for use in the sustainable treatment of industrial effluent. At present, while not without faults, it is concluded that the use of either chitin or nanoparticles hold the most potential for "greener" cadmium removal.

In the end, there are no universal solutions, and techniques explored for cadmium removal from industrial effluent must be tailored to fit the unique situations, such as material availability, level of contamination, and monetary resources, of each location where the removal is to be performed. As Paul Anastas once noted, it is important to "meet the need" and "minimize waste."[34] If in one location crab shell waste is abundant and readily available, that may be a viable option for use in cadmium adsorption, whereas the transportation and costs may mean it's not a viable option somewhere else. Similarly, as techniques have a variety of adsorption capacities depending on the initial concentration of cadmium, the sorbent should ideally be optimized for the level of contamination of the water, in order to minimize waste.

AUTHOR INFORMATION

Corresponding Author

* Jill Bachelder: jill.bachelder@gmail.com

Funding Sources

No funding was received in producing this review.

ACKNOWLEDGMENT

Many thanks to Dr. Audrey Moores and Dr. Robin Rogers for their guidance and support throughout the process of putting this journal together. In addition, thank you to the members of CHEM 462, McGill's Green Chemistry class, as well as the editors of the McGill Green Chemistry Journal.

ABBREVIATIONS

Mg/g, milligrams cadmium adsorbed per gram of sorbent.

REFERENCES

(1) Organization, W. H., Cadmium in drinking-water: background document for development of WHO guidelines for drinking-water quality. **2004**.

(2) Bhattacharya, A. K.; Venkobachar, C., Removal of cadmium (II) by low cost adsorbents. *Journal of Environmental Engineering* **1984,** *110* (1), 110-122.

(3) Benguella, B.; Benaissa, H., Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies. *Water Research* **2002,** *36* (10), 2463-2474.

(4) Namasivayam, C.; Ranganathan, K., Removal of Cd(II) from wastewater by adsorption on "waste" Fe(III)Cr(III) hydroxide. *Water Research* **1995,** *29* (7), 1737-1744.

(5) Sludge treatment, reuse and disposal. http://www.unep.or.jp/ietc/publications/freshwater/sb_summary/11.asp (accessed Dec 1).

(6) Barakat, M. A., New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry* **2011,** *4* (4), 361-377.

(7) Fu, F.; Wang, Q., Removal of heavy metal ions from wastewaters: a review. *Journal of environmental management* **2011,** *92* (3), 407-418.

(8) Malik, A. H.; Khan, Z. M.; Mahmood, Q.; Nasreen, S.; Bhatti, Z. A., Perspectives of low cost arsenic remediation of drinking water in Pakistan and other countries. *Journal of hazardous materials* **2009,** *168* (1), 1-12.

(9)Jha, M. K.; Kumar, V.; Jeong, J.; Lee, J.-c., Review on solvent extraction of cadmium from various solutions. *Hydrometallurgy* **2012,** *111*, 1-9.

(10) Hahne, H.; Kroontje, W., Significance of pH and chloride concentration on behavior of heavy metal pollutants: mercury (II), cadmium (II), zinc (II), and lead (II). *Journal of Environmental Quality* **1973,** *2* (4), 444-450.

(11) Pacheco, S.; Tapia, J.; Medina, M.; Rodriguez, R., Cadmium ions adsorption in simulated wastewater using structured alumina–silica nanoparticles. *Journal of Non-Crystalline Solids* **2006,** *352* (52–54), 5475-5481.

(12) Matheickal, J. T.; Yu, Q.; Woodburn, G. M., Biosorption of cadmium (II) from aqueous solutions by pre-treated biomass of marine alga Durvillaea potatorum. *Water Research* **1999,** *33* (2), 335-342.

(13) Aris, A. Z.; Ismail, F.; Ng, H. Y.; Praveena, S. M., An experimental and modelling study of selected heavy metals removal from aqueous solution using Scylla serrata as biosorbent. *Pertanika Journal of Science & Technology* **2014,** *22* (2), 553-566.

(14) Krishnan, S.; Cancilla, A.; Jervis, R., Industrial wastewater treatment for toxic heavy metals using natural materials as adsorbants. *Journal of Radioanalytical and Nuclear Chemistry* **1987,** *110* (2), 373-378.

(15) Jha, I. N.; Iyengar, L.; Rao, A. V. S. P., Removal of Cadmium Using Chitosan. *Journal of Environmental Engineering* **1988,** *114* (4), 962-974.

(16) Chaney, R. L.; Hundemann, P. T., Use of peat moss columns to remove cadmium from wastewaters. *Journal (Water Pollution Control Federation)* **1979**, 17-21.

(17) Priesnitz, W. Ask Natural Life: Does Peat Moss Have a Place In the Ecological Garden? http://www.life.ca/naturallife/0712/asknlpeat.html (accessed Nov 7, 2016).

(18) Klimmek, S.; Stan, H. J.; Wilke, A.; Bunke, G.; Buchholz, R., Comparative Analysis of the Biosorption of Cadmium, Lead, Nickel, and Zinc by Algae. *Environmental Science & Technology* **2001,** *35* (21), 4283-4288.

(19) Arıca, M. Y.; Kaçar, Y.; Genç, Ö., Entrapment of white-rot fungus Trametes versicolor in Ca-alginate beads: preparation and biosorption kinetic analysis for cadmium removal from an aqueous solution. *Bioresource Technology* **2001,** *80* (2), 121-129.

(20) Ansari, M. I.; Malik, A., Biosorption of nickel and cadmium by metal resistant bacterial isolates from agricultural soil irrigated with industrial wastewater. *Bioresource Technology* **2007,** *98* (16), 3149-3153.

(21) Gupta, V. K.; Rastogi, A., Equilibrium and kinetic modelling of cadmium(II) biosorption by nonliving algal biomass Oedogonium sp. from aqueous phase. *Journal of Hazardous Materials* **2008,** *153* (1–2), 759-766.

(22) Brandt, A.; Gräsvik, J.; Hallett, J. P.; Welton, T., Deconstruction of lignocellulosic biomass with ionic liquids. *Green Chemistry* **2013,** *15* (3), 550-583.

(23) Kesraoui-Ouki, S.; Cheeseman, C. R.; Perry, R., Natural zeolite utilisation in pollution control: A review of applications to metals' effluents. *Journal of Chemical Technology & Biotechnology* **1994,** *59* (2), 121-126.

(24) Shawabkeh, R.; Al-Harahsheh, A.; Hami, M.; Khlaifat, A., Conversion of oil shale ash into zeolite for cadmium and lead removal from wastewater. *Fuel* **2004,** *83* (7), 981-985.

(25) Xu, M.; Hadi, P.; Chen, G.; McKay, G., Removal of cadmium ions from wastewater using innovative electronic waste-derived material. *Journal of Hazardous Materials* **2014,** *273*, 118-123.

(26) Hua, M.; Zhang, S.; Pan, B.; Zhang, W.; Lv, L.; Zhang, Q., Heavy metal removal from water/wastewater by nanosized metal oxides: a review. *Journal of Hazardous Materials* **2012,** *211*, 317-331.

(27) Hu, J.; Chen, G.; Lo, I. M. C., Selective Removal of Heavy Metals from Industrial Wastewater Using Maghemite Nanoparticle: Performance and Mechanisms. *Journal of Environmental Engineering* **2006,** *132* (7), 709-715.

(28) Shen, Y. F.; Tang, J.; Nie, Z. H.; Wang, Y. D.; Ren, Y.; Zuo, L., Preparation and application of magnetic Fe3O4 nanoparticles for wastewater purification. *Separation and Purification Technology* **2009,** *68* (3), 312-319.

(29) Hristovski, K.; Baumgardner, A.; Westerhoff, P., Selecting metal oxide nanomaterials for arsenic removal in fixed bed columns: From nanopowders to aggregated nanoparticle media. *Journal of Hazardous Materials* **2007,** *147* (1–2), 265-274.

(30) Gupta, V. K.; Nayak, A., Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe2O3 nanoparticles. *Chemical Engineering Journal* **2012,** *180*, 81-90.

(31) Huang, F.; Shen, Y.; Xie, A.; Zhu, J.; Zhang, C.; Li, S.; Zhu, J., Study on synthesis and properties of hydroxyapatite nanorods and its complex containing biopolymer. *Journal of Materials Science* **2007,** *42* (20), 8599-8605.

(32) Salah, T. A.; Mohammad, A. M.; Hassan, M. A.; El-Anadouli, B. E., Development of nano-hydroxyapatite/chitosan composite for cadmium ions removal in wastewater treatment. *Journal of the Taiwan Institute of Chemical Engineers* **2014,** *45* (4), 1571-1577.

(33) Jung, C.-R.; Lin, Y.-T.; Hwang, B.-F., Ozone, particulate matter, and newly diagnosed Alzheimer's disease: A population-based cohort study in Taiwan. *Journal of Alzheimer's Disease* **2015,** *44* (2), 573-584.

(34) Anastas, P. T.; Zimmerman, J. B., Peer reviewed: design through the 12 principles of green engineering. *Environmental science & technology* **2003,** *37* (5), 94A-101A.