# The McGill Green Chemistry Journal

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# About the McGill Green Chemistry Journal

The McGill Green Chemistry Journal consists of articles written by McGill students, which report and critique issues related to the 12 Principles of Green Chemistry. The journal broadens the definition of green chemistry by accepting the perspectives offered by the authors. The published articles highlight different ways for sustainable chemistry to directly and indirectly improve people's lives. The articles cover the following subjects:

- Design of more sustainable reactions and chemicals
- Chemistry to reduce waste production
- Analytical techniques for hazardous chemicals
- The societal effects of green chemistry
- Evaluation of the sustainability of current chemical processes and methods

# A Letter from the Editors

The world we live in is in a precarious state; one that will require technological advances and a shift to sustainable practices to ensure the prosperity of current and future generations. As chemists, we have the ability to greatly impact the world and help society make informed decisions. Current pressing issues including climate change, resource scarcity, access to energy and pollution can be ameliorated by advances in green chemistry. Green chemistry is the philosophy and practice of reducing the negative impact and increasing the sustainability of chemistry. It is for this reason that we have chosen to focus on this quickly developing field in this journal.

There is a distinct lack of focus on green chemistry in core chemistry undergraduate classes, meaning all learning must be done independently if the student's specific chemistry department does not value sustainability enough to offer courses in it. This peer-reviewed journal will hopefully act as a beacon for students trying to develop their own sense of sustainability and interest in green chemistry.

This student-run journal is designed to give McGill students a platform to publish work on the scientific advances in green chemistry and to develop writing skills and interest in the topic.

In our first year, the making of this journal has been a learning experience for all of those involved. We hope our work will enable future student interest in publishing in this field. Furthermore, we hope to inspire students graduating from the McGill University Chemistry Department to pursue research and careers that employ green chemistry.

Thank you,

Irene Carrasco
Editor-In-Chief

Sheena Louisia
Allen Li
Ross Koby
Associate Editors

# A Critical Essay: Supercritical CO2 Dyeing, a Key to Textile Dyeing's Sustainable Future

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*KEYWORDS: Supercritical $CO_2$, Textile Industry, Polyester, Waterless, Sustainable*

**ABSTRACT:** Energy is scarce.[1] Water is scarce.[2] Carbon dioxide is plentiful.[3] With this in mind, an efficient process that reduces both energy and water consumption[4] at the expense of carbon dioxide in the textile industry – the most water polluting of the industrial sectors[5] - must be applied at once. In this critical essay strong regulations and strategic subsidies are proposed as the remaining factors needed for the successful widespread implementation of supercritical carbon dioxide (scCO2) polyester dyeing technology in the textile industry. The technology has been developed[4], pilot plants have been tested successfully[6] and large companies have taken up the technology[7]. However, the technology is still considered to be in the pilot stage.[7] Thus, what remains to successfully commercialize the technology is to combine regulation on wastewater discharge that will force the industry to change their processes with strategic subsidies. This essay demonstrates that the chemistry and technology required for this commercialization is available and it is time to use it to solve the grave problem that is textile dyeing water pollution.

## THE TEXTILE INDUSTRY'S PROBLEM

The textile industry's high water consumption in its dyeing processes[8] and lack of effluent discharge legislation[5] have made it one of manufacturing's largest water consumers[7]. The conventional wet textile dyeing process is inefficient, with an estimated 200 000 tons of unused dye emitted by the industry in its wastewater each year.[5] As many wastewater treatment plants are not equipped to deal with these resistant effluents and with variation in effluent chemical composition for different dyeing plants, a large portion of these dyes escape into the environment.[5] Once in the environment, these dyes persist as a result of their high stability and resistance to biological degradation.[5] This stability is due in large part to 70% of the world's organic dyes being comprised of azo dyes.[5] The problem arises in that these dyes contain azo groups of general formula:

R-N=N-R', with the R's pertaining to arenes.

These arenes destabilize the molecule's system and in turn stabilize the azo dye greatly. Unfortunately, it is this stability that leads to both the longevity of these dyes in the environment and their success in the textile industry. The industry requires its dyes to withstand harsh conditions, namely soap, bleach, water, high temperatures and light[5], making azo dyes an ideal option, as long as their toxicity and persistence are overlooked. Overlooking these two effects however has shown great disruption in aquatic ecosystems. Primarily through the impediment of photosynthesis and oxygenation from the reduction of water transparency and the negative health impacts from the carcinogenic, mutagenic and synergistic properties of certain dye components (i.e. azo dyes, chlorine, heavy metals).[5]

Considering the harmful environmental effects of this effluent, the textile industry must be held accountable for its waste. One form of accountability has been seen in countries that charge companies for their water supply and discharge.[7] This has motivated them to modify their processes to reduce their costs.[7] However, this pricing does not encompass all of the effects that the wastewater has on the environment and is limited to certain countries. Based on this trend from putting a price on the water and discharge, regulation on wastewater discharged must be implemented in each country to push industry to adopt waterless technology to remain competitive.

## THE WATERLESS SOLUTION

The textile industry's problem of high water consumption and contamination can be eliminated with the elimination of water from the dyeing process. Switching from wet dyeing to dyeing with supercritical CO2 leads to an increase in both productivity and energy savings[4] and a reduced environmental impact[9] for the textile industry.

The increase in productivity is a result of scCO2's chemical properties. Above critical point, CO2 has both liquid and gas properties, allowing for hydrophobic dyes to dissolve into it.[10] Paired with a low-viscosity and gas-like diffusion, dyeing with scCO2 has been shown to produce shorter dyeing times than wet dyeing.[10] Additionally, chemicals and auxiliaries are reduced[4] as there is better dye diffusion in scCO2 and a more even spreading of the dye than in water. This reduction is further enhanced through the possible optimization[11] of dye and CO2 compatibility. Stains from salts, notably calcium and magnesium, would be eliminated[10] with the use of scCO2 dyeing, once again increasing the productivity of the process by eliminating the need of stain removal. There are also temperature controllable dyes and density controllable dyes[4] which increase productivity as they allow for the control on the dye outcome through temperature and pressure changes.

Not only does this switch increase productivity, it also reduces energy consumption. A 2013 study by the Department of Apparel Manufacturing Management and technology at Shanto Mariam Univeristy in Dhaka, Bangladesh compared the wet and dry methods and found the dry process to require only 20% of the wet method's energy.[10] Energy savings are primarily a result of eliminating the wet dyeing's drying step[4] and the water pre and post dyeing steps (notably washing, scouring, bleaching and finishing steps[10]). These steps account for 100-145L of water on average per 1kg of textile material dyed.[10] Energy use would also be reduced in terms of cleaning the water of impurities at the beginning of the wet process and treating the wastewater at the end of it. The aforementioned process time reduction would also reduce the energy input per kg of dyed textile. This energy reduction would have an economic benefit for the dyer. A 2005 economic analysis of a 1000-L supercritical dyeing machine by the University of Delft in the Netherlands found that although an scCO2 machine required an initial investment five times greater than that of an aqueous machine, the scCO2 dyed 1 kg of polyester for 0.35€ while the aqueous dyed it for 0.9€.[12] Over time, this difference was found to have a 50% reduction in process costs for the scCO2 method compared to the wet process[12]. This supports the viability of sc$CO_2$ textile dyeing as the initial investment in the new technology can be offset by the significant energy reduction as compared to the wet process.

Economic benefits aside, this energy reduction has the added effect of reducing pollutant emissions from fossil fuel dependent textile dyeing mills.[10] Thus, a company that adopts this technology will pay less to fuel its process as well as reduce its CO2, nitrous oxide, and sulfurous dioxide emissions.[7]

The most notable way that this technology reduces the textile industry's environmental impact however is through the removal of water from the process. A waterless process eliminates both the sector's demand for clean water and its discharge of wastewater into the environment. This contributes to ease the global strain for clean water as well as prevent water pollution that intensifies this strain and harms aquatic ecosystems. The use of scCO2 prevents pollution as a result of successful dye separation from CO2 through depressurization at the end of the process.[12]This allows for easy collection of the dye at the end of the process, as opposed to the wet process where dye separation from the wastewater is very difficult[5]. Further, it allows for CO2 recycling[12], a process that has been optimized to 90% recyclability[7]. Finally, the use of CO2 as the solvent for this process is environmentally favourable as it is nontoxic and nonflammable and its linear structure and non-polarity classify it as an inert gas in many conditions.[4] With CO2 being a stable and well-studied molecule, it is easier to work with than the hazardous and variable wastewater from wet processes.

## THE PILOT PLANTS

Over the past 15 years successful pilot plants have emerged for supercritical CO2 textile dyeing across the globe. In 2000 the North Carolina State University College of textiles started up a pilot-plant machine that concluded that the scCO2 dyeing process of polyester was technologically and economically feasible.[4] In 2008, an Italian pilot plant at the Polytechnic University of Turin produced scCO2 dyed polyester yarn bobbins with low crocking, high reproducibility and dye evenness.[6] It recorded an impressive dye process time of 1.5hrs, (compared to the conventional wet process's 3-4hours) which provided strong support for scCO2 dyeing's potential to increase the textile industry's productivity. Soon after, a technical scale machine at the Delft University of Technology in the Netherlands reproduced short dye times (2hrs) as well as even dyeing.[12] This machine also showed final product fiber strength comparable to wet dyeing and 95% efficient recycling of CO2.[12] More recently, in 2014, the Soochow University College of Textile and Clothing Engineering developed a scCO2 rope dyeing pilot plant which produced commercially viable products with low crocking and high colour diffusivity.[11] These successful plants are all indicators of scCo2 dyeing's commercial potential and realization of this technology's pilot state. It is now time for regulation and subsidies to step in.

## THE CURRENT COMMERCIALIZATION

The commercialization of scCO2 polyester dyeing has begun, and there is evidence of companies that have successfully upscaled this technology and introduced it into the textile dyeing market. The current spearheading company in this commercialization is DyeCoo Textile Systems[7]. The Dutch company has patented its method of scCO2 dyeing[13], and signed contracts with major companies such as Nike and Adidas[14]. Further, it boasts the ability to bring dyeing to water scarce environments[14], which could open up the world geographically to the dyeing industry. In collaboration with DyeCoo, the Yeh Group - a Thai textile company specializing in performance polyester - has now implemented commercial-scale scCO2 machine in its mills[7]. As a result, it is now branding its fabrics as DryDye™ fabrics[15], which are consequently distributed around the world with the DryDye™ certification. These two companies are examples of the feasibility of commercializing scCO2 technology in the textile industry. In addition to these companies, there are also manufacturers that wish to shift to scCO2 technology with alternative options. Applied Separations, a US manufacturer of supercritical systems works together with companies that wish to develop their own scCO2 equipment. It has developed scCO2 polyester dyeing equipment at the scale of both pilot plants and small production systems.[16] This shows that there is a demand for scCO2 polyester dyeing technology; subsequently supporting scCO2 dyeing's commercialization viability.

## THE CRITICS

Critics of the scCO2 dyeing process argue that the main obstacles for this technology's commercialization are its high investment costs and its inability to dye natural fibers. However, I argue that the first can be solved with strategic price subsidies[17] and the second is already in its developmental stage.[7] First, the subsidies would make scCO2 dyeing technology available to the textile industry sooner than would be possible without the program. Through the use of a strategic price subsidy program, the technology's feasibility would be taken into account and there would be a continuous adjustment to competitive pricing.[17] The combination of these two requirements would ensure the subsidy's contribution to the new technology's longevity in the industry. The second problem that of natural fibers not being compatible with scCO2 is only a temporary problem. Research is being conducted at many sites that has improved natural fibers' dyeability. One notable example is the 100% dye fixation of cotton using scCO2 dyeing technology in combination with fluorotriazine reactive dyes[18]. A further example is that of the Delft University of Technology's development of pretreatment methods using methanol and modification of cosolvents that also demonstrated an increase in dye fixation. Even though scCO2 dyeing of natural fibers is not yet ready to be commercialized, it will benefit greatly from the implementation of scCO2 dyeing infrastructure for polyester, as the latter will facilitate the former's entrance into the market. Thus, although these two problems are valid concerns for the adoption of the technology, neither is an irresolvable impediment to its commercialization.

## CONCLUSION

To conclude, now is the time for supercritical CO2 polyester dyeing technology to be upscaled and commercialized in the textile industry. Regulation and subsidies are critical to this commercialization as the technology has been developed and the pilot and large scale plants implemented with successful results. The current rate of textile wastewater discharge is hazardous for both the environment and society as clean water becomes increasingly scarce. If the textile industry is truly focused on sustainable manufacturing, as stated in their goals for this year's World Textile Summit[19], it is crucial that it implements supercritical CO2 polyester dyeing at once.

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## ABBREVIATIONS

scCO2, supercritical carbon dioxide

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# A Super-Critical Review of Supercritical Fluids: Can SCF's Replace Traditional Solvents?

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*KEYWORDS: Supercritical Fluids, Analytical techniques, Pharmaceuticals, Waste Treatment, Traditional Solvents, Organic Solvents*

**ABSTRACT:** Recently, a great deal of attention has been directed towards finding alternatives to traditional solvents. The chemical industry, as a whole, relies heavily on solvents, which has contributed to the large volume of solvent related waste produced to date. This waste is not only toxic to humans but can cause adverse effects to the surrounding environment and ecosystems and as such a substitute is required. Some of the proposed ideas include solid state reactions, greener solvents and alternative solvent systems. This article focuses on supercritical fluids (SCF's) as an alternative solvent system. The applications and advantages of these solvents are analyzed to determine whether or not SCF's are a viable replacement to the traditional solvents. SCF's are extremely versatile and have great environmental benefits relative to traditional organic solvents, however the use of these solvents is not widespread nor are they sufficiently developed to feasibly replace solvents used today. Regardless, SCF's present an area into which certain solvent uses can be diverted in order to mitigate the environmental effects of the current situation while searching for a more practical replacement.

## INTRODUCTION

Presently, solvents occupy most of the focus in the realm of green chemistry, whether it be optimizing solid-state reactions, investigating ways to recycle solvent waste or conducting research on greener solvent systems. Motivating this work is the realization that while solvents play crucial roles in various chemical reactions they are not always necessary and in some cases may hinder optimal reaction conditions. In addition, the replacement of these traditional systems can eliminate the vast amount of solvent related waste. For example, in pharmaceutical manufacturing alone, solvents make up 80 % of the raw materials used in the process and this is only expected to increase [1]. Solvents are commonly employed for their benefits such as mass transfer, heat transfer, dilution of reagents to ensure selectivity and potential stabilization of transition states.

The environmental impact from solvent waste of chemical industries underscores the current need to find "greener" and more sustainable alternatives. Supercritical fluids (SCF's) are one of the many green solvents which have received a fair amount of attention in the past 20 – 30 years. As a result, several published works have investigated the properties and uses of these solvents. Supercritical fluid is a term that refers to a substance exposed to temperatures and pressures above the corresponding critical point. There are a number of commonly studied SCF's including: carbon dioxide ($ScCO_2$), water ($ScH_2O$), propane ($ScC_3H_8$), methanol ($ScCH_3OH$) and nitrous oxide ($ScN_2O$) among others. Of these, $ScCO_2$, is the most commonly used, this is because of its critical pressure (73 atm) and critical temperature (approximately 31°C) [2]. Most SCF's have very little environmental impact and are non-toxic, non-flammable and relatively cheap, making these solvents a great potential alternative to the systems already in place. This review seeks to present some of the applications of SCF's in order to assess their efficacy as replacements to traditional solvents.

## ANALYTICAL APPLICATIONS

SCF's are used in two main analytical techniques Supercritical Fluid Extraction (SFE) and Supercritical Fluid Chromatography (SFC). SCF's offer great benefits to the aforementioned techniques as a result of their tuneable solvent properties. The process of liquid extraction can be adapted to accommodate SCF's and is relatively simple to perform. A pump is used to produce a given pressure of extraction fluid that is transferred to a temperature-controlled container which remains above the critical temperature of the solvent of interest [3], [4]. The analyte of interest is then added to the SCF. Following this the extracted product and residual SCF are removed and sent to a collection vessel that is held at ambient pressure. Once the mixture is transferred the SCF then quickly converts to its gaseous form leaving only the desired products. The use of SCF's offers multiple benefits, one being that above the critical point a solvent will exhibit characteristics of both a gas and a liquid [5]. For instance, the gaseous nature of SCF's leads to an increase in mass transfer of the solvent. This increase is due to the lower viscosity and larger diffusivity observed in SCF's [3]. As a result of the reduction in mass transfer limitations, extractions performed using SCF's often result in less time required to complete the process as compared to liquid extractions. For instance, common SFE's can take place in 10 – 60 minutes while, a traditional liquid extraction can take up to several days [3], [5]. A comparative study was performed in which PAH's were extracted from an adsorbent material using both SFE and a traditional extraction method. The results indicated that both methods offered the same extraction efficiencies, but SFE showed a decreased extraction time [5]. Furthermore, the solvent properties of SCF's can be varied greatly by small changes in temperature and pressure allowing multiple extractions to be performed using one given solvent. Above the critical point of a given substance, small changes in the pressure cause significant changes in the density, accounting for the adjustable solvent characteristics [3 – 5]. This property is well known and successive extractions of different compounds using the same SCF have been reported previously. One such example is VOC's found within urban air particulates. When the extraction process is performed using $ScCO_2$ at constant temperature, alkanes can be extracted at 75 atm while polyaromatic hydrocarbons (PAH's) remain in the sample matrix until the pressure is increased to 300 atm [6]. Further examples of tunable solvating character are present in $ScCO_2$ which, at low pressure favours less polar analytes and at higher pressure will favour more polar and higher molecular weight analytes [5]. Therefore, as opposed to traditional extractions in which multiple solvents must be employed in order to extract all desired products, SCF's present a convenient way to remove multiple products without changing the solvent but rather changing the physical conditions [3]. Once the analyte has been extracted, the SCF is removed by simply bringing the sample to ambient pressure. On the other hand, with liquid-liquid extractions, the analyte would then have to be concentrated, resulting in increased energy usage and labour to obtain the desired product as well as potential degradation of the product, which could take place in cases of lengthy concentration steps [3]. In the case of thermally sensitive products, SCF's are a good alternative to traditional solvents as some of them have critical temperatures below 40°C [3].

Most of the advantages previously discussed carry over to Supercritical Fluid Chromatography (SFC), since chromatography generally relies on the partitioning of the desired analyte between the mobile phase (SCF) and the stationary phase. Hence, the ability to alter the solvating properties of SCF's with changes in temperature and pressure offers numerous advantages to SFC. $ScCO_2$, is a commonly used supercritical fluid for SFC because of its low critical temperature, which allows for the separation of thermally labile compounds [7], [8]. However, a challenge arises when trying to separate polar analytes since at lower pressures $ScCO_2$ shows minimal solvating power for polar compounds. This is overcome by adding a small amount of modifier to the sample, such as methanol (5 – 30 %), which increases the polarity of the SCF. Therefore, it works best with compounds of low polarity but can be adapted to those of moderately high polarity if necessary. In addition, the mild operating conditions used in SFC, with $ScCO_2$ as the mobile phase, allows it to be easily adapted to liquid chromatography (LC) and Gas Chromatography (GC) instrumentation [8]. There has even been reported coupling of SFC to spectroscopic methods including UV/Vis, FTIR, MS and $^1H$ NMR [8 - 13]. Although the use of SFC might seem limited due to the restricted solvating characteristics of ScCO2, it has already been employed for the separation of many different compounds such as highly polar antibiotics, natural products such as sterols, terpenes, fatty acids and cannabinoids and is even used in chiral separations of enantiomeric compounds [7], [8], [14]. Furthermore, this method can offer advantages over traditional chromatographic techniques like the ability to separate mixtures at lower temperatures than GC and in shorter periods of time than LC [8]. Moreover, the methods associated with SFC are quite diverse with both capillary SFC (cSFC) and packed column SFC (pSFC) having already been developed [14].

The examples presented above are not the only analytical applications of SCF's. Research has shown that SCF's can be used in tandem with electrochemical and gravimetric methods among others [3]. Unfortunately, the implementation of many of these techniques is limited by the high costs required for slightly modified equipment [15]. However, the examples outlined present the versatile nature of this solvent and highlights both the benefits and drawbacks of replacing traditional solvents in analytical applications with SCF's.

## PHARMACEUTICAL APPLICATIONS

As previously indicated, supercritical fluid chromatography is a widely studied technique. Moreover, it has been used in pharmaceutical research in order to separate a wide variety of compounds, including enantiomers, where research has shown that through the use of SFC, better resolution of chiral compounds can be obtained as opposed to other HPLC methodologies [15]. Besides the use of SCF's to purify compounds, these solvents can also be used in the synthesis of certain drugs in order to improve the delivery of the compound. The most common methods are Solution Enhanced Dispersion by Supercritical fluids (SEDS) and Rapid Expansion of Supercritical Solutions (RESS). The former uses an SCF to act as an antisolvent to precipitate the material, while the in the latter the SCF rapidly expands, due to a pressure difference which causes the dissolved material to precipitate out of solution very quickly as small particles. In both of these techniques, the material of interest is introduced to the SCF, commonly $ScCO_2$, at a high pressure in order to produce ultrafine particles. This is mostly used to increase the bioavailability of such drugs by reducing the particle size and increasing the surface area [17 - 20]. Additional advantages include; high purity product, control over particle morphism and ability to process thermally sensitive compounds. Furthermore, for this process, the use of $ScCO_2$ in place of traditional organic solvents offers fundamental environmental benefits [18]. Like the previous methods described, the use of $ScCO_2$ allows this process to be conducted under mild conditions while producing crystals that are solvent free and require no added surfactants [16]. Additionally, traditional methods of crystal formation such as spray drying, milling, lyophilisation and controlled precipitation can cause particle size inhomogeneity, low yields and temperature induced protein inactivation, all of which are undesirable characteristics in sustainable processing methods [16]. Thus, SCF's can offer more than a medium in which one can conduct reactions, they can also aid in particle size alteration in order to increase bioavailability of a given drug.

## WASTE TREATMENT

SCF's can also be applied in the field of waste treatment. $ScH_2O$ can be used to treat organic waste by oxidizing it to produce $CO_2$, $H_2O$ and $N_2$ in a process referred to as Supercritical Water Oxidation (SCWO) [21]. The process is carried out at 600 °C and 23 MPa, at which point most organic compounds become soluble in $ScH_2O$. This change in solubility is due to the decrease in dielectric constant and ionic product of the solvent [22]. As a result, $ScH_2O$ acts as a non-polar solvent that is miscible with most gases such as $O_2$ and promotes the rapid oxidation of the waste water [22]. Other materials contained in the waste stream, like inorganic salts, remain insoluble and can be precipitated out of the solution and collected separately [23]. The efficiency of this process can reach values of up to 99 % with a process time of under 10 seconds. Furthermore, this pathway offers the additional advantage of destroying hazardous waste and separating inorganics in a single reactor [23]. Additionally, this process does not allow for the production of other common air pollutants, such as $NO_x$ and $SO_2$, which would otherwise be formed in the incineration of such waste [22], [23]. The configuration commonly used is a pipe reactor however this type of reactor has the disadvantage of plugging if the waste stream, once treated, produces a large amount of inorganic salts [23]. However, there have been patents put forward to handle this problem, wherein the reactor contains two zones, one in which the SCF is contained and a second zone containing cold water at the same pressure as the $ScH_2O$. The reactor operates as follows; as the organic waste is oxidized the corresponding gaseous products are vented from the top of the reactor, while the solid materials produced will sink into the cold water layer. Constant stirring is maintained in this layer to form a slurry that can then be easily removed [23]. Yet there have been difficulties in fully optimizing this process due to the corrosive nature of $ScH_2O$ and the by products of SCWO which eventually lead to the degradation of the reactor vessel. Nevertheless, active research is being conducted to bring SCWO to an industrial scale [22], [23].

SCF's also show promise in the production of chemically recycled plastics. Recently, significant focus has been placed on plastic recycling due to the realization that the degradation of such plastics is almost impossible under normal biotic and abiotic conditions. This has lead to problems such as landfill overflow and the Great Gyre Problem. There have been some attempts to find alternatives to the current products used, such as PLA a polymer which is biodegradable under certain conditions. However, no definite solution has been found. Another area of research within this field is the chemical degradation of plastics by SCF's. By combining certain polymers with SCF's it is possible to depolymerize them to the corresponding monomers quicker and in a more selective manner than traditional methods. The monomers obtained are of decent quality such that they can be recycled [24], [25]. Condensation polymers can be depolymerized by solvolysis using supercritical water or alcohol. Previous research has shown that complete depolymerization of PET to monomer sized units can take place in $ScCH_3OH$ in a short time span of 1200 seconds without a catalyst, [24 - 28]. Addition polymers, like resins commonly found in electronics, are constructed out of materials such as phenols which have a high thermal stability. When combined with $ScH_2O$ and a slight $Na_2CO_3$ modifier, these materials can be decomposed into the corresponding monomers in as short a period of time as 30 minutes with yields reaching 90 % [24], [25].

## ROLES OF SCF'S IN CHEMICAL REACTIONS

SCF's, because of their versatile nature, have been studied in various reactions either as the solvent medium or as actively participating in the reaction. By altering certain properties, such as the density, pressure, dielectric constant etc., it is possible to increase the reaction rate, yield and selectivity [28]. In fact, previous literature presents the study of SCF's in many well-known chemical reactions [29]. Hence, the ability to tune the chemical properties of these solvents by altering the physical conditions presents certain experimental consideration that should be taken into account. Changes in the pressure under which the SCF is contained can impact the density of the fluid immensely and consequently, the solvating ability of said fluid. Through the use of SCF's it may be possible to carry out traditionally heterogeneous reactions in the homogeneous state. One example of this is reactions which involve polymeric substrates that experience rate limitations when conducted heterogeneously. In addition, it is necessary to consider the temperature under which the reaction will be carried out. For instance, lower temperatures will cause the reaction rates to decrease while higher temperatures may cause catalytic decomposition [30]. In the case of pyrolysis, it is observed that conducting the reaction at lower temperatures can reduce unwanted by-products and has been shown to increase yield, selectivity and product separation [28]. Furthermore, it is necessary to consider the reactive nature of the SCF being employed. One consequence of using SCF's in chemical synthesis is that these solvents ca partake in the reaction under certain conditions. However, this property is actually utilized in certain reactions such as the hydrogenation of $CO_2$ to produce common organic molecules, such as formaldehyde. Of the many reactions that have been studied in SCF's, three of the most well-known are presented below. These are: hydrogenation, hydroformylation and oxidation.

**Hydrogenation:** The rate of many hydrogenation reactions is dependent on the concentration of hydrogen in solution as well as the diffusion of $H_2$ once dissolved. However, this is limited by the immiscibility of $H_2$ in many organic solvents [31]. Because of the miscible nature of SCF's with certain gases, it is possible to significantly increase the concentration of hydrogen in solution. Furthermore, the increased diffusivity present in most SCF's allows the reaction to proceed at significantly increased rates [30 - 32]. Previous studies have shown that this increase in rate lies exclusively with the increase in hydrogen concentration as catalytic activity is not shown to increase when the reaction is carried out in SCF's [32]. Moreover, SCF's have been advantageous in the production of many hydrogenation products including, fats and oils, small organic compounds and enantioselective products. Considering that the conversion of vegetable oils into saturated fats is a huge industry, using SCF's would be greatly advantageous. The widespread use of SCF's would initially result in the replacement of traditional solvents and ultimately a large reduction in the environmental impact caused by such solvents [31]. Hence, the ability to replace the current solvents with $ScCO_2$, which is non-flammable, non-toxic and environmentally benign would present many "green" benefits [31], [33].

**Hydroformylation:** This process is very similar to hydrogenation in that it traditionally uses liquid solvents, gaseous reagents and a solid catalyst and presents great industrial importance as the products of this reaction go onto many secondary applications [30], [33]. Unlike the hydrogenation reaction, the reaction rate for hydroformylation is not greatly altered when carried out in SCF's since the reaction is homogeneous when carried out in organic solvents. However, there have been observed increases in catalytic selectivity when conducting the reaction in SCF's such that the desired product is obtained in higher yields [29], [30], [32].

**Oxidation:** There have also been many studies where SCF's are used in oxidation reactions, some of which have yielded certain heterogeneous catalyzed reactions such as the steel catalyzed oxidation of cumene, the CoO catalyzed oxidation of toluene or supercritical water oxidation as previously discussed [30]. The benefit here, similar to the previous examples, is the miscibility of $O_2$ with most SCF's allowing for greater mass transfer [29], [33]. Some studies have been performed on homogeneous oxidation reactions with SCF's such as epoxidation reactions that can afford enantioselective products in the presence of specific catalysts, sulfoxidation reactions where the use of an SCF promotes diastereoselectivity and even oxidation of alkanes to produce functionalized molecules, such as the conversion of cyclohexane to cyclohexanone albeit in lower yields [29], [30], [32]. Another interesting application of SCF's, with respect to oxidation, is the use of partial oxidation. Methane has been studied as a potential fuel source, however there are challenges associated with the storage and transport of this material. Partial oxidation of methane yields methanol and other higher order hydrocarbons, which are easier to transport and store. Unfortunately, this reaction is yet to be optimized and shows very poor yields [31]. In addition to the synthetic pathways described above, there has also been research invested into the use of SCF's to increase total aerobic oxidation of organics [29].

Although not explicitly discussed herein, there are a vast number of reactions in which SCF's have been substituted in order to observe the impact on reaction rates, selectivity, yield etc. As presented, it is clear that in some cases it is largely beneficial to employ SCF's in place of the traditional solvents not only for their environmental benefits, but also for their potential to improve the metrics associated with the reaction of interest.

## CONCLUSION

Solvent use contributes tremendously to the environmental impact of most chemical industries. Solvents are used in the pharmaceutical industry, automotive industry, textiles, dry cleaning, paints, plastics, rubbers etc. However, it is clear that simply halting the production of solvents would do more harm than good. Therefore, it is necessary to find some alternatives to the traditional methods used, whether greener solvents are introduced, solvents are removed from the process altogether or alternative solvent systems are adopted. The many applications previously presented indicate that there is a possibility for SCF's to replace traditional solvents in some aspects. More specifically, the use of SCF's as the mobile phase in some common analytic techniques, the potential use of SCF's in the pharmaceutical industry, the ability to treat waste using SCF's or substituting SCF's in well-known reactions all in an attempt to replace the solvents traditionally used. Unfortunately, there are several applications where it is not feasible to simply replace the solvent with a SCF. Therefore, SCF's can clearly offer a replacement to traditional solvents in many aspects and in these cases it would be greatly beneficial to replace the solvents. However, SCF's cannot completely substitute the solvents used today and solve the current crises. SCF's offer an environmentally friendly transition state, during which a greener and more viable alternative can be sought.

## AUTHOR INFORMATION

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## ABBREVIATIONS

SCF, Supercritical Fluid; $ScH_2O$, Supercritical Water; $ScCO_2$, Supercritical Carbon Dioxide; SCWO, Supercritical Water Oxidation; Polyaromatic Hydrocarbons, PAH; Supercritical Fluid Extraction, SFE; Supercritical Fluid Chromatography, SFC; Volatile Organic Compounds, VOC's; Mass Spectrometry, MS; Fourier Transform Infrared Spectroscopy, FTIR; Proton Nuclear Magnetic Resonance, $^1H$ NMR; Solution Enhanced Dispersion by Supercritical fluids, SEDS; Rapid Expansion of Supercritical Solutions, RESS; High Performance Liquid Chromatography, HPLC; Polylactic Acid, PLA.

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# Carbon Dioxide Copolymerization: How Green Is It?

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*KEYWORDS* *Copolymerization; Carbon Dioxide; Epoxides; Catalysts; Polycarbonates; Organometallic Complexes*

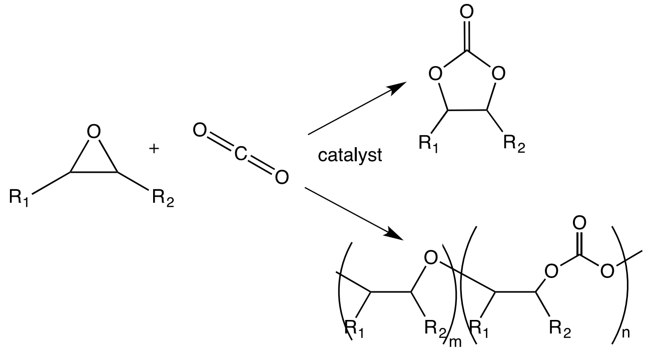
**ABSTRACT:** Carbon dioxide is one of the most abundant carbon resources available, however its activation and subsequent utilization, is a difficult process. In recent years, this field has been of great interest since carbon dioxide is one greenhouse gas contributing to climate change. The intent of this article is to present 3 case studies of specific methods of catalysis used in carbon dioxide copolymerization, in order to evaluate the "greenness" of each method. The various catalysts are synthesized with slightly different priorities in mind, so each method will be evaluated to see if these priorities align with the principles of green chemistry. The chosen catalytic systems presented in each case study are a β-diiminate zinc catalyst, an Iron catalyst, and a Palladium catalyst. Not only will the characteristics of the products be examined, but also the renewability of the starting materials and the catalyst. The need to find alternative feedstocks for creating copolymers, as well as catalysts with high activity at mild conditions, is of great concern if the field wants to reach a green standard. Highlighted overall is the need to be conscious of all aspects of a process in order to achieve sustainable methods.

## INTRODUCTION

Carbon Dioxide ($CO_2$) copolymerization was originally designed to be a green technique due to its use of the greenhouse gas, $CO_2$, as a reactant. $CO_2$ is a cost effective, non-toxic, and abundant reagent.[2] Using it to create polycarbonates has been a process of great interest, since polycarbonate-based plastics can have many desirable properties, such as high transparency and UV stability[3] and polycarbonates have many lucrative applications in food and drink containers, household appliance parts, components of electronic devices, reusable bottles, and many other products.[3] Polymers provide a method of recycling the carbon dioxide into products we need.

The general pathway shown in scheme 1 depicts the two possible products that can be obtained. The top product, a cyclic carbonate is the kinetic product, while the bottom product, an aliphatic polycarbonate is the thermodynamic product.[4] Pioneering work on this process was performed by S. Inoue and colleagues who, in 1969, discovered that $CO_2$ and propylene oxide can copolymerize in the presence of diethyl Zinc in water to produce polycarbonates.[5] Since this discovery, there have been numerous catalysts synthesized for the copolymerization of carbon dioxide. The majority of these catalysts are organometallic compounds.[6] The ligands have been varied over the years to examine how sterics or chirality[7] of the catalyst can influence copolymerization. More recently, the "greenness" of the process has been called into question. The amount of carbon dioxide actually consumed can trivial.[6] The impact the copolymerization of atmospheric $CO_2$ would have on global emissions is minimal.[8] However $CO_2$ is a waste product of many processes,[9] thus utilization of emitted $CO_2$ would be a way to valorize this waste.

There are several obstacles in the entire process that need to be solved. The source of this carbon dioxide is not necessarily green either. Existing processes are very energy intensive.[10] Thus the capture of waste CO2 is an active field of research currently. There are pilot projects in the works, however it is by no means a simple process.[10] Carbon dioxide waste needs to be scrubbed (or stripped out), purified, and concentrated before it can be stored for use.[11] So depending on the reactants, the final polymer product may not be a particularly green or a sustainable product.



**Scheme 1. General Copolymerization Reaction[4] to yield either a cyclic carbonate (top product) or a polycarbonate with possible ether linkages.**

In order to illustrate the vast differences of catalysis in this field, three current methods will be evaluated using four different qualities. The first will be the amount of $CO_2$ incorporated into the final copolymer by analysis of carbonate linkage % The carbonate linkage percentage will be calculated using the following equation.[12]

$$\%\ \text{Carbonate} = \frac{\text{(copolymer carbonate linkages)}}{\text{(copolymer carbonate + ether linkages)}} \qquad (1)$$

Looking at the source of the starting material will assess the renewability of the reagents. If the production of the reagents requires large amounts of energy, or is a long process that produces other wastes, this does not embody the ideas of green chemistry.[13] Energy efficiency, waste prevention and use of renewable feedstocks are green chemistry principles[13] that should be considered when choosing reagents.

The same factors will influence the factor of the renewability of the catalyst. If the catalyst is made from abundant starting materials and its synthesis is not an energy intensive process, green standards are likely to be met.

Finally, the biodegradability of final product will be taken into account. Biodegradable polymers are designed to degrade in the presence of the action of living organisms.[14] A common example of a biodegradable polymer is poly(lactic) acid.[14]

Methods to be analyzed will include the use of β-diiminate zinc catalysts to produce biodegradable polymers,[15] catalysts using iron, a more sustainable metal,[16] and a novel palladium catalyst that employs butadiene instead of epoxides in the copolymerization process.[1] Each method was chosen based on a different "green" factor specific to each process.

β-diiminate (BDI) zinc catalysts were chosen for this case study due to the ability to produce biodegradable polymers.[15] Approximately 150 million tons of plastics are produced every year, and the majority of those are non-biodegradable and are manufactured using energy intensive processes, often using petroleum-based starting materials.[8] Thus to reduce the amount of waste plastics, the biodegradability of the copolymer is of great importance. The zinc catalyst chosen embodied this trait.

An iron catalyst was considered since Iron is one of the most abundant metals in Earth's upper crust.[17] This catalyst also shows activity at atmospheric pressure, which has a lower energy demand than those processes requiring elevated pressures.[17] Iron's accessibility and potential to reduce energy costs makes it a green option for this process

Finally, the use of conjugated dienes with a palladium catalyst was chosen to contrast the other methods of catalysis since it uses a precious metal, as well as a diene as a starting material.[1] The use of a precious metal is not a green choice. However, the use of a conjugated diene allows the elimination of the epoxidation step. With the elimination of a step, energy is saved and the waste from that particular step can be reduced.[8] Both the pros and cons of this method are to be evaluated, in order to decide how green this catalysis really is.

**Β-diiminate Zinc Catalysts.** Since the first catalyst discovered for copolymerization was a zinc diethyl complex,[5] the most traditional of the catalysis methods analyzed is the use of a β-diiminate zinc catalyst, (Figure 1). In particular D. Moore and co-workers, synthesized highly active zinc catalysts to produce biodegradable polymers, specifically heterotactic and syndiotactic poly(lactic) acid.[18] Using bulky β-diiminate ligands, each containing two nitrogen atoms, and a zinc atom, these compounds have achieved narrow polydispersity indices (PDI) where PDI = 1.10 – 1.16. The rate of reaction can be manipulated via ligand choice and configuration.[15] The polydispersity of a polymer corresponds to the uniformity of the polymer length, this is important for the commercial or industrial processes downstream from the production. The narrower the polydispersity index, the more desirable the product for consumers and the more likely this process could eventually be commercialized. Interestingly, this catalyst seems to be the most effective when it forms a loosely associated dimer complex.[15] This mechanistic aspect has influenced more recent research of M. Kember and colleagues to synthesize dizinc catalysts, that have been found to be highly active at atmospheric pressure[19] and maintained a high percentage (>99%) of carbonate linkages at lower pressure. [19]

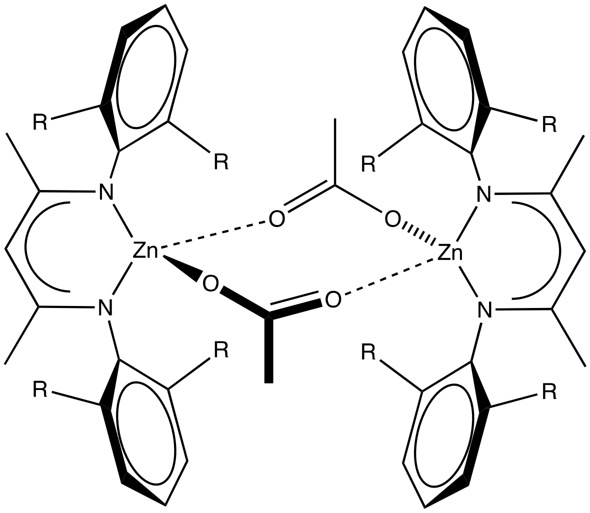
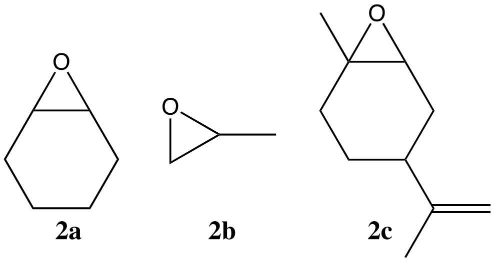


**Figure 1**. Loosely associated dimer of the β-diiminate zinc catalyst.[15] This is the most active form of the catalyst.

If this process were to be commercialized, the process would need to be reevaluated from a green perspective. As mentioned before, carbon dioxide copolymerization is often labeled green on the sole basis that carbon dioxide is consumed. A carbonate linkage in the polymer signifies the incorporation of a carbon dioxide molecule since the epoxide itself will not create a carbonyl moiety in the polymer chain. In the absence of carbon dioxide, the catalyst may catalyze the formation of an ether bond between subsequent epoxide molecules.[12] For β-diiminate zinc catalysts, the copolymerization with cyclohexane oxide (CHO), Coates and co-workers reported a high percentage of carbonate linkages.[15] Most of the BDI zinc complexes produced polymers with 94 % – 99 % carbonate linkages.[15] Zinc is an abundant, cost-effective and sustainable metal.[20] Therefore, this choice abides by the green principle stating to use renewable feedstocks.[13] Also to be considered is the renewability of the reagents. As previously described, carbon dioxide is abundant, cheap, and in excess on our planet although issues are presented in its capture and storage.[10] However, the epoxide, cyclohexene oxide (CHO) or propylene oxide (PO), with which the $CO_2$ copolymerizes, is much less sustainable. These traditional choices are derived from petrochemicals, such as cyclohexene and propylene, which undergo industrial epoxidation using heterogeneous catalysis.[21] While technically petrochemicals are renewable, it is estimated that they will be depleted or become uneconomical within the next century.[12] The development of an environmentally benign catalytic system for olefin epoxidation is still a challenging endeavor in the field.[22]

However, there has been successful work using BDI zinc catalysts to copolymerize limonene, a naturally occurring cyclic monoterpene, with similarities to CHO.[23] (Figure 2)



**2a** **2b** **2c**

**Figure 2**. Comparison of epoxides used, (2a) Cyclohexene Oxide. (2b) Propylene Oxide. (2c) Limonene Oxide.

This is an advantageous alternative since limonene is one of the most common terpenes, and is produced by over 300 different plants.[23] Limonene and carbon dioxide copolymers are biodegradable and can be synthesized under mild conditions.[23] In comparison with the β-diiminate zinc catalysts made by D. Moore and co-workers[18], the dizinc catalysts synthesized by M. Kember and colleagues[19] embody the previously mentioned green qualities but remain active at lower pressures, with comparable turnover numbers (TON) and turnover frequencies (TOF).[19] This is advantageous due to the reduced energy input of the reaction.[19] The copolymers of Kember's dimetallic catalyst maintain the high percentages (>99 %) of carbonate linkages, and ether linkages were not detected.[19] Ether linkages would indicate polymerization without the incorporation of carbon dioxide so it is important that these are minimized to have maximal $CO_2$ consumption.[6]

**Iron Catalysis, a Sustainable Metal Choice.** Iron is one of the most abundant metals on Earth. It has a low toxicity, and is necessary for metabolic processes in many animals, plants, and microorganisms.[24] Its abundance in nature makes for a cost-effective, environmentally friendly green choice.[17] With these qualities known, somehow Iron seemed to slip under the radar of the majority of research in copolymerization catalysts until relatively recent years. The first report of a highly active Iron catalyst for carbon dioxide copolymerization was in 2011 by A. Buchard and colleagues.[12] This group created a bimetallic iron (III) catalyst that showed notable activity with CHO at atmospheric pressure.[12] Creating an active catalyst at lower $CO_2$ pressures reduces the energy consumption of the entire process.[12] This bi-metallic catalyst demonstrated a narrow polydispersity index of 1.13.[12] Two years later, the first iron catalyst able to effectively copolymerize $CO_2$ and propylene oxide (PO) was reported by K. Nakano and co-workers,[16] using iron-corrole complexes (figure 3). Using this complex, crystalline copolymers were observed.[16] Varying the degree of crystallinity can change the mechanical properties of the polymer, although too high crystallinity will cause the polymer to become brittle.[25] It is important to be able to control this factor in order to obtain the desired final product. The fact that this catalyst can increase the crystallinity is significant because it allows for manipulation of mechanical qualities in the final product, which would be appealing for commercial use.[26] Crystalline polymers are desirable for use as gas-barrier films in food, medicine, and electronics packaging.[26] While quite effective at 10 atm pressure, this bimetallic iron (III) catalyst was not as effective at lower $CO_2$ pressures.[12]

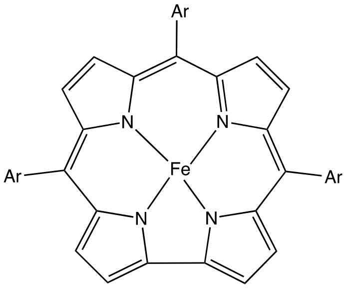
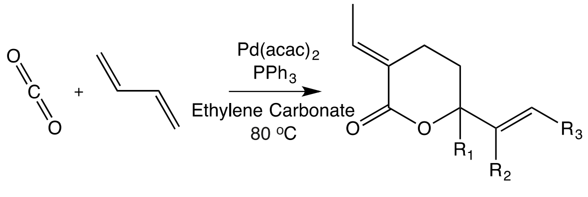


**Figure 3**. Example of a Simple Iron-Corrole Catalyst.[16]

For iron catalysts, a major green aspect is the availability, abundance, and low cost[16] of the catalytic metal centre. It is also environmentally benign[16] in the case of contamination or industrial accident. The diiron catalyst has demonstrated activity at atmospheric pressure, however this copolymer was of sub-optimal standards with only 66% carbonate linkages.[12]. If the pressure was increased to 10 atm, the result was a dramatic improvement on the quality of the polymer with greater than 99% carbonate linkages, and only trace amounts of a cyclic carbonate by-product.[12] This indicates that quality polymers can be synthesized using a diiron catalyst, however changes need to be made before atmospheric pressure copolymerization will be effective. The iron-corrole catalyst for $CO_2$ copolymerization with PO did not incorporate notable amounts of $CO_2$, the greatest carbonate linkage % found to be 62%, at increased pressure.[16] Although, the iron-corrole catalyst reported by K. Nakano and colleagues was the first to be able to catalyze the copolymerization reaction with propylene oxide,[16] there are still improvements to be made before this catalyst can be active at atmospheric pressure.

**Use of Alkenes in Place of Epoxides via Palladium Catalysis.** The majority of copolymerization reactions involve carbon dioxide and an epoxide, a fairly reactive species due to ring strain.[23] Starting with an alkene eliminates the synthetic step of adding the epoxide across the double bond.[8] In 1975, attempts at copolymerization reactions with butadiene and carbon dioxide were reported.[27] However, only oligomers with low molecular weight could be achieved.[27] In 1983, the activation of carbon dioxide to create lactones was studied,[28] but this process was not expanded past the synthesis of lactones. These results left each method relatively untouched for decades. Neither the $CO_2$ copolymerization of butadiene, or the $CO_2$ utilization to create lactones were connected until R. Nakano and co-workers, developed the novel idea of creating a metastable lactone for subsequent copolymerization.[1]



**Scheme 2. First reaction in the process to obtain the lactone intermediate before subsequent copolymerization.[1]**

Although the copolymerization reaction between carbon dioxide and butadiene has finally created polymers of desirable qualities, is this process actually green? One major pro for this process is that it incorporates up to 33 mol% of $CO_2$, which is comparable to the theoretical maximum.[1] Since this process incorporates carbon dioxide into the lactone intermediate (scheme 2), the carbonate linkages of the final polymer are not reported like the previous catalysts.[1] However, it is stated that 33 mol% is near the theoretical maximum incorporation of $CO_2$,[1] thus comparable to the 94 – 99 % carbonate linkages reported in copolymerization reactions with CHO and PO.[12, 15-16, 19] It also boasts a narrow polydispersity index of 1.6, along with a high yield and high selectivity.

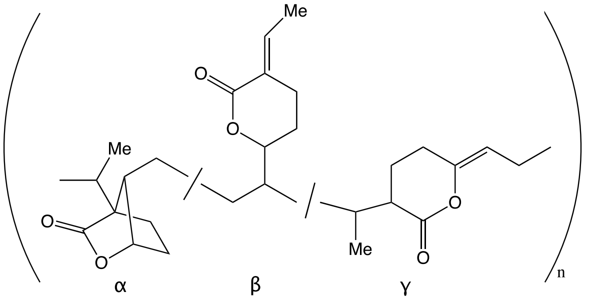


**Figure 4.** Polymer created via lactone polymerization.[1]

However, the metal catalyst used to activate the carbon dioxide to react with the butadiene is made of palladium. Palladium is a precious metal, so it is expensive and not a renewable resource.[29] The catalyst loading of palladium/diene is 1:750 in effective experiments.[1] While organometallic catalysts, such as the dizinc catalyst discussed, obtained successful results with a lower catalyst loading of dizinc catalyst/CHO of 1:1000.[19] It should also be noted that short alkenes used in this process, such as butadiene and isoprene, are petroleum based and generally derived from by-products in oil refining.[30] Butadiene is produced specifically from steam cracking, an energy intensive oil-refining process.[30] Therefore, these unsaturated alkenes are not a sustainable alternative to epoxides.[30] Although, this method produced polymers with comparable carbon dioxide incorporation to the zinc and iron methods, the high price and rarity of Palladium, along with the extra step in the copolymerization process, are not green choices. In addition to the non-renewable sources of conjugated dienes, the starting material, and the non-biodegradability of the final copolymer, one cannot justify deeming this process 'green.'

**Table 1. Comparison of Catalysts using discussed Qualities:**

| Catalyst | Carbon Dioxide Incorporated (%)[a, b] | Pressure needed for copolymerization (atm) | Renewability of Starting Material | Renewability of Catalyst | Biodegradability of the Copolymer |
|---|---|---|---|---|---|
| BDI Zinc | 94 – 99[a] | 1.36 | Yes, if using Limonene Oxide | Yes | Yes |
| DiZinc | >99[a] | 1 | No | Yes | No |
| Bimetallic Iron(III) | 99[a] | 10 | No | Yes | No |
| Iron-Corrole | 62 | 19.7 | No | Yes | No |
| Palladium | 33 mol%[b] | 1 | No | No | No |

[a]Carbonate linkages were the measurement used to assess the amount of carbon dioxide incorporated. [b]Mole percent was the measurement of to assess the amount of carbon dioxide incorporated. Note that 33 mol% is near the theoretical maximum,[1] comparable to 95-99 % carbonate linkages.

**Future Research.** Currently, a variety of chemical techniques are being employed to approach this process. To grasp a better understanding of the mechanism of polymerization using these catalysts, the reaction can be computationally modeled.[31] For example, the BDI Zinc catalyst previously described has been modeled by Morokuma *et al*[32] who mapped out a plausible sequence of reactions for the $CO_2$-epoxide copolymerization, using ethylene oxide. They predicted carbon dioxide would weakly coordinate to the coordinatively unsaturated zinc-bound polymeric alkoxide. [32] They identified the transition state of this mechanism as the breaking epoxide bond, and the following ring-opening step by the polymeric carbonate to be the rate-determining step. This modeling can be applied to other similar catalysts for this process, and the transition state and rate-determining steps of the reaction will provide insight into future catalyst design.[32] Using different models and basis sets, the enthalpies and free energies of copolymerization with different reagents can also be analyzed to aid in design of better catalysts.[31]

There has also been research into metal free catalysis. A notable example of this was put forward by N. Aoyagi and colleagues,[33] who used secondary and primary ammonium iodides to activate carbon dioxide and synthesize cyclic carbonates.[33] However, this catalysis has yet to report applications in the creation of copolymers. The fact that this catalyst is able to activate carbon dioxide is an important advancement to demonstrate that metal-free catalysts are viable alternatives. It is still important to analyze the renewability of these catalysts, because they are metal free does not automatically make them green. Conscious choices will have to be made in sourcing the starting material of the catalyst.

One type of catalysis that seems to be missing in this field is the use of nanoparticles. Immobilized catalysts have been used for carbon dioxide copolymerization,[34] so the heterogeneity of nanoparticles may be suitable for the copolymerization process. Nanoparticles also provide many tunable qualities such as size, shape, and composition.[35] Due to the small size but high surface area of nanoparticles, the cost per function is minimized.[3] This makes nanocatalysis attractive for industrial processes.[36] Since there has been significant development in the research of nanoparticles in recent years, it could be an idea worth exploring.

## CONCLUSIONS

It is clear that there is still a lot of work to be done in this field. A commercializable catalyst that upholds green standards has not yet been realized. The BDI zinc catalyst is able to synthesize biodegradable polymers,[15] while the dizinc catalyst shows high activity at atmospheric pressure.[19] The bimetallic iron (III) catalyst can create polymers of high crystallinity.[12] While the palladium catalyst is able to incorporate $CO_2$ into a polymer starting with a conjugated diene.[1] In this critique of three example methods, it is clear that different catalysts have certain advantages but also disadvantages. Both zinc and iron routes of catalysis use CHO and PO, which are not yet sourced from renewable feedstocks.[22] Thus, the process also needs to be adjusted to favour renewable starting materials. Using petrochemical derived hydrocarbons and epoxides[30] on an industrial scale would not be a green option. For that reason, research into the copolymerization of renewable, naturally occurring or derived starting material also needs to be a priority. However, BDI zinc catalysis of limonene oxide, produces a biodegradable copolymer from a renewable feedstock using mild conditions.[23] Of the results chronicled in this article, this process best embodies the principles of green chemistry.[13]

Also included in this critique was the novel technique to copolymerize carbon dioxide with conjugated dienes via a lactone intermediate. As discussed previously, the use of palladium, an intermediary step, and use of non-renewable feedstocks[13], is not indicative of a green process. This emphasizes the fact that there is research currently done in the field that hardly embodies any principles of green chemistry. One cannot generalize an entire field since some of the ways to perform this reaction are green. It is dangerous to make assumptions, the reader needs to be aware of this, and critically evaluate the information given before deciding if a process is green or not.

Unfortunately, all of this research field cannot be considered green until a viable method of carbon dioxide capture and storage is available.[10-11] In order to maximize the valorization of the waste product, $CO_2$, this method needs to be energy efficient, to ensure the green standards of the $CO_2$ copolymerization process are not negated by the effort of obtaining the starting material. As of 2014, there were pilot projects under way to optimize carbon capture and storage on a large scale.[10] With the world focused on limiting $CO_2$ emissions,[11] this technology will be in focus over the next few years. Hopefully, this will mean the realization of a completely green $CO_2$ copolymerization process.

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## ABBREVIATIONS

$CO_2$, Carbon Dioxide. CHO, cyclohexene oxide. PO, propylene oxide. PDI, Polydispersity Index. BDI, β-diiminate.

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# Making Something From Nothing: Quantifying the potential of biogas from organic waste in Canada

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*KEYWORDS: Biogas, organic waste, Canada, biomethane, green chemistry.*

**ABSTRACT:** The use of organic waste materials as a biogas feedstock presents multifaceted environmental benefits. In addition to reducing dependence on fossil fuel sources for energy, diversion of organic waste material to biogas plants will reduce greenhouse gas emissions and pollution caused by the current prevailing disposal methods of organic waste materials. Canada is a country rich in biomass with large argicuture and forestry sectors producing large amounts of organic waste, creating potential for organic waste as an energy renewable energy resource. This study quantifies the possible energy produced if all sources of organic waste were wholly converted to biogas.

## 1. INTRODUCTION

Increased global awareness of climate change has created an impetus for the research and development of renewable sources of energy, including biogas. Biogas is the product of anaerobic digestion of biomass, including energy crops and organic waste materials, that can be used for electricity and heat, or converted to biomethane for use in the natural gas network.[1] Production of biogas specifically from organic waste materials, such as agriculture and forestry residue, livestock waste, municipal waste, and wastewater sludge, has the added environmental advantages of diverting waste from landfills, reducing landfill methane and carbon dioxide emissions, and preventing toxification of soil and groundwater (see Figure 1). In Canada, unused organic waste materials are responsible for 10% of greenhouse gas emissions each year.[2] Thus introduction of centralized biogas plants in Canada could directly reduce greenhouse gas emissions in addition to reducing dependence on fossil fuels.

Organic waste material, especially municipal solid waste and livestock waste, is a significant source of methane emissions. Methane is a greenhouse gas 21 times more potent than carbon dioxide in terms of global warming potential.[3] Mitigation of this greenhouse gas is thus a crucial concern in climate change efforts. Unlike other greenhouse gases however, as a hydrocarbon, methane is also a fuel. Natural gas is a commonly used fuel source that is comprised predominantly of methane, highlighting the usability of methane as a fuel source. This presents an intriguing strategy for the mitigation of methane emissions from organic waste: if it were possible to collect all of the organic waste material and deliver it to an anaerobic digester, the methane produced by its decomposition would not be released to the atmosphere, but used for energy.

Biogas plants exist around the world today, using anaerobic digesters to convert biomass into biogas—a gas mixture that is primarily composed of methane. In addition to reducing methane emissions and creating energy out of what was once garbage, this strategy would divert volume from landfills and prevent other harmful effects of unregulated anaerobic digestion of organic matter, such as eutrophication and air and groundwater pollution.[4] Further, in addition to methane, biogas production produces a nutrient-rich digestate that can be used as a fertilizer.[5] Produced on a large-scale, this could displace a significant amount of chemical fertilizers used in the agricultural industry, which are produced by the highly energy intensive haber-bosch process.

Biogas produced from waste materials in Canada is currently an untapped hydrocarbon resource that, unlike petroleum-based hydrocarbon resources, is more environmentally detrimental if left unused. This paper serves to quantify the potential for large-scale biogas production from waste materials in Canada.

## 2. METHODS

Data on the feedstock inventories in Canada was obtained from a study by Wood and Layzell.[6] The amount of dry matter in livestock manure was estimated based on a study by Levin et al to be 14.3%, 25.5%, and 10.1% for cows, poultry, and swine respectively.[2] The amount of dry matter in the wastewater sludge was estimated to be 4% based on a study by Berlgund et al.[7] The organic fraction of dry municipal solid waste was taken to be 40% based on a study by Chornet et al.[8] The conversion factors of dry matter to biogas yield were adapted from the study by Berglund et al.[7] The published conversion factor for manure was 7 GJ/dry tonne for swine manure and 6.2 GJ/dry tonne for cow manure.[7] In this study, the conversion factor the manure from cows, pigs, and poultry combined was taken to be 5.5 GJ/dry tonne to account for the lower biogas yield of poultry manure.[9] The conversion factor for agricultural and forestry waste was approximated to be 7 GJ/dry tonne, based on the published conversion factor for straw.[7]

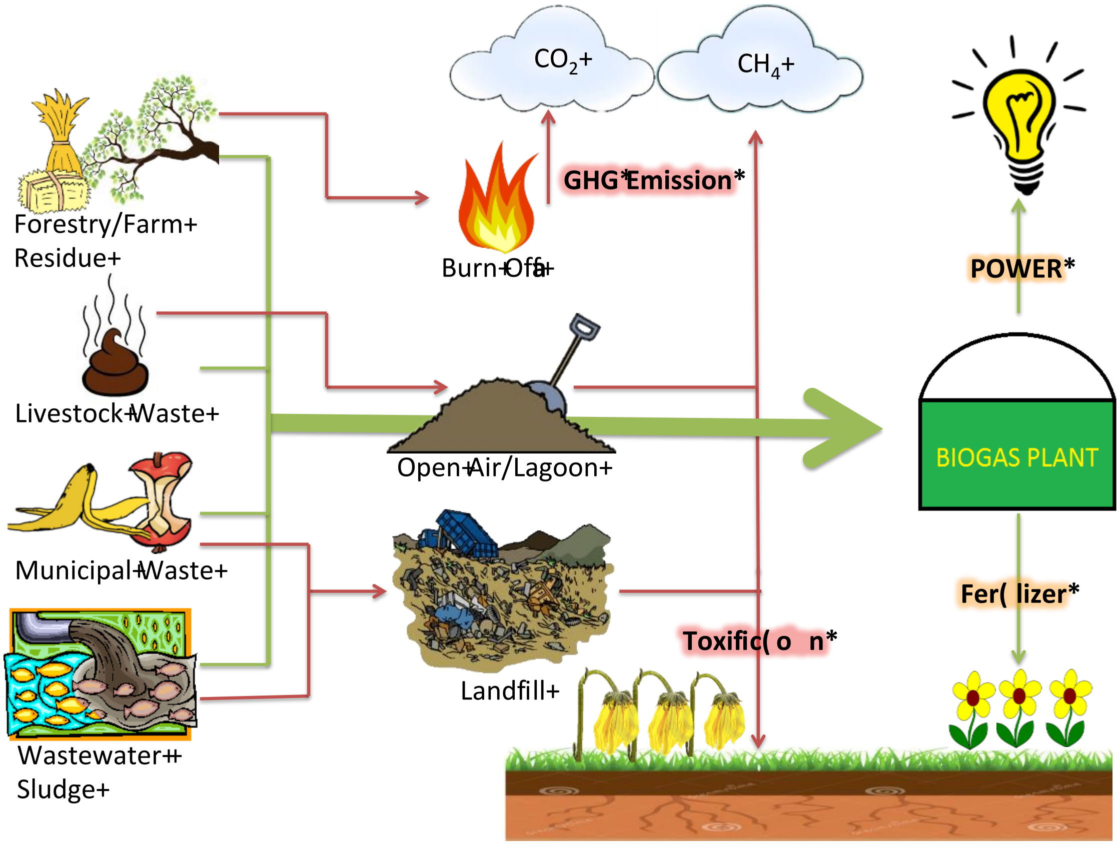

**Figure 1.** Schematic diagram of the benefits of diverting organic waste to biogas production.

## 3. HOW IT WORKS

Anaerobic digestion of organic material is a process involving a variety of microbial communities. There are four stages of anaerobic digestion: hydrolysis, acidogenesis, acetogenesis, and methanogenesis, each one making use of a different type of microorganism.[10] A schematic of the entire process can be found in Figure 2.

The first step in anaerobic digestion is hydrolysis. During this process, the feedstock material is broken down into its basic substituents via enzyme-mediated digestion. Extracellular enzymes secreted by bacteria, such as proteases and amylases, convert the macromolecules present in the feedstock material into compounds suitable for use as food by microorganisms.[10] Proteins, carbohydrates, and lipids are metabolised into amino acids, monosaccharides, and long chain fatty acids.

In the second stage, called acidogenesis, the monomers produced in hydrolysis are further digested by acidogenic bacteria into short chain organic acids (such as acetic, formic, and butyric acid) and alcohols (methanol, ethanol). Some hydrogen and carbon dioxide is also produced during this stage.[11]

The short chain acids and alcohols (except methanol) produced resulting from acidogenesis are further degraded by acetogenic bacteria into carbon dioxide, hydrogen and acetic acid in the third stage of anaerobic digestion, acetogenesis. This stage is acutely sensitive to the partial pressure of hydrogen. As hydrogen is a major product of acetogenesis, an elevated hydrogen partial pressure will render the conversion processes thermodynamically unfavourable.[12] Hydrogen scavenging bacteria are thus another critical bacterial family in the anaerobic digestion process, as they act to keep the partial pressure of hydrogen low in the reaction vessel.[11]

The fourth and final stage of anaerobic digestion is methanogenesis. During this stage, the acetic acid, hydrogen, and carbon dioxide formed in the acidogenesis and acetogenesis stages, as well as the methanol formed during the acidogenesis stage, are converted into methane

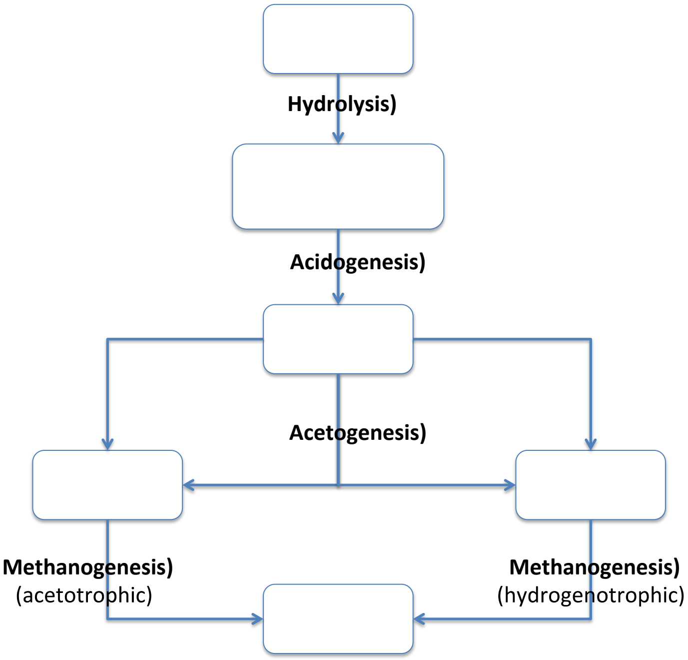

Figure 2: Schematic diagram of anaerobic digestion processes.

by acetotrophic methanogenesis, hydrogenotrophic methanogenesis, or methylotrophic methanogenesis. The stoichiometric equations for these conversions are found in Equation 1, 2, and 3 respectively.[13]

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad (1)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (2)$$

$$4CH_3OH + 6H_2 \rightarrow 3CH_4 + 2H_2O \qquad (3)$$

The amounts of hydrogen, acetic acid, and methanol produced in the first three stages of anaerobic digestion will depend on the composition of the feedstock.[11] Thus, different feedstocks vary widely in the relative amounts of methane and carbon dioxide in the biogas they produce. Typically the methane content of biogas falls between 50-75%. The biogas can be converted to electricity and heat, or upgraded to pure methane (called biomethane) using a biogas upgrader facility, which can then be supplied to the natural gas grid.

## 4. ORGANIC WASTE POTENTIAL IN CANADA

Typical feedstocks for biogas production include energy crops and organic waste residues. Energy crops, such as maize and clover, are crops grown specifically for the purpose of biogas production. While biogas from energy crops is renewable source of energy, there are several drawbacks to this approach. Production of energy crops on a large scale requires a substantial energy input for the cultivation and harvest of the crops. Tractors and machinery used in these steps often rely on petroleum-based fuels, further limiting the benefits of biogas from energy crops.

Organic waste materials used for biogas production include agriculture and forestry residues, livestock residue, municipal solid waste, and wastewater sludge. Unlike energy crops, the production of biogas from organic waste material does not require the manufacture of feedstock material and thus the only energy input is that involved with the collection of waste.[14] Additionally, as the prevailing disposal methods of organic waste are environmentally detrimental, diversion of these waste materials to biogas production presents additional environmental benefits of greenhouse gas emissions (see Figure 1).

This paper outlines four major sources of organic waste that have potential to be used for biogas production in Canada, and quantifies the potential energy production if these materials were wholly converted to biogas (see Table 1).

### 4.1 LIVESTOCK WASTE

Livestock manure is an organic waste material that is extremely hazardous to the environment if left unused. In the United States in 2005, 50.8 million metric tonnes of carbon dioxide equivalent resulted from methane and nitrous oxide emissions solely due to livestock manure.[15] Normally, manure is stored either in lagoons (i.e. buried under ground) or in open-air and left to decompose. In addition to the foul odour, decomposition in these conditions leads to many problems, namely the production of methane and nitrous oxide, as well as air pollutants such as hydrogen sulphide and ammonia.[15] The ammonia produced has the additional issues of groundwater contamination and eutrophication of the soil.[16] In short, when treated as waste, manure is highly problematic and environmentally volatile. However, as an organic material, manure has an alternate destiny as a feedstock for biogas.

**Table 1: Quantities of dry manure produced by agricultural livestock in Canada.**

| Livestock | Number of Animals[17] | Manure Produced (Mt/year)[6] | % Dry Matter[2] | Total Dry Matter (Mt/year) |
|---|---|---|---|---|
| Cows | 7,594,465 | 100 | 14.3 | 14.3 |
| Poultry | 126,159,529 | 2 | 25.5 | 0.51 |
| Swine | 13,913,001 | 26 | 13 | 3.38 |
| Total | 147,666,995 | 128 | -- | 18.19 |

**Table 2: Overview of biogas potential by feedstock source.**

| **Organic Material** | **Dry Matter (Mt)** | **Biogas Potential per dry tonne (GJ)** | **Total Biogas Potential (PJ)** | **Total Biogas potential (TWh)** |
|---|---|---|---|---|
| Livestock Waste | 18.19 | 5.5 | 100.045 | 27.79 |
| MSW | 6.016 | 12.4 | 186.4660788 | 75.12 |
| Wastewater Sludge | 15486.64 | 22 | 0.34070608 | 51.80 |
| Agriculture Residue | 38.632 | 7 | 270.424 | 156.99 |
| Forestry Residue | 80.74088 | 7 | 565.18616 | 0.09464 |
| Total | | | 1122.461945 | 311.79 |

In Canada, 128 million tonnes of manure are produced each year from cows, swine and poultry.[6] Table 1 shows the dry matter content of manure by Livestock species in Canada. If instead of decomposing on site, this manure were collected and brought to an anaerobic digester, it could be converted into approximately 100 PJ of energy (see Table 2). In addition to mitigating methane and nitrous oxide emission, conversion to biogas could solve manure's waste management problems and turn manure into a renewable energy resource.

## 4.2 MUNICIPAL SOLID WASTE (MSW)

There are three categories of municipal solid waste: urban residential waste; industrial, commercial, and institutional waste; and landscaping and construction waste. About 40% of the dry weight of municipal solid waste is organic, and therefore usable as a biogas feedstock. Unused, these waste materials end up in landfills, where they are degraded to form methane that is released to the atmosphere. Landfill emissions are the largest source of anthropomorphic methane in the United States.[18] Much of the organic material in landfills is a result of food waste. In North America, 300 kg of food per capita is wasted annually by consumers and production to retailing.[19] In the U.S., 40% of food that reaches the consumer is thrown away—the equivalent of 20 pounds per person per month.[20] The total municipal solid waste production in Canada is nearly 23 million tonnes (wet). If the organic fraction was diverted into biogas production, it would result in approximately 186 PJ of energy.

## 4.3 WASTEWATER SLUDGE

Another waste form that has potential as a biogas feedstock is wastewater sludge: the material filtered out of wastewater, including sewage. This sludge is mostly organic material and can produce the most methane per dry kg out of all of the feedstocks mentioned in this paper. Wastewater sludge is another troublesome waste that is major source of marine pollution. Its high capacity for conversion to methane as well as the sheer quantity produced in developed countries makes wastewater sludge an ideal candidate as a biogas feedstock. With heightened water treatment standards being introduced, the amount wastewater sludge collected around the world is ever increasing. In Canada, 390,000 tonnes of wastewater sludge is created each year, presenting a significant source for biogas production.

## 4.4 FORESTRY AND AGRICULTURE RESIDUE

Agricultural residue is what is left in a field after the harvest: stalks, stems, leaves—the non-food portions of agricultural production. While it is beneficial to leave part of the residue after harvest to protect soil, the amount of sustainably removable residue is still a significant source for biogas production at 40 million dry tonnes. Current disposal methods for harvest residue often include burn-off, which results in significant carbon dioxide emissions. The use of harvest residue for biogas production could prevent this source of emissions in addition to creating 270 PJ of energy each year in Canada.

Forestry waste includes the non-stem portions of the trees—i.e. the branches and leaves. The forestry industry in Canada is immense, with an annual harvest of over 1 million hectares every year, the residue amounts to 90 million dry tonnes.

## 4.5 SUMMARY OF ORGANIC WASTE POTENTIAL IN CANADA

Table 2 illustrates the potential energy from biogas if each source of organic waste were wholly diverted to a biogas plant. The total amount of energy created from organic wastes was found to be over 300 GWh, the equivalent of 190 million barrels of oil.[21] The organic waste from forestry and agricultural sectors are the largest sources of energy, accounting for 230 GWh combined. The total biogas potential from all organic wastes could power over 50% of Canada for a year.

## 5. CONCLUSION

Organic waste materials available in Canada have the potential to produce a significant amount of energy with limited input costs, as the feedstock material would otherwise be waste. The available feedstocks for biogas production are prevalent enough to produce more than 300 GWh of electricity if combined, which could account for over 50% of Canada's yearly electricity consumption. While the organization and infrastructure is not yet in place, the potential environmental advantages to using this fuel provide an impetus to make biogas a mainstream energy source.

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# Strategies for the Reduction of Methane Emissions and Harnessing for Use as an Alternative Energy Resource: A Review.

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**KEYWORDS: Methane, methane emissions, greenhouse gases, environment, alternative energy resource**

**ABSTRACT:** Methane gas is a greenhouse gas over 20 times more potent than carbon dioxide and is produced in four principal sectors: the oil and gas industry, the agricultural industry, from landfill waste, and as a byproduct of coal mining. Apart from being detrimental to the environment, the emission of methane into the atmosphere is also a waste of an energy resource. In this review, the sources of methane emission and current methods used to mitigate emissions or to harness them for use are presented and evaluated. It was found that the harnessing and use of emitted methane for an alternative fuel source has been explored to varying degrees depending on the sector: in the oil and gas industry the detection of emitted methane is still a challenge, whereas in the agricultural, landfill, and coal mining sectors the harnessing of methane gas for use is becoming more popular, though flaring is still an option in these sectors.

## 1. INTRODUCTION

In the past several decades, societal attention has shifted increasingly toward greenhouse gas emissions and the problems they pose, as well as the solutions presented to solve these problems. Emission sources as reported by the United States Environmental Protection Agency (EPA) include: electricity (31%), transportation (27%), industry (21%), commercial and residential (12%), and agricultural (9%) emissions.1 Greenhouse gases (GHGs) include: carbon dioxide (82%), methane (10%), nitrous oxide (5%), and fluorinated gases (3%).1

Greenhouse gases play an important role in trapping heat in the atmosphere and maintaining global temperatures necessary for life on Earth. Trapping too much heat, however, can lead to a global rise in temperature, a phenomenon known as global warming. Climate change that results from global warming is of significant importance as it directly affects the survival of many lifeforms on Earth2 by impacting the habitats in which they live. To combat global warming, much research has been conducted on the matter of reducing greenhouse gas emissions.

Carbon dioxide has been a main concern as emissions are found to account for 80% of all GHG contributions to global warming3. The second most prevalent GHG is methane, which accounts for 10% of GHG contributions to global warming3. Although CO2 is the primary GHG emitted through human activities (there is 200 times as much CO2 in the atmosphere as there is methane4), methane is more potent, with a global warming potential (GWP) 3.7 times that of CO2 on a molar basis3. Therefore, while methane does not linger in the atmosphere for as long as CO2 does, its higher GWP means that it is far more effective than CO2 at absorbing and trapping heat in the atmosphere, and it is initially far more devastating to the climate.

Methane emissions have many sources, including: natural gas and petroleum systems (29%), enteric fermentation (26%), landfills (18%), coal mining (10%), and manure management (10%).1 Global warming is also causing the release of methane hydrates frozen in permafrost.

Recently, studies have been conducted on the harnessing and reduction of methane emissions. The EPA proposed the first-ever rule to directly limit methane emissions from oil and gas operations in 2015.5 This would instill regulations to reduce wasteful methane emissions in the near future. Studies have also been conducted on the harnessing and use of emitted methane gas in the environment, including methane hydrates as a fuel source6 and the use of methane emissions from livestock, landfills, and coal mining for an alternative fuel source through a combustion reaction.

In this review, methods for the harnessing, use, and reduction of methane emissions will be explored.

## 2. METHANE EMISSION SOURCES AND RECYCLING PROCESSES

In order to better understand the recycling processes of methane, it is important to first understand the sources from which methane is emitted. Globally, over 60% of total methane emissions come from human activities.[1] By understanding how methane is emitted from each source, it becomes possible to devise methods for the reduction and recycling of methane emissions.

### 2.1. Agriculture

The agricultural sector is the primary source of methane emissions from human activities globally[1]. Enteric fermentation is responsible for 26% of methane emissions, while manure management is responsible for 10%.[1] These emission sources are considered human-related because humans farm the animals responsible for the emissions and raise them for food.

Enteric fermentation is the digestive process whereby microorganisms break down carbohydrates for absorption into the bloodstream of an animal. Methane is produced in the rumen as part of this process, and it is emitted through belching by the animal or passed out as flatulence.

Livestock manure is a valuable resource for nutrients and an excellent soil amendment that improves soil quality, tilth, and productivity.[9] It is also a source of methane production during the anaerobic decomposition of its organic matter in storage. Storage conditions such as temperature, oxygen level (aeration), moisture, and sources of nutrients greatly affect emissions.[9]

#### 2.1.1. Agricultural methane emission reduction and harnessing strategies

Methane emitted as part of livestock digestion is difficult, though not impossible, to mitigate. Cattle diet plays a huge part in emissions, so feeding strategies naturally play a part as well. Experiments done by Agriculture and Agri-Food Canada (AAFC), for example, have shown that an increase in dietary fat by feeding crushed oilseeds such as sunflower, canola, and flaxseeds, reduce methane emissions from livestock by up to as much as 20%.[10] The use of a methane inhibitor (3-nitrooxypropanol, or 3NOP, outside the scope of this paper)[11] was found to persistently decrease methane emissions by enteric fermentation by 30%, without negatively affecting animal productivity. Other methods for the mitigation of enteric emissions include management practices that reduce animal numbers on beef and dairy farms[10], as well as vaccines that target the methanogens present in animal rumen[12].

For the remaining emissions emitted by livestock, recent methane harnessing strategies have been developed, including a backpack for cows for the collection of methane gas emissions[13]. This method extracts 300 L of methane a day from the animals' digestive tracts and converts the gas into enough energy to run a car for 24 hours.[13]

Enteric fermentation is not the only factor for agricultural emissions, however, and livestock manure should also be addressed. Its value as an excellent soil amendment, as mentioned above, prompts storage at various farming locations worldwide. In storage, the

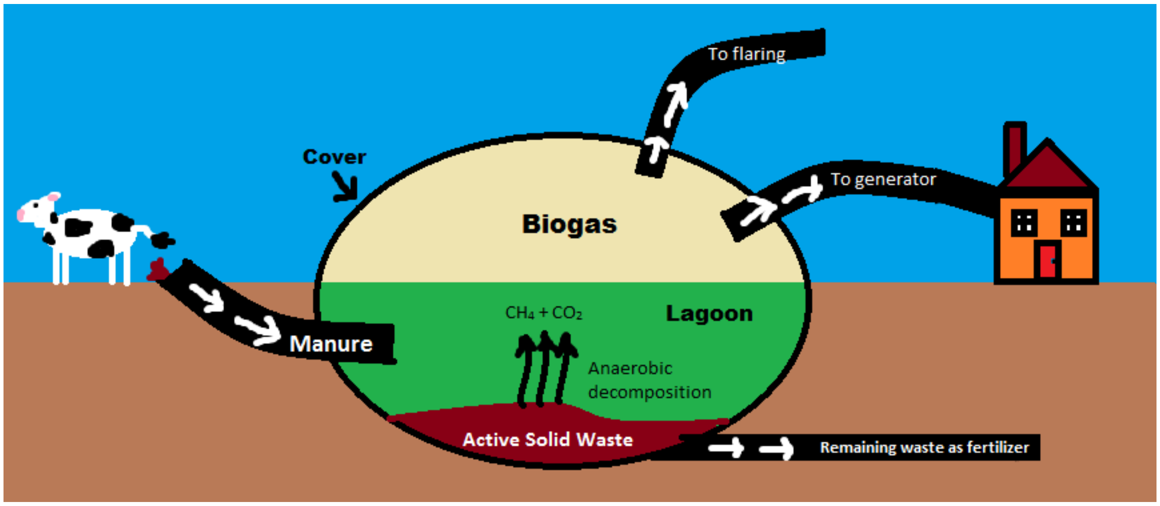

**Figure 1.** The anaerobic decomposition of manure in a lagoon forming methane biogas, to be used as an alternative energy source or flared to the environment. Remaining manure can be used as fertilizer.

amount of methane emitted depends upon: the amount of manure, the animal type, the manure handling method, and the environmental conditions.[9] Liquid manure storage, such as in ponds, lagoons, and holding tanks, leads to anaerobic conditions; the decomposition of manure in these conditions can emit up to 80% of manure-based methane emissions.[9] Solid storage, on the other hand, comprises a more aerobic environment, and emits little to no methane.

Waste management methods for manure include covered lagoons, whereby a cover is placed on the surface of the tank or lagoon used for storage; the trapped gases are subsequently flared and exhausted to the atmosphere as the less potent $CO_2$, or burned inside a generator for an alternative energy source.[9] Covers can reduce methane emissions by 80%[9] and provide good odor control as well. Digesters are also used to process waste for the production of methane gas under anaerobic conditions.[9] The gas can be used as an alternative energy source and the remaining manure can be used as fertilizer. A typical lagoon is shown in Figure 1 below.

## 2.2. Oil and gas industry

The second biggest source of methane emissions as denoted by the EPA stems from the natural gas and petroleum industry, better known as the oil and gas industry. This sector is responsible for 29%[1] of emissions from human activities in the US. Emission sources from the oil and gas industry include leaks in natural gas transmission facilities such as pipelines and compressor stations, as well as leaks in upstream oil and gas production facilities, especially from solution gas.[7] For both safety and climate change reasons, the elimination of methane emissions from these sources can only be beneficial. In addition, these emissions are a source of wasted energy, which, if captured, can be used as fuel for useful energy.[7]

### 2.2.1. Industry methane emission reduction strategies

As mentioned above, the EPA has proposed national standards to directly regulate methane emissions from the oil and gas industry just recently. Although currently unfinalized, the rule is expected to have an impact on methane pollution for new and modified sources in the industry.[5] Regulation of emissions is an important step for mitigation of leakage, due to the variety of ways in which leakage can occur: loose screws, leaky storage tanks, corroded pipes, outdated compressors, inefficient pneumatic systems, condenser valves stuck open.[8]

Replacement of outdated equipment prone to leakage could aid in stopping leakages, as well as the installation of new technology to capture leaks where they occur. Unfortunately, it is difficult to determine when and where a certain pipe will leak in hundreds of miles of pipelines, or when a certain valve or storage tank will suddenly burst open[8]. Therefore, the current approach to dealing with fugitive emissions has been to impose regulations (as noted above) and to investigate methods for the better detection of leakages. Thus far, infrared cameras have been put to use for the purpose of leakage detection, however, better detection systems are needed, as they are too labor-intensive and fail to find many leaks[8]. Cameras mounted on drones have been explored[8], but they do not last long and the development of lighter sensors is required to prolong flight time.

## 2.3. Landfills

Landfills account for 18%[1] of human activity-related methane emissions in the US. Much like manure, methane is produced in landfills during the anaerobic decomposition of the organic matter present. As such, emission levels differ from landfill to landfill depending on site-specific characteristics such as the kind of waste present and its composition, as well as the climate of the landfill in question.

### 2.3.1. Landfill emission reduction and harnessing strategies

Landfill waste can be mitigated first and foremost by limiting waste production not only in the industrial setting but the office and household settings as well. This can be achieved by reusing objects before subjecting them to the waste bin and simple tasks such as composting organic waste instead of throwing it out. In fact, increased recycling and alternative waste disposal methods are contributing to a forecasted decline in landfill methane emissions, by reducing the rate of waste going into the landfills.[15]

For waste that does end up in landfills emitting methane gas, rules such as the Emission Guidelines set by the EPA[16] ensure that methane emission is controlled by setting an emissions threshold at which a landfill must install controls. Landfill gas recovery plants exist to capture and use emitted methane as a renewable energy source in many countries including: Canada, Germany, Sweden, Finland, and the United States, to name a few.[17] The world's largest biogas plant has a 140 megawatt (MW) capacity and is expected to cut coal use by up to 40% in Vaasa, central Finland, where it was built.[18] Current landfill methane emission mitigation strategies appear optimistic for the short term: Northern European countries such as Sweden and Norway burn waste as a major source of energy.[19] Recently, they have even had to import garbage as they had run out of waste to burn. In the event that demand far exceeds supply for trash worldwide, this would mean no more methane emissions from landfill sources, and attention would then be drawn to harnessing from other sources as mentioned in this article.

## 2.4. Coal mines

Coal mines are the fourth-largest source of methane emissions from human activities, and are responsible for 10%[1] of emissions in the US. Methane gas and coal are formed together during coalification, and methane is stored within coal seams and the rock strata surrounding the seams.[20] It is released when natural erosion, faulting, or mining causes the pressure within the coal bed to drop.[20] Underground mines tend to release more methane than surface mines, because storage capacity is increased with pressure, which increases with depth. According to the EPA, underground coal mines liberate 29 to 40 x $10^9$ $m^3$ of methane annually, of which less than 2.3 x $10^9$ $m^3$ is used for fuel.[21] Abandoned mines also play a part in methane emissions, and a study done by the EPA concludes that, along with coal handling and surface mines, they represent approximately 26% of total emissions from the coal mining industry.[22]

### 2.4.1. Coal mine methane emission reduction and harnessing strategies

As mentioned above, underground coal mines liberate 29 to 40 x $10^9$ $m^3$ of methane annually, of which less than 2.3 x $10^9$ $m^3$ is used for fuel.[21] The remaining methane is emitted to the atmosphere and represents the loss of a valuable energy source[21]; methane is also detrimental to the environment as a major greenhouse gas. Thus, methods for the capture and use of methane emitted from coal mines have been developed.[20-21] As methane is the primary constituent of natural gas, current uses for coal mine methane include: heating and cooking at mine facilities and nearby residences, boiler fuel, and electricity generation.[21] In the US, some mines even sell the gas to natural gas distributors.[21]

Methane emissions from ventilation air shafts used during mining can be lowered in several ways: by using the ventilation air as the combustion air in surface installations at the mine site, by the oxidation of methane to carbon dioxide, or by thermal incineration.[20] The use of ventilation air as combustion air has been noted to be unlikely to use more than a small portion of the total available air[20], making this an unlikely one-shot solution to the problem. Both thermal incineration and oxidation of methane produce carbon dioxide (the primary greenhouse gas, although less potent), so this is not the best solution either, unless coupled to an energy recovery system.

The use of boreholes, or narrow shafts bored into the ground, for methane drainage provide an effective way of reducing the risk of gas outbursts by decreasing the pressure of the coal bed near the mine workings[23].

Once a mine is abandoned, the methane emission decreases but does not completely stop. Abandoned mines can liberate methane at a near-steady rate for an extended period of time.[23] Flooding of the mines can inhibit gas emissions and buildups in the empty spaces; this would also help to mitigate the danger level of working in active mines nearby[23]. Methane emissions from abandoned mines can also be reduced by properly sealing the mine, eliminating unintentional venting of methane[23].

Finally, it should be noted that, with the advancement of technology and various other methods for electricity and energy generation (hydroelectricity, wind turbines, solar generators), perhaps the method of coal mining should take a backseat. After all, the only way to ensure 0% methane emissions from coal mining would be to stop mining activities altogether, but this is beyond the scope of this paper.

## 3. SUMMARY AND FUTURE PROSPECTS

Methane is a greenhouse gas over 20 times more potent than carbon dioxide on a pound-for-pound basis over a 100 year time period.[1] It is emitted primarily from four major sectors: the agricultural industry, the oil and gas industry, from landfill waste, and from the coal mining industry. The emission of methane gas from these sectors into the atmosphere not only has a negative impact on the environment, but also represents a wasted energy resource. Across each sector, various methods have been applied to limit the amount of emissions; in the oil and gas industry, however, efforts are still being made for the proper detection of leakages. The theme behind the methods applied to each sector follows roughly the same format: a rule or regulation is implanted, and measures are taken to follow that rule. Energy harnessing has been explored in the agricultural, landfill, and coal mining sectors, with exceptional results using landfill waste in particular. This is usually achieved through a combustion process, whereby methane is converted to $CO_2$ and water. The expulsion of this $CO_2$ into the atmosphere is justified by noting that, if methane were not to be used as an alternative fuel source, it would be expelled into the atmosphere anyway, and cause more than 20 times the damage than would $CO_2$. In addition, another fuel source would be used, adding to the greenhouse gas emissions.

For future research, better methane detection technologies must be developed for the oil and gas industry, as this would allow for the better pinpointing of leak locations and thus more precise methods to stop fugitive emissions. Better capture and use methods for emitted methane should also be investigated to maximize the full potential of emissions.

## AUTHOR INFORMATION

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# Environmental decay, incommensurate methane emission and feasible future solutions for the treatment of a greenhouse gas

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KEYWORDS: *Absorption, greenhouse gasses, framework, ionic, nanofibers*

**ABSTRACT:** The human growth in the last decades has required the supply of food, energy and fuel in a high demand. These three necessities are related with one issue: green house gas emission. This may not appear directly related to the supply of goods, but secondary activities are responsible for this problem such as organic waste disposals, natural gas extraction and combustion of fossil fuels. These and other similar activities have raised methane concentration in the environment, causing an increase in temperature and natural disaster frequency. For this reason, methane emissions have been chosen as a target problem to be solved. Some opportunities to reduce this greenhouse gas are the implementation of physical chemical and spectroscopic methods such as: time correlation tracer systems, sorption modeling for coal-bed methane production, use of ionic liquids for methane capture and methane decomposition by catalyst to create carbon nanofibers. Several of these small-scale applications have shown significant results for methane reduction. This paper reviews the significant results for methane reduction of the aforementioned physical, chemical and spectroscopic methods.

## INTRODUCTION

Over the pass of the years, the chemical composition of the atmosphere has been altered producing a change in environmental conditions, such as the increment of temperature. This has led to an increase in natural disasters, for instance hurricanes, tornadoes, floods, typhoons, droughts, wildfires, etc.[1] Methane is one cause of many of environmental deterioration, producing a growth in the greenhouse effect [2]. Global activities such as fossil fuel production, distribution and use; intensive livestock farming; and the creation of abounding landfill and waste disposals, generate the exponential emission of this gas [3]. With the well-known consequences of the preceding activities, humans must propose alternatives to reduce the inherent global warming created by the greenhouse effect.

Scientists may be doing research for creating a new branch of chemistry, for example: innovating low-cost and environmentally friendly processes, namely methods for recycling and purifying water and technologies for storing energy coming from renewable sources. However, a small portion is proposing solutions to improve climate conditions that are damaged and getting worse.

The purpose of this paper is to give a review of the environmental situation as well as to provide ideas and proposals of what can be done for the environmental concern and the treatment of immeasurable methane emission by using technologies and processes already developed by scientists.

Many possible options to solve this current global condition are convenient, for example: the employment of methane sorption models, the decomposition of methane to heavier hydrocarbons and its conversion to reusable goods. With the prior proposals to improve the environmental situation, a slight reduction of catastrophic side effects in the near future may be possible

## DISCUSSION

The composition of the atmosphere is 78% nitrogen, 21% oxygen, 0.9% argon, 0.0375% carbon dioxide and 0.003% as trace elements. This composition has remained the same for the past 200 million years [4]. However, it wasn't until the beginning of the industrial revolution in the mid-18th century when the impact of human activities began to grow, especially the use of fossil fuels and their combustion[5]. This led to the creation of greenhouse gases and aerosols that modify the atmosphere composition. Hydrocarbons were not uniquely responsible for the initiation of ambient impact effects, the emission of chlorofluorocarbons, chlorine and bromine compounds were also a cause of the ozone layer depletion.

As Figure 1 illustrates, the increase in temperature over the years since the first half of 18th century due to the industrial revolution [6].

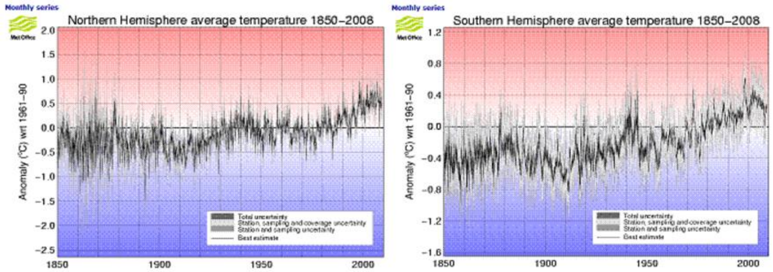


**Figure 1.**[6] Graphics for Northern and Southern Hemisphere average temperature along the past 150 years. Graphics plotting temperature versus years.

Moreover, the greenhouse effect is the phenomena that permits the solar radiation (visible radiation) absorption through a transparent medium, but the emitting radiation from the Earth to the space (infrared radiation) is blocked by it. This trapped radiation causes the heating of the Earth's surface, increasing its temperature. The primary cause for this effect is attributed to carbon dioxide ($CO_2$) which has increased 30% since industrial times, [5] and is still increasing with a rate of 0.4% per year according to the records and documentation of Mauna Loa Observatory[7] as illustrated in Figure 2.

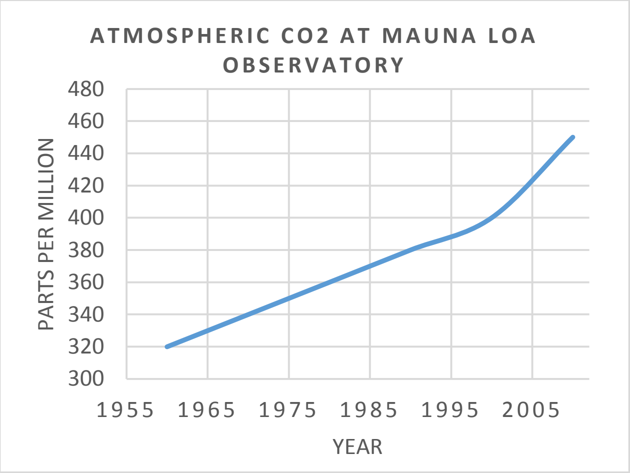


**Figure 2.**[7] Graphic of carbon dioxide increase in ppm reported by the Institution of Oceanography. Scripps Institution of Oceanography NOAA Earth System Research Laboratory.

However, $CO_2$ is not the only greenhouse gas resulting from anthropogenic activities, methane and nitrous oxide must also be taken into consideration.

The main characteristic of these gases is the increment on Earth's temperature that consequently generates an impact on climate change and natural disasters. According to the IPCC, an increase in greenhouse gasses in the atmosphere will probably increment temperatures, which will lead to the emergence of droughts, intense storms, tropical cyclones and mid- latitude storms[8]. In Figure 3, the graphs demonstrate that the change in climate, besides affecting temperatures, produces an increase of weather-related natural disasters. An example of this is: the formation of storms by decreasing the temperature difference between the poles and the equator. The warmer temperatures at latitude 0 will increase the water vapor in the atmosphere generating a humid and hotter environment. From the convection currents, the poles will receive warmer air drafts taking these regions out of temperature equilibria. Subsequently, as the temperature increases, concentration of water vapor in the atmosphere increases, as well as the probabilities of storm formation with greater potential. The increase of temperature over land, change of temperature difference between equator and poles and humidity increase could provoke intense cycles of droughts and floods [9].

According to the Climate Analysis Indicator Tool, China and the U.S are the main countries for greenhouse gas emissions, and methane is the second highest emitted gas in the U.S.[10]. Although $CH_4$ emissions are small compared to those of carbon dioxide ($CO_2$), the lifetime in atmosphere of $CH_4$ is 12 years. The global warming potential (it refers to how much energy the emissions of one ton of a gas will absorb over a given period of time[11]) is 28-36 compared to $CO_2$ that it is *1*, and the most hazardous property of $CH_4$ is that it is can absorb $CO_2$ in much higher concentrations which, in turn, will lead to greater impacts on climate change.

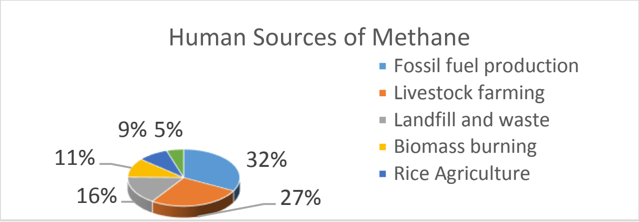


**Figure 3**[9]. Different graphs to illustrate divergent temperature behavior in distinct cases.

There exist two types of methane emissions. The natural emissions correspond to a 36% of the total emissions, while human emissions account the 64% total including landfills, livestock farming and fossil fuel use (see Figure 4)[3].

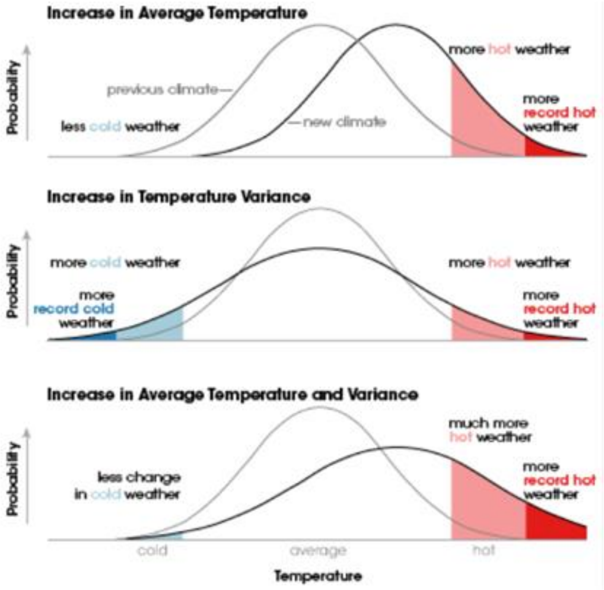


**Figure 4**[12]. Pie chart for the human sources of methane

The methane concentration in the atmosphere has increased in the last two centuries because of the population growth and the increase in human activities. In the past, the methane concentration was between 350-800 ppb but after the 1850's, the concentration levels have raised 2.5 times larger [12].

Fossil fuels production and use occupies the 32% of the overall emissions and they are mainly produced when fuels are extracted from the earth (natural gas, petroleum, and coal) but also during their handling, transportation and refinement. It has been calculated that 110 million tonnes of methane are produced due to these activities [3].

Livestock farming is also a big contributor of methane by the enteric fermentation in animals proportioning the 27% of emissions. This emission has increased the last few decades because of the large growth of livestock populations worldwide producing an increase of 90 million tonnes of methane annually [13]. Landfills and waste dumps generate methane due to the decomposition of biodegradable organic material, and it produces 55 million tonnes annually.

As population grows every year, as does human waste, increasing the number of landfills. As more organic waste is produced, anaerobic degradation increases the methane production. But not only solid material wastes enhance this problem, but also wastewater from residential and industrial sources can be a problem [3].

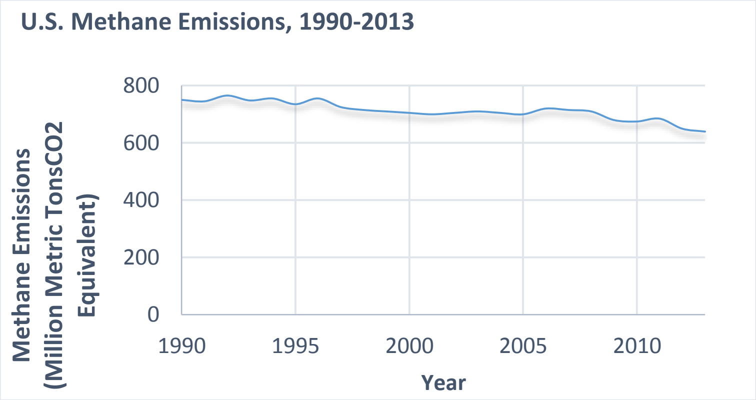
Biomass burning, rice agriculture and biofuels represent a minimum percentage of methane emission, but they contribute 69 million tonnes annually [3].

As it was reviewed, production of methane is inherent in all human daily activities and as long as we continue inhabiting this planet, greenhouse gasses will continue existing. For the prevalence of an equilibria between our wellbeing and the continuity of quotidian activities, standards or mitigation opportunities should be applied to achieve better environmental conditions. An example of this is illustrated in the graph of Figure 5, where U.S reduced a by 15% the $CH_4$ emissions in a period of 23 years [11].

**Figure 5**. U.S. Methane Emissions, 1990-2013

Some reduction opportunities for methane have been set by the U.S Department of State such as the renewal of extraction, handling and transportation equipment for natural gas which will reduce the number of gas leaks [14]. Another proposal is that of manure management strategies at livestock operations[15] and the implementation of methods to capture methane in landfills as a reduction strategy[16].

On 1 October 2010, 37 government partners and the European Commission launched *The Global Methane Initiative* (GMI) to face the climate change developing new technologies for cleaner energies [17]. An example of this is the implementation of bio digesters in local farms in the U.S region. At the moment, this has been a great step for society to deal with climate problems and the decrease of greenhouse gasses production. However, more than establishing initiatives can be done.



University research groups have focused on investigating and developing new technologies for the generation of energy from renewable sources. These technologies include solar radiation, construction of hydroelectric power plants, assembly of windmills, hydrogen fuel cells and the replacement of common fuel sources as hydrocarbon derivatives. Methane is a hydrocarbon derivative, it is a side product of human activities that cannot be removed unless the chemistry of biodegradation, fermentation and combustion is completely changed. Because methane is an unavoidable gas, we can take advantage of its chemical properties that allow it to be used as fuel. Instead of letting methane flows directly to the upper atmosphere, it should be trapped and reused.

One of many pioneers in making use of methane emission and trapping was the Linköping University in Sweden. Their research was principally focused on the quantification of methane oxidation and its recovery applying a time Correlation Tracer System with Fourier Transform Infrared (absorption spectroscopy) as a detection instrument in combination with nitrous oxide ($N_2O$) as a tracer gas. Their studies were carried out in open and closed landfills, confirming that closed landfills had a higher percentage of oxidized methane than open fields, reporting a gas recovery between the 14-65% according to it lead to the U.S environmental Protection Agency to create a sector called AgStar [20], the one that implements the use of methane system recovery from livestock waste creating a cost-effective source of renewable energy. The beginning of this research began trying to reduce methane from landfills, but besides doing it, methane capture for its reuse was also achieved. The advantage of applying this technology in large scale will be in certain way sustainable. The unique inconvenient for popularizing this, is the high cost of the absorption instrument employed for methane detection.

Nevertheless, the prior technology is not the only one available for the reuse of methane. Another possibility is applying sorption modeling for coalbed methane production and carbon dioxide sequestration [21]. This works by the pumping of $H_2O$ into the coal seams, and this will produce the recovery of coalbed methane. This last is a form of natural gas which has become a good source of energy. This is an important proposal due to the high emission during mining activities[22]. Despite of the great performance reported, the large scale implementation of this technique seems to be non-significant. The reason for this is due to the adsorption capacity decrease as the moisture in the medium increases, reducing the pore sizes of the coal by the water absorption

Another possibility for methane recovery could be using ionic liquids. The creation of composites, especially with camphor sulfonate ion derivatives and a polyaniline, will enhance the methane detection and lead to the absorption of its molecules [23]. The advantage of this technology is that it could be scaled to a greater magnitude because absorption is done in the range of 25-65 degrees Celsius.

However, production of energy is not the sole driver for attributing importance to methane. Methane can function as raw material for the production of new materials. For example the methane decomposition by catalyst like cobalt supported with aluminum, magnesium, silicon and titanium induce the formation of carbon nanofibers and nanotubes. These two last components have been of great relevance because they are nanoscale carbon materials which have a wide application field such as hydrogen storage, chemical sensor, catalytic supports and field emission display features. This is possible because of their magnetic, electronic, chemical and mechanical properties provided by their nanoscale structures [24].

One more application for methane usage is the creation of permanent porous materials with high methane volumetric storage capacity known as metal-organic frameworks [25]. This kind of material can solve the problem for future hydrogen fuel vehicles by substituting them. The main reason for this is because hydrogen as a fuel is highly flammable and its storage is not easy as compared to normal fossil fuel derivatives.

## CONCLUSIONS

As it has been reviewed, technologies for trapping and reusing methane have been enhanced with the years and it is expected that in a close future these technological and scientific advances could be exploited as much as possible and enhance methane recycling. As the last examples presented, it is expected that those technologies get even more developed for a large scale application, and methane can be use as feedstock for other products and applications rather than only energy as the unique product. The applications presented in this paper review are not the only ones as there exist more cost-effective opportunities for the reduction of methane emissions. However, in order to efficiently use the applications developed in the laboratory on an industrial scale, more research still needs to be done.

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# On Selectivity and Stability: Can Metal Organic Framework be a Green Industrial Catalyst?

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*KEYWORDS : MOFs, ZIFs, Industrial catalysis*

**ABSTRACT:** There is much focus on improving zeolite's selectivity and stability for greener catalysis in industry. Metal Organic Frameworks (MOFs), as another class of porous material, can be readily tuned for their selectivity due to ease of functionalization. However, their thermal and chemical stability may not high enough. A new type of MOF, called Zeolitic Imidazolate Framework (ZIF), is meeting this challenge of stability, while still capable of easy modification for higher selectivity and even stability. Thus, the ZIF may be a better candidate for the development of greener catalysts that drive down the environmental impact from the chemical industries.

In discussions of porous materials used in industry, a controversial issue is whether Metal Organic Frameworks (MOFs) are better candidates than zeolites for the development of green industrial catalyst. While some argue that MOFs can be more selective for absorbing or even converting waste and hazardous chemicals[1], others contend that MOFs lack the stability for recovery and reusability[2]. These two positions seem to be irreconcilable. However, a closer examination of the field allows us to see that a class of MOF, called Zeolitic Imidazolate Framework (ZIF), can not only be modified easily for increased selectivity, but also stability. These properties will allow chemical industries to further lower their processes' environmental impacts.

Despite the success of zeolites as industrial catalyst, there remains a push towards greater selectivity and stability. Zeolites are framework materials made of silica and aluminum (See Fig. 1). Their porosity, structural robustness, and catalytic activity make them suitable for industrial catalysis. 9 out of 10 industrial chemical processes utilize heterogeneous catalysts[3]. While this global market is estimated to be between 15-20 billions USD per year, 35% of it constitutes zeolite based or supported metal catalyst[4]. Due to their structural stability as solid acidic catalysts, zeolites have been used by the refining and petrochemical industry to reduce waste product, replace hazardous acid catalysts, and prevent plant corrosion[5]. On the other hand, due to their selectivity, they are being used to absorb more specific waste compounds[6], or used as catalyst for synthesis of fine chemicals[5]. Compared to the homogeneous catalysts that are more widely employed in the fine chemical industries, heterogeneous catalysts like zeolite could yield significant lower amount of waste from washwater stream, salts, and heavy metal[6]. Selectivity and stability of a catalyst seem to be the key that allows industries to lessen their processes' environmental impacts.

Unfortunately, only a relatively small fraction of new zeolites has been discovered, compared to millions of zeolite structures that have been postulated. This, Yaghi *et. al.* argue, is due to a lack of general synthetic method for zeolites.[1] MOFs could be functionalized more easily. This has yielded porous materials that have greater selectivity towards certain molecules[7].

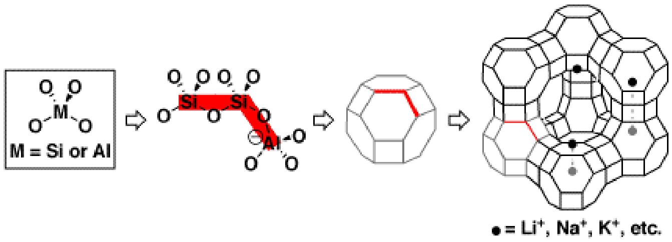

**Figure 1**. From Silica and Aluminum to the Zeolite Framework. (Figure from Professor T. Poon's research website[8].)

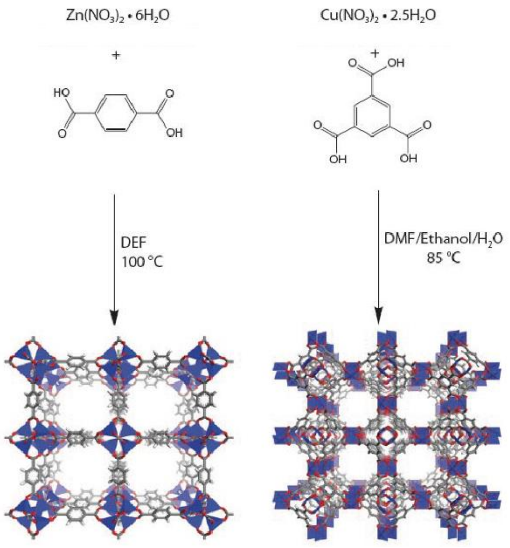

**Figure 2**. From Hydrated Metal Salts and Organic Linkers to Metal Organic Framework (Figure adapted from Sigma Aldrich[9])

Researchers in the field have demonstrated that pore size and functionalities of MOFs could be engineered easily for selectivity. MOFs, like zeolites, are porous framework material, but they are constructed from metal and organic "linkers" (See Fig. 2). 1) Prior to the synthesis of MOF, one can choose from many different organic linkers, metals, and solvent conditions to build a porous material of desired topology and property. Specifically, by changing the size and the chemical functionalities of the organic linkers, researchers could vary structure and property of the resulting pore cavity[1]. 2) Such modification is not always possible, Cohen argues, as it is restricted by the synthetic conditions for MOFs (e.g., long hours of heating at 100°C or solvent incompatibility)[10]. A second strategy addresses this challenge by allowing the addition of chemical functionalities *after* crystal formation, termed Post Synthetic Modification (PSM)[10]. PSM also makes purification easier because the crystal and the chemical solution are in a different phase[10]. 3) In response to the very same challenge, the group of Yaghi developed a high throughput synthesis method, allowing the thousands of combination with different solvent, linkers, and metals to be tested simultaneously and quickly[11]. MOFs with a wide range of pore size and functionalities were subsequently generated, some of which could be scaled up into gram quantities. With these three strategies, researchers can easily give their MOFs different topology, functionalities, and pore sizes, which are relevant to engineering a material's selectivity towards specific molecules.

Published in *Science*[12], Long and co-worker's work showed that the topology of MOFs have a direct impact on their selectivity towards isomers of hexane. Their newly identified framework, $Fe_2(BDP)_3$, is capable of separating linear hexane from its branched isomers, a process that is implicated in the production of high-quality gasoline (BDP = 1,4-benzenedipyrazolate). The sharply angled pore walls that are also very flat are not encountered in zeolites. (See Fig. 3) The researchers reasoned that the sharp crevices between the wall of pores can retain linear hexane chain more readily, thus allowing its branched isomers to flow through. Such a feature is not encountered in zeolites probably because the metal node in a MOF has a higher coordination number, allowing greater structural diversity; whereas, those in zeolites do not (Fe of MOF vs. Si of Zeolite). MOFs have a greater selection of metal nodes than zeolites, making MOFs' topology more tunable for selectivity.

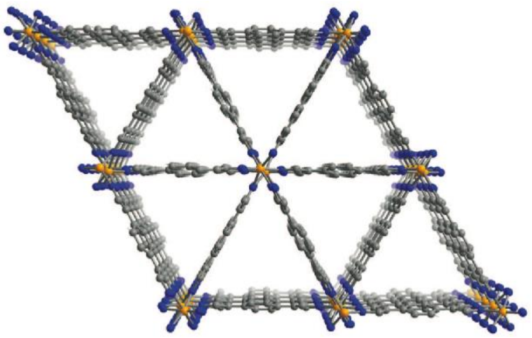

**Figure 3**. The Sharply Angled and Flat Pore Walls of $Fe_2(BDP)_3$ Framework (Figure adapted with permission from AAAS[12]).

On the other hand, Yaghi *et. al.* showed that MOFs with the same topology, but varied sizes and functionalities of pore cavity, also exhibit different level of selectivity[13]. Their MOFs take up $CO_2$ in levels of selectivity that corresponds to the dipole moment strength of their organic linker's substituents: –Cl, -CN, -Me, -Br, to $-NO_2$ (See Fig 4.). $-NO_2$ is the most selective, then -CN, -Br, -Cl, then -$C_6H_6$, -Me, and finally -H. The chemical functionalities of the linkers could be used to rationally tune MOFs' selectivity towards a molecule.

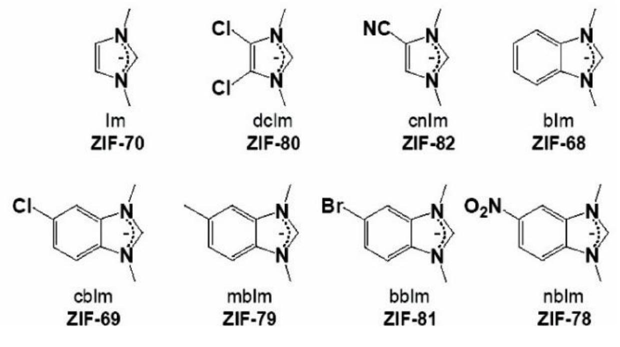

**Figure 4**. Substituents on the Imidazolate Organic Linker for Selective Absorption of $CO_2$ (Figure adapted with permission from Ref. 11. Copyright (2009) American Chemical Society.)

Despite such control over selectivity, some researchers argue that MOFs are not suitable for industrial catalysts due to their low thermal and chemical stability. Zeolites used in petroleum cracking, for example, often experience harsh conditions: a temperature of around 450 to 750°C, and a pressure at 70 atm[14]. They are widely used not just because of their catalytic properties but also their structural robustness. For the most commonly studied MOF (MOF-5), the highest temperature it can tolerate in $N_2$ is 300°C[15]. Efforts have been made to increase this limit, but it still falls way below zeolites' over 1000°C of tolerance[16]. Furthermore, MOFs may not be able to withstand impurities from flue or synthesis gas present in an industrial process. For example, it may be hard to scrub off strong acids like $SO_4$ if the MOF's structural integrity tolerates it at all[2]. Humidity poses yet another challenge to the structure for carbon dioxide capture or conversion[2]. MOFs can be easily functionalized, but if the structures are not robust enough to endure harsh conditions, it will unlikely be practical for industrial purposes.

Notwithstanding, a recent class of MOF, called Zeolitic Imidazolate Framework (ZIF), was shown to have increased thermal and chemical stability relative to its MOF predecessors. As a mimic of zeolite, which composed mainly of silica, a ZIF is composed of transition metal ions and imidazolate links. (See Fig. 5). Using thermal gravimetric analysis, Yaghi and co-worker found a type of ZIF (ZIF-8) that could withstand thermal heat in $N_2$ gas up to 550°C[17]—a 250°C increase from 300°C of MOF-5. They also tested ZIF-8 in boiling water and in organic solvents that are typical of an industrial process—benzene or methanol—for 7 days; ZIF-8 maintained its structural integrity as indicated by powder x-ray diffraction pattern. As a relatively new class of MOFs, ZIFs have the potential to reach even higher thermal and chemical stability for industrial catalytic purposes.

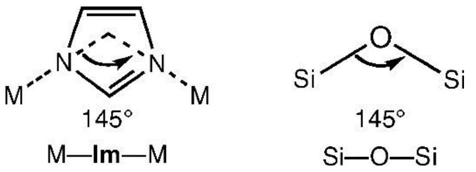

**Figure 5**. Zeolite-type Tetrahedral Topology Resulted from 145° between metals in ZIF (Left) or the Si in zeolites (Right). (Figure adapted with permission from Ref. 15. Copyright (2010) American Chemical Society.)

ZIFs can in fact be generated by high throughput method developed in Yaghi's lab[11]. Through this method, ZIFs' functionality and stability can be optimized simultaneously. In particular, Banerjee et. al. demonstrated that they could put two different linkers together into a single crystal (heterolinker) with one phase instead of multiple phases (i.e., each cavity has the same composition of two different linkers and not a distribution of cavities with different compositions.) The heterolinkers give rise to additional functional complexity, so that some of the structures exhibit higher selectivity towards $CO_2$ over CO. They are stable up to 390°C and in boiling benzene, methanol, and water for 7 days. High throughput method provides a fast way to generate ZIFs that have both higher stability and higher selectivity towards specific molecules.

Recent development on ZIF's stability towards humidity[18] further suggests that functionality can be used to improve stability. In industrial $CO_2$ capture, humidity can influence the performance of an adsorbent. By using hydrophobic linkers (-Br, -Cl, -Me on imidazole), the researchers developed a ZIF that is capable of taking up the same moderate amount of $CO_2$ in humid or dry conditions. The ZIF can tolerate heat up to 450°C and boiling water for up to 7 days. One plausible explanation is that hydrophobic cavities created by the substituent repels water molecules from entering and subsequently damaging the structure through hydrolysis. This protects the integrity of the functionalities that serve to capture CO2. Indeed, not only can the functionalities be tuned to have selective capturing, but also have higher stability towards undesirable conditions.

To summarize, we saw that although the metals and the linkers give MOFs higher selectivity by taking on different topology and functionality, their practical industrial application will rely on their thermal and chemical stability. Recent efforts in mimicking zeolites have resulted in a new class of MOF, namely ZIFs, that addresses these challenges through their improved stability in harsh conditions. High throughput method can be used to quickly generate ZIF of increased stability but also increased selectivity by introducing more than one linker. Further, the functionality that the linkers bear can be designed such that it further protects the structure from adverse conditions. ZIFs' selectivity and stability can be easily modified. Although all the examples of MOFs drawn here are limited to *capturing* chemicals and not to *catalyzing* reactions per se, MOFs have been shown to exhibit a wide range of catalytic activity[19]. In this regard, researchers have used post-synthetic modifications to generate ZIF that has catalytic activity and retained thermal stability[20].

Selectivity and stability allow industries to significantly cut down on the use of hazardous chemicals and production of waste[5-6]. The findings in this paper have important consequences for the green application of MOFs in industry. In particular, ZIF could be an ideal candidate for the future development of industrial catalysts, whose stability and selectivity could be engineered to significantly drive down the environmental impacts that industrial chemical processes make.

## ACKNOWLEDGMENT

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## ABBREVIATIONS

MOF, metal organic framework; ZIF, zeolitic imidazolate framework; PSM, post synthetic modification.

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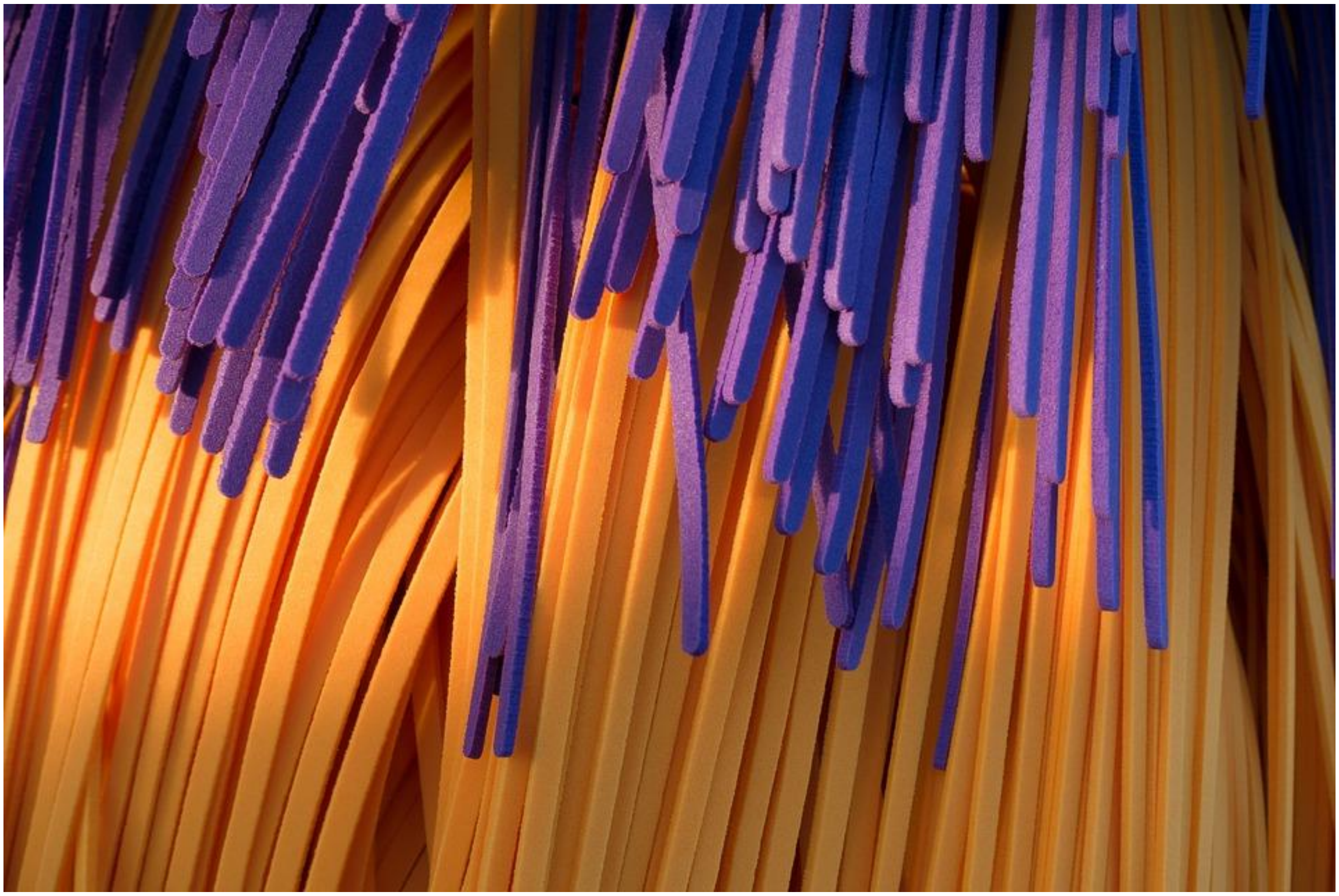

# Synthesis of Polyurethane Using Castor Oil Based and Kraft Lignin Based Polyols: A Review

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*KEYWORDS : Polyols; Castor Oil; Kraft Lignin; Polyurethane;*

**ABSTRACT:** There is an increasing demand for renewable, sustainable and environmentally friendly materials to make polyols instead of petroleum based material. The aim of this review is focused on chemical and non-chemical methods to make bio-based polyol, which are used in the synthesis of polyurethane products. Castor oil based and kraft lignin based methods are both shown to have comparable or even better effects on the properties of the polyurethane compared to the conventional petroleum based polyurethane. The kraft lignin based method is concluded to be a more suitable alternative to our conventional petroleum based method.

## 1. INTRODUCTION

Polyurethane (PU) is an important class of polymer that has a variety of applications, such as in coatings, adhesives, elastomers, foams, and fibers [1]. Polyurethanes are made by reacting polyols with polyisocyanates, and its structure and properties can be varied by using appropriate polyols [2]. Today, most of the polyols used in the manufacture of polyurethanes are derived from the petroleum industry [3,4]. However, petroleum is non renewable, has an increasing trend in cost, and its industrial processes raise environmental concerns due to greenhouse gas emission. Thus, materials that are renewable and environmentally friendly are required for future sustainability. The use of vegetable oil and natural lignin derived from woods are the "green" alternative options. Vegetable oil is an interesting option due to its ready availability, inherent sustainability, bio-degradability and low cost [2,5]. Lignin is one of the most abundant aromatic substances on Earth [6,7], and it is derived from wood during pulp and paper making processes [8]. Lignin is also attractive due to its low cost, sustainability and ready availability.

The aim of this manuscript is to describe the use of castor oil and kraft lignin in the synthesis of polyols and the overall properties of polyurethanes made from castor-oil based and kraft lignin based polyols.

## 2. CASTOR OIL

Castor oil by nature contains at least 80% of ricinoleic acid [9]. Ricinoleic acid is an unsaturated fatty acid formed with 18 carbons and it contains a hydroxyl functional group at 12th carbon, which can react with polyisocyanate to form polyurethane [9]. The average number of hydroxyl group per castor oil triglyceride is about 2.7 (figure 1) [5].

### 2.1 Synthesis of castor oil-based polyols

The triglyceride of castor oil already contains hydroxyl group which can act as reactive site for polycyanate, but the hydroxyl number is relatively low (157 mg KOH g$^{-1}$) compared to the commercial polyols (392 mg KOH g$^{-1}$) [3,5]. This results in a soft polyurethane due to low cross-linking density [5]. Hydroxyl number is the weight of KOH (mg) that will neutralize the acetic anhydride capable of reacting by acetylation with 1 g of polyol [8]. It is calculated by multiplying total hydroxyl value in the polyol by the molecular weight of KOH [8]. In order to overcome the low hydroxyl number of castor oil, different approaches have been made.

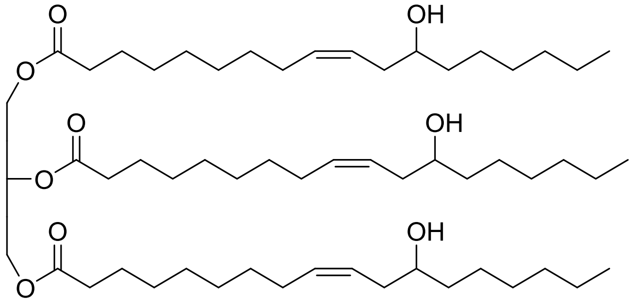
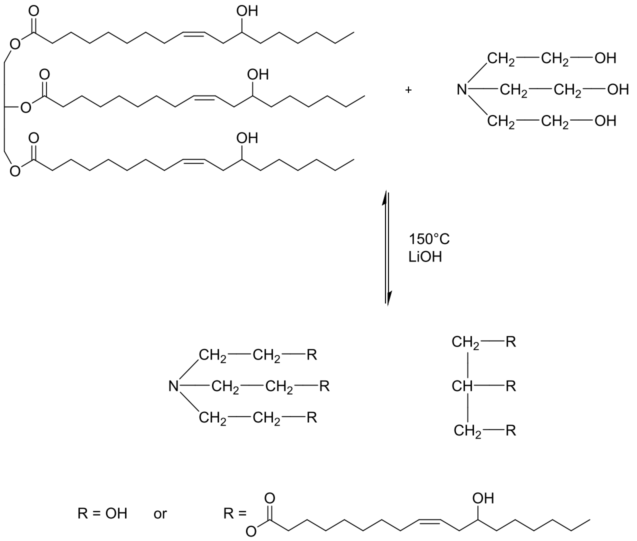


**Figure 1. Structure of triglyceride in castor oil**

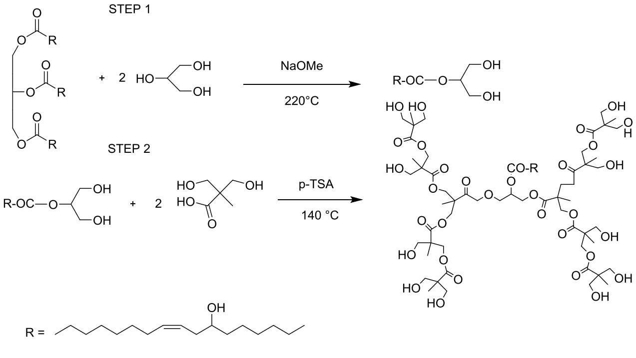
Mosiewicki *et al.* [3] used the alcoholysis reaction to increase the number of hydroxyl group in castor oil. The alcoholysis was performed by reacting castor oil with triethanolamine in the presence of lithium hydroxide as catalyst at 150 °C. The chemical reaction is presented in the scheme 1. After the reaction, the hydroxyl number of the polyol was determined to be 449 mg KOH g$^{-1}$ with a viscosity of 670 cP, compared to the commercial polyol, 392 mg KOH g$^{-1}$ with a viscosity of 12500 cP. When polyurethane foam was made using each of these polyols, the castor oil based foam had thermal conductivity, thermal stability and mechanical properties comparable or even better than the commercial polyol based foam. With addition of filler (wood flour in the experiment) in the foam, castor oil based foam had increased thermal stability, but decreased mechanical properties and increased thermal conductivity, which are important components in polyurethane foam. Thus slight improvements are required for such drawback, but it is still a good alternative to replace petroleum-based polyols.

**Scheme 1. Synthesis of polyol from castor oil using alcoholysis**



Teramoto *et al.* [10] used glycerol, which is a 10% byproduct of biodiesel production from vegetable oil [11], as a mixture with castor oil to overcome the disadvantage of low hydroxyl number when using castor oil alone. No polyol was synthesized in their study, but rather the castor oil was directly used with glycerol at differing ratio of castor oil/glycerol. The mixture of castor oil/glycerol was reacted with a dissocyanate compound, PEA-TDI, to yield polyurethane elastomers, and its bio-degradability increased with an increase of castor oil/glycerol ratio. However, even with the use of glycerol, direct use of castor oil is limited to the production of elastomer and other products having very weak intermolecular forces due to the intrinsic property of castor oil having a poor hydroxyl number within its structure.

De *et al.* [12] synthesized hyperbranched polyester polyol (HBPP) from castor oil by a two step method. The first step was the alcoholysis reaction between castor oil and glycerol using sodium hydroxide as catalyst at 220 °C to form monoglyceride of castor oil. In the second step, the monoglyceride of castor oil was undergoes esterification reaction with 2,2-bis(hydroxylmethyl)propionic acid using p-toluene sulfonic acid (p-TSA) as catalyst at 140 °C. The chemical reaction is presented in the scheme 2.



**Scheme 2. Synthesis of HBPP from castor oil**

The hydroxyl number of the synthesized HBPP was determined to be 420 ± 8 mg KOH g$^{-1}$. Instead of synthesizing a polyurethane, De *et al.* synthesized a hyperbranched epoxy from HBPP. The synthesized epoxy had an outstanding toughness, flexibility, elasticity, with acceptable biodegradability and thermostability. Even though hyperbranched epoxy and polyurethane are different polymers, HBPP could possibly contribute to the mechanical properties and thermostability of polyurethane, thus using HBPP for polyurethane synthesis could be an interesting study.

Zhang *et al.* [13] synthesized castor oil based flame-retardant polyol (COFPL) in a three step process. First step was the glycerolysis reaction between castor oil and glycerol using sodium methoxide and triethanolamine as catalysts at 180°C, producing castor oil monoglycerides and diglycerides. In the second step, castor oil monoglycerides and diglycerides were epoxidized using formic acid, phosphoric acid and hydrogen peroxide. In the third step, the epoxidized products were mixed with toluene, diethyl phosphate and triphenylphosphine, producing COFPL with 3% in phosphorus content.

The synthesized polyurethane foam from COFPL showed extremely high degree of crosslinking density, highlighting the good mechanical property. The Limiting oxygen index test (LOI), which is a test to measure the fire resistance of a material, indicated LOI value increase to 24.3% compared to normal polyurethane foam, thus COFPL based polyurethane had excellent fire resistance.

Zhang *et al.* [2] synthesized soy-castor oil based polyol from epoxidized soybean oil and castor oil fatty acid. The castor oil was saponified into fatty acid by heating with sodium hydroxide solution, and the resulting fatty acid was mixed with epoxidized soybean oil to form the polyols. At the ratio of 1: 2 for castor oil and epoxidized soybean oil, the polyurethane film showed higher thermal and mechanical properties compared to castor oil based polyol and methoxylated soybean oil based polyol. Only vegetable oils are used as raw materials in the absence of catalysts and solvents to synthesize the polyol, making this method a green process.

## 3. KRAFT LIGNIN

Lignin is an amorphous polymer derived from *p*-coumaryl alcohol, coniferyl alcohol, and/or sinapyl alcohol [14]. the three structures are shown in figure 2.

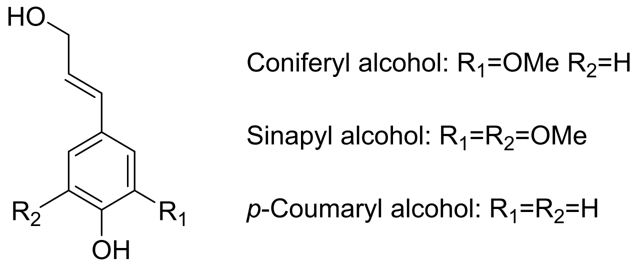
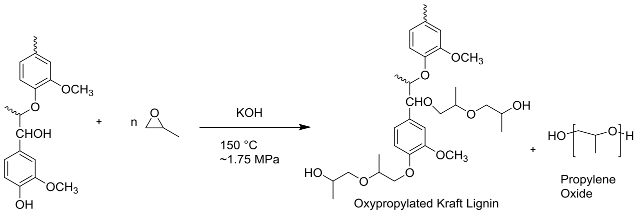


**Figure 2. Three building blocks of lignin**

Lignin contains a large number of aliphatic and phenolic hydroxyl groups, which offers good reactive sites for polyisocyanates [1]. The main source of lignin nowadays is from the kraft pulping process, and its byproduct, the black liquor, contains 30-34% of lignin[7]. About 55 million metric tons of lignin are produced each year in the form of black liquor [6].

3.1 The use of kraft lignin for polyols

Li *et al.* [1], made a liquid polyol by oxypropylation reaction from kraft pine lignin. The purchased kraft lignin was dried, and mixed with propylene oxide and potassium hydroxide under heating. The reaction is described in scheme 3.



**Scheme 3. Kraft lignin oxypropylation reaction**

The reaction produced oxypropylated kraft lignin, which is a chain extension of kraft lignin, and propylene oxide oligomers, which is an important co-polyol that decreases viscosity and glass transition temperature of lignin polyol. The synthesized kraft lignin polyol had a hydroxyl value of 387 mg KOH $g^{-1}$. When the following polyol was reacted to form a polyurethane foam, the foam exhibited good mechanical properties due to the high crosslinking of the polyol. This method did not require adding extra polyol such as glycerol, and the oxypropylated lignin polyol could solely be used for polyurethane foam with better mechanical properties than commercial polyurethane foam.

Mahmood *et al.* [15] produced kraft lignin based polyol via direct alkaline hydrolysis. The lignin was reacted with distilled water using sodium hydroxide as a sole catalyst at a temperature increasing up to 350°C, without any organic solvent and capping agent. The resulting kraft lignin based polyol had aliphatic-hydroxyl number in the range of 236-352 mg KOH $g^{-1}$, which is a suitable value for synthesis of polyurethane foam.

It is important to note that in general, the aromatic hydroxyl group has higher reactivity than the aliphatic hydroxyl group, and because of this property, kraft lignin is more readily used as a filler rather than a polyol precursor [16]. The kraft lignin has both aromatic and aliphatic hydroxyl group within its structure, thus it is favourable to use it directly without making any chemical modification to form a polyol.

Chahar *et al.*[17] used kraft lignin from black liquor that is similar to the one produced by paper industry and combined it with a polyol, poly(ethyleneglycol), of different molecular weight ranging from 300 to 4000. The mixture was directly used without chemical modification of kraft lignin, since it could already act as a polyol. The mixture was reacted with 2,4-diisocyanate using stannous octoate as a catalyst to synthesize a polyurethane coating. Higher concentration of polyethylene glycol contributed to the softness and stickiness, while the increase in lignin concentration contributed to the brittleness and poor adhesion property. However, controlling the amount of lignin and polyol resulted in better adhesion and shear strength properties, and the increased thermal stability of the coating was observed with the increase of lignin use.

Similarly, Hatakeyama *et al.* [18] studied the effect of the ratio of kraft lignin and poly(ethyleneglycol) polyol on the mechanical and thermal properties of the synthesized polyurethane foam. The results showed increased rigidity with the increase of lignin due to high crosslinking between hydroxyl and polyisocyanate groups. In terms of thermal stability, the use of kraft lignin increased the glass transition temperature of the polyurethane foam, and its value was competitive to the petroleum based foam.

Pan *et al.*[19] studied the effect of replacing polyether polyol by the kraft lignin. Polyether-modified polysiloxane was used as a surfactant, and Tin(II)-isooctoate was used as a catalyst. The reagents were used with a blowing agent and reacted with methyl diphenyl diisocyanate to form polyurethane foam. The polyether triol was replaced with kraft lignin up to 28% (w/w), and the foam had good structure and mechanical properties at 19-23% (w/w) in kraft lignin content.

## 4. SUMMARY AND DISCUSSION

It has been shown that the castor oil-based polyol and kraft lignin-based polyol are good alternatives for replacement of petroleum-based polyol in the synthesis of polyurethane products. In general, when the castor oil-based polyol and kraft lignin-based polyol are synthesized into polyurethane, both show a competitive or even better performance in terms of mechanical and thermal properties. In some cases, more studies and improvements are needed to overcome some drawbacks.

Using unreacted castor oil as a sole reagent for synthesis of polyurethane is not a preferred pathway, since it does not contain enough hydroxyl group that offers reactive site for isocyanate. Thus the synthesis of castor oil into polyols is highly favored to increase its hydroxyl number. Castor oil based polyol can be made from the alcoholysis and glycolysis reactions, and the synthesis can be done under solvent free conditions using a catalyst. For more complex polyol such as COFPL by Zhang *et al*, the synthesis may require more uses of solvents and additional catalysts. The renewability, bio-degradability and sustainability of the starting material make castor oil based polyol a viable alternative for polyol and polyurethane industry.

Kraft lignin can be chemically modified to yield a lignin based polyol, or it can be directly used as a sole reagent and mixed with the existing commercially used petroleum based polyol to synthesize polyurethane products. Oxypropylation and alkaline hydrolysis are main synthetic pathways known from the literature to derive polyols from kraft lignin. Both methods involve a simple catalyst, and uses no organic solvents or capping agent. The kraft lignin contains both aromatic and aliphatic hydroxyl groups which can act as reactive sites for isocyanate, thus recent studies incorporated commercial polyols such as poly(ethylene glycol) and polyether triol with kraft lignin to synthesize polyurethane products. With the kraft lignin method, a portion of petroleum based polyol can be directly replaced by kraft lignin without undergoing a chemical modification.

One major drawback for both methods is that the chemical reactions do not occur at a mild condition and require controlled temperature and pressure.

Helling *et al.* [20] conducted a life cycle assessment (LCA) for the production of polyol using castor oil, soybean oil and petrochemical. It was found that if each polyol is made using the same polymerizing initiator, propylene oxide (PO), the castor oil and soybean oil would use 33% to 64% of the fossil resources compared to the petrochemical based polyol. The oil based polyol also generates -13%( sequestration) to 46% greenhouse gas emission compared to the petrochemical based polyol.

Bernier *et al.* [21] also conducted a life cycle assessment of kraft lignin for polymer applications. The environmental impact of kraft lignin is directly related to the kraft pulping process, since 130 million tonnes of kraft pulp corresponds to total release of 55 million tonnes of kraft lignin [6]. Optimizing the use of $CO_2$, $H_2SO_4$ and NaOH in the kraft pulping process could further minimized the environmental impacts of kraft lignin. The lignin can originate from different pulping processes such as kraft, sulfite, soda or organosolv and from different feedstock such as hardwood, softwood and straw, thus the property of the synthesized polyol and its environmental impacts can vary from one type to another. The life cycle environmental impacts of many types of lignin are still undocumented.

It is difficult to choose which method between castor-oil based or kraft lignin based is better in terms of physical and thermal properties of the synthesized polyurethane, since both methods are determined to have a competitive performance to the petroleum-based polyurethane. Also, both methods for the synthesis of polyol are designed to use least or no amount of solvents and use a simple catalyst.

However, looking at how both materials are derived and their ready applicability into the synthesis of polyurethane foam, the kraft lignin seem to be more a attractive option than castor oil.

Kraft lignin is extracted from the industrial waste (black liquor) that is produced during the kraft pulping process. Black liquor contains about 30-34% of lignin [7], and it is used as burning fuel, but it is not cleaner than a natural gas [21] in terms of atmospheric emission. Thus, using the black liquor as a lignin source is an efficient way to treat and use this industrial waste. On the other hand, castor oil is derived from the raw material, castor plants. Considering factors such as tractor fuel, pump power and fertilizer required for farming, the cost for making castor oil may be more expensive than kraft lignin.

The extracted kraft lignin can be modified into liquid polyol, but due to its rich hydroxyl property it can also be used directly in the synthesis polyurethane products and replace a portion of the commercial petroleum based polyols. Castor oil, as mentioned previously, does not contain high value of hydroxyl group to react with isocyanate, and it is a weak reagent to be used directly in the synthesis of polyurethane without undergoing chemical modification. In most cases, castor oil has to be converted into a liquid polyol to produce different variety of polyurethane products that are comparable to the petroleum based polyurethane.

Being able to use a material without undergoing a chemical reaction is a great advantage. In the methods seen for castor oil in the previous section, the alcoholysis and glycolysis involve reaction at a temperature up to 220 °C. Also for kraft lignin, the oxypropylation and hydrolysis reaction requires controlled temperature and pressure for the reactions to occur. These reactions do not occur at a mild condition, thus they require an energy input, which is a drawback for both methods in terms of energy cost. However, compared to the petroleum based polyol synthesis, which requires multiple steps such as dehydrogenation, steam cracking and fluid catalytic cracking for making the compounds necessary for the reaction[22], castor-oil and kraft lignin based polyol synthesis are much simpler, less expensive, and the reaction processes are environmentally benign in terms of greenhouse gas emission.

## 5.CONCLUSION AND OUTLOOK

With the increase in demands of renewable, sustainable and environmentally friendly materials, the vegetable oil and natural lignin attracts more and more interests of researchers in the synthesis of polyols for polyurethane manufacturing. Castor oil and kraft lignin are among the green options for making polyols used in polyurethane. Different strategies involving a chemical or non chemical modification for synthesizing polyols were reviewed in this manuscript. Between the two proposed methods, kraft lignin is concluded to be a more favorable alternative than castor oil.

The castor oil based method requires to use castor as raw material, whereas the kraft lignin is extracted from the industrial waste in the pulping process, allowing for efficient waste treatment finding and use for byproducts. Also, the kraft lignin can readily be used without chemical modification and can replace a portion of petrochemical based polyol to synthesize polyurethane products.

Nevertheless, researchers are still working to discover alternatives that can replace petrochemical-based polyols for polyurethane synthesis. Vegetable oils and wood lignin will continue to be the focus of research.

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## ABBREVIATIONS

HBPP, Hyperbranched polyester polyol; COFPL, Castor oil based flame retardant polyol; LOI, Oxygen index test;

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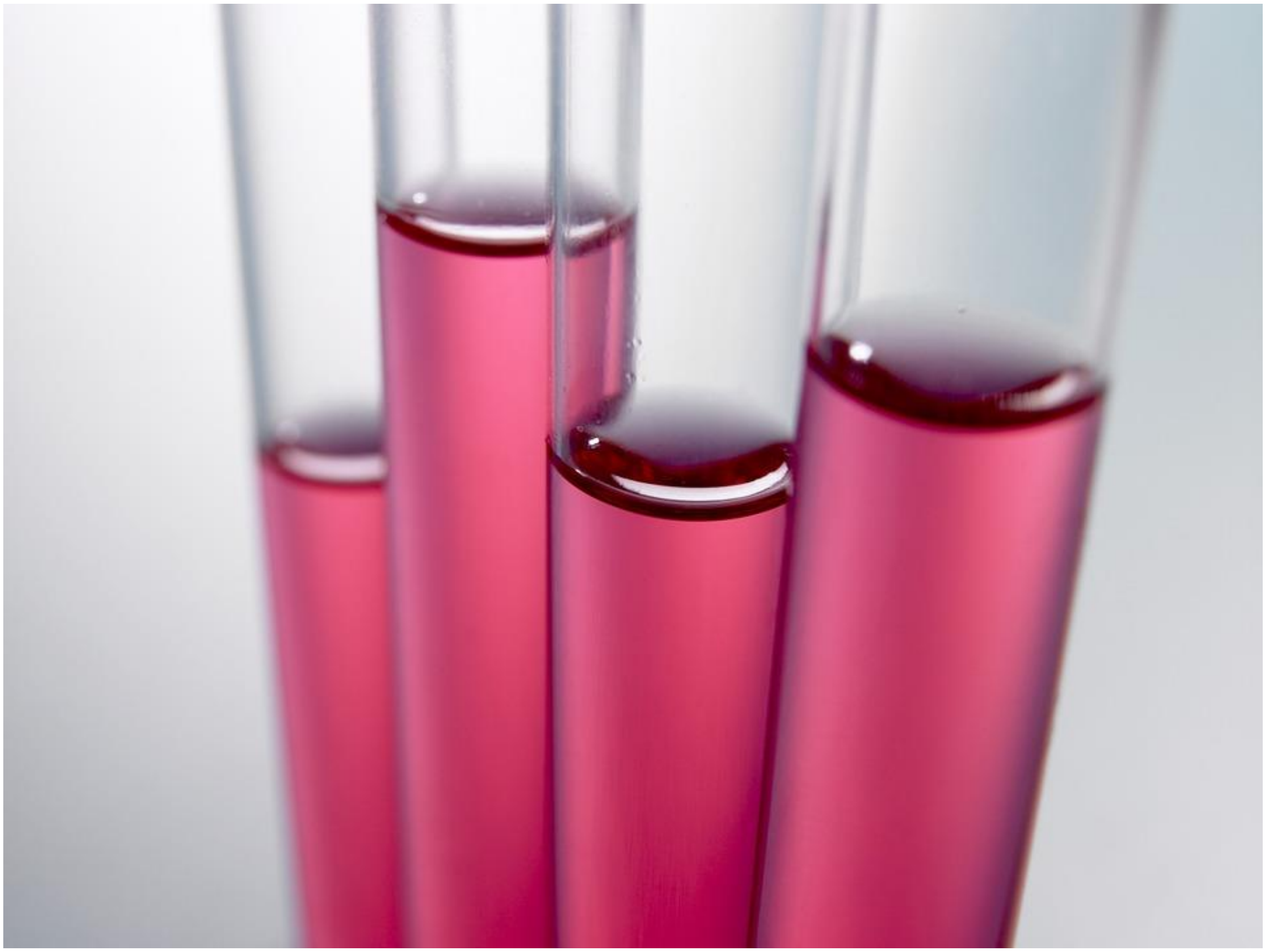

# Green Alternatives for the Synthesis of Metal Nanoparticles

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*KEYWORDS: Metal nanoparticle, green nanoscience, alternative synthesis, solution-based synthesis, biological synthesis*

**ABSTRACT:** Metal nanoparticles are major components of the nanorevolution. Synthesis of metal nanoparticles is traditionally achieved through solution-based methods, however increased concern over green chemistry has led to the development of alternative syntheses. An essential element of a greener nanoscience is to develop alternative syntheses and make them known. Such alternatives include photochemical, electrochemical, mechanochemical and biological methodologies. This review introduces these alternative methods and how they can viewed as environmentally friendly, hazardless and sustainable. A particular focus is given to solution-based and biological nanoparticle syntheses. The solution-based method offers control over the size and shape of the nanoparticles, but is not easily scalable. The biological method offers the great advantage of employing renewable feedstock, benign solvents and the possibility of making a wide range of nanoparticles. However this route has been found to be rather long and to yield polydispersed nanoparticles. Multiple successful syntheses are described and, depending on the availability of materials and equipment to the scientist, these methods can lead to a more environmentally friendly synthesis of metal nanoparticles.

As the nanorevolution grows with ever increasing funding, concerns have been voiced over the employment of novel nanomaterials with regards to human safety and the environment[1]. With the wide range of promising applications that could use nanomaterials, much research should also go towards making nanotechnology environmentally friendly and hazardless. One such solution would be the application of a green nanoscience to ameliorate current processes by eliminating waste and hazardous materials all through a nanomaterial's life cycle[1]. Green nanoscience, like green chemistry, attempts to reduce or eliminate hazards to human health and the environment through product design and process optimization of nanomaterials[1]. Green nanoscience conforms to the 12 principles of green chemistry postulated by Paul Anastas[1,2,3]. Making nanoscience greener through green chemistry is a major concern for the future application of nanotechnology. Hutchison[1] described three ways in which research should be approached for a greener nanoscience:

1. Develop safer alternative materials
2. Identify the design rules for new nanomaterials
3. Reduce the hazards and increase the efficiency of nanomaterials production

Metal nanoparticles are of considerable interest because of their numerous physical, optical, electrical and catalytic properties (Figure 1)[4]. The physical properties of these nanoparticles leads to different applications, for example the catalytic performance of gold nanoparticles (AuNPs) is highly influenced by their size and shape[5,6]. Thus a size and shape controllable synthesis of nanoparticles is of great utility for their specific application. Nanoparticles are usually synthesised with four ingredients: the metal salt, a solvent, a reducing agent and a protecting agent. Many methods are commonly used, mainly the solution-based methods[4,57-21] that use water as a solvent, various reducing and protecting agents and heat. The Turkevich method[7,8], which uses sodium citrate as the reducing and protecting agent with heat, results in the spherical synthesis of 2 to 150 nm AuNPs, has been found to be one of the more popular options for nanoparticle synthesis. The success of the method for its simplicity and size and shape control is undeniable, however this method has faced challenges in large scale production[10,26,27]. In addition, the push for a greener chemistry for nanoparticle production has sparked considerable interest in cleaner synthesis methods. Photochemical[4,28,29], electrochemical[30-34], mechanochemical[35-38], biological[13,39-81] methods are already well-developed subjects of research. In addition, the use of microwave[82-88], ionic liquids[89-93], super critical fluids[94,95] and sonication[96-98] have resulted in successful nanoparticle synthesis. The ideal synthesis should be able, by simply modifying the initial conditions, yield a wide range of nanoparticle size while being monodisperse, soluble in aqueous and organic solvents, utilize benign reagents and be inexpensive. Another consideration should be the use of a chemical which can both act as a reducing and protecting agent yielding a better atom economy.

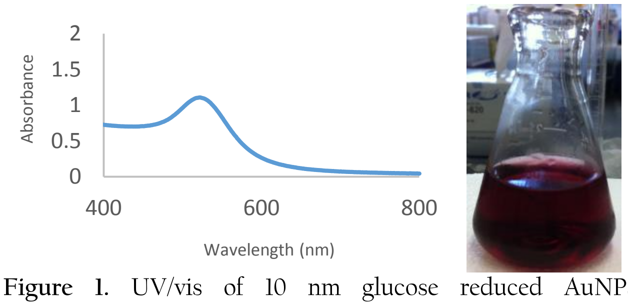
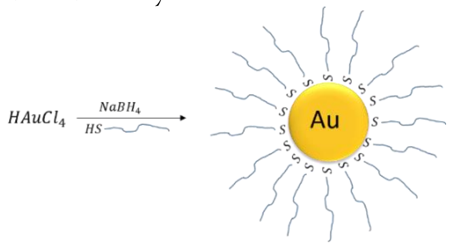


**Figure 1.** UV/vis of 10 nm glucose reduced AuNPs, demonstrating the surface plasmon resonance band

There are two main ways to synthesize metal nanoparticles: the bottom-up and top-down approaches[40,41]. The bottom up approach (self-assembly) employs small building blocks, such as molecules, and, one by one, these blocks are assembled to form larger structures. Chemical and biological methods are commonly used for this approach, which when employed to nanoparticle synthesis can led to nanoparticles with fewer defects, more homogeneous composition and a better control of size and shape[40]. In the top-down approach, a bulk material is reduced in size by means of physical or chemical interactions[40]. Methods such as lithography, etching, electro-explosion, sputtering, mechanochemical milling and laser ablation processes are currently employed[41]. However the top-down method results in numerous defects such as imperfection of the surface structure[40]. The intent of this review is to introduce the multiple alternatives by which metal nanoparticles can be synthesized, satisfying Hutchison's[1] first criterion for a greener nanoscience. This should permit the nanoscientist to take a justified decision depending on the size and shape desired as well as the availability of certain materials and equipment. A particular focus is given to biological synthesis and solution-based methods. Microwave, ionic liquids, super critical fluids and sonication will be encapsulated by solution-based methods. Photochemical, electrochemical and mechanochemical routes will briefly be discussed.

## SOLUTION-BASED METHODS:

Solution-based methods are extremely simple. A solution of metal salt is added to a reducing agent like sodium borohydride and a protecting agent like thiols. In the case of AuNPs the reducing agent reduces $Au^{III}$ to $Au^{0}$, leading to the formation of the nanoparticles[4] (Scheme 1). The Turkevich method[7,8], later improved by Frens[9], has been widely considered to be one of the most successful methods for AuNP synthesis (Figure 2). However this method has severe limitations, such as the low colloid content and the exclusivity of water as a solvent[10]. Another well know method, developed by Brust et al.[11], employs a two phase (water-toluene) reduction of $HAuCl_4$ with sodium borohydride and alkanethiols. The two phased system permits the formation of water and organic soluble colloids[10]. The downsides of this reaction are the small sized colloids, 1 to 10 nm, high polydispersity and cost, as well as the usage of a harsh reducing agent[10,11,12]. Sodium borohydride, hydrazine hydrate, *etc.* may lead to absorption of hazardous chemicals on the surface of nanoparticles which could then lead to undesired toxicity[13].



**Scheme 1: Formation of thiol protected AuNPs by $NaBH_4$ reduction**

The use of oleyamine (OLA) as a reducing and stabilising agent[10,14] has attracted some attention since OLA offers the advantage of being commercially available and inexpensive[10]. The nanoparticle size can be tuned by the amount of OLA added to the reaction mixture and it can be prepared in aqueous or organic solvents[10,14]. Another interesting synthesis involves the use of β-D glucose (dextrose) as a reducing agent[15,16]. β-D glucose has the advantage of being environmentally benign and renewable[15]. The extent of the reduction can be controlled by monitoring the temperature and the pH of the reaction[15]. The β-D glucose reduced nanoparticles can be stabilised by starch[15]. These nanoparticles could be compatible with a biological medium[15]. β-D glucose can also act as the protecting agent in the form of a negatively charged monolayer of gluconic acid[16].

Seed mediated synthesis has often been employed for the formation of nanospheres and nanorods[16,17]. In this process, a nanoparticle is synthesized and subsequently used as a seed for further growth of the particle. To do so, small nanoparticles in solution are used as the seeds. To obtain negatively charged nanoparticles, the seed solution can be added to an ethanolic solution with 4-mercaptobenzoic acid (4-MBA) at pH 8 and to obtain positively charged particles, ascorbic acid can be used with cetylmethylammonium bromide (CTAB) as the protecting agent[16]. This method permits the control of nanoparticle size and nanoparticle interactions with the surrounding medium. Roberts et al.[18] have successfully developed a seed mediated synthesis of palladium nanoparticles. They used a 3.4 nm sized seed prepared by an ascorbic acid reduction and carboxymethyl cellulose (CMC) as the protecting agent. These seeds were then placed in a solution of $Pd^{2+}$ and ascorbic acid to reduce the free ions which then accumulated on the seed. This method offers an easy control of the nanoparticle size by using non-toxic reducing and protecting agents in ascorbic acid and CMC[18].

Multiple other environmentally friendly reducing agents as well as ascorbic acid, such as amine borane complex[5], caffeine[19], tea extracts[19], heparin[20], chitosan[20], starch[21] and CMC[22] have been used in successful nanoparticle synthesis.

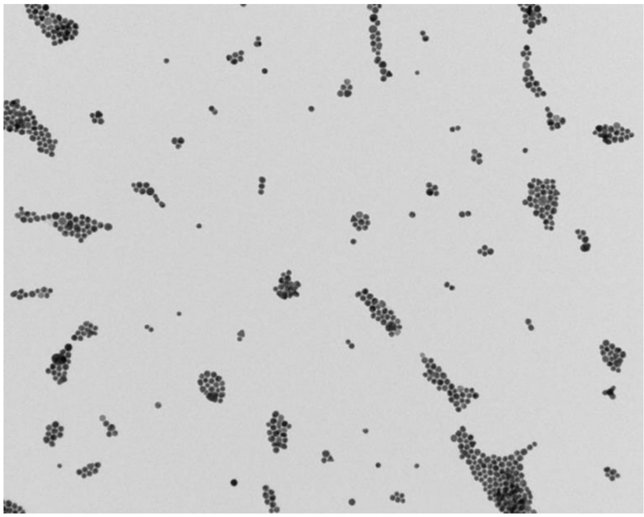


**Figure 2.** TEM image of 20 nm citrate reduced AuNPs

*MICROWAVE ASSISTED METHOD:*

The use of microwave irradiation (MW) has been actively employed for organic transformations in non-solid and solid state reactions[82-84]. Pericyclic, cyclisation, aromatic substitution and alkylation reactions are just few reactions that can easily be performed under MW irradiation[82-84]. MW offers numerous advantages such as shorter reaction completion times and homogenous heating[83]. These advantages may be extremely useful for large scale nanoparticle synthesis as the mixing and distribution of heat are critical for controlling the size distribution of the nanoparticles[26]. Large scale synthesis of silver nanoparticles (AgNPs) has been demonstrated by Yin et al.[26] by using silver nitrate, trisodium citrate and formaldehyde. This resulted in a higher yield and improved selectivity when employing MW heating as opposed to heating with convection. However the use of formaldehyde, a volatile organic compound (VOC), as a reducing agent and solvent should be avoided. A much cleaner synthesis involves ethanol as a reducing agent and polyvinylpyrrolidone (PVP) as protecting agent[85]. Ethanol, being a benign solvent, and PVP, which is non-toxic and soluble in many solvents[31], makes for a greener alternative. PVP has also been used as both the stabilising and protecting agent[31,86]. CMC, being a biomaterial applied in the food and medical industries, has also been employed simultaneously as both a protecting and a reducing agent[87]. A quite nice synthesis was performed using β-D glucose as the reducing agent and starch as the protecting agent to obtain 1 to 8 nm AgNPs using MW irradiation[15].

*IONIC LIQUIDS:*

Ionic liquids (ILs) have been perceived as an alternative solvent compared to organic solvents, due to their undetectable vapor pressure[89]. The great advantage of using ILs for nanoparticle synthesis is that they can be tuned to serve as both the reducing and protecting agent[12,83] . ILs are ionic compounds, therefore solvation and protection of metal ions is superior in ILs compared to conventional organic solvents[12]. ILs form a protective layer which provides both steric and electronic protection against agglomeration[90]. Alcohol ionic liquids (AILs) have been used due to their great reducing capabilities in the formation of AuNPs[12]. Using (HEMMor)($BF_4$), Kim et al.[12] have reported that nanoparticle size is dependent on the size of the alkyl chain; particles were smaller for longer chains. Imidazole ILs such as 1-n-butyl-3-methylimidazolium, have been shown to be efficient green catalyst for several reactions in multiphase reactions[90]. Dupont and Scholten[90] offer an extensive review of the use of ILs for nanoparticle synthesis and list a large number of syntheses in ILs.

*SUPERCRITICAL FLUIDS AND SONICATION:*

Supercritical fluids (SCFs) have been proposed as an attractive alternative for nanoparticle synthesis due to their gas-like diffusivities, continuously tunable solvent power and ease of complete elimination at the end of the process[94]. Supercritical $CO_2$ has been the most often used SCF due to its relatively low price and environmental friendliness[94]. Supercritical water ($scH_2O$) has also been used for the synthesis Ce, Fe, Al, Ti, Cu and Zn metal oxides, however the formation of metal nanoparticles is hampered by the formation of metal oxides[95]. Supercritical alcohols, such as methanol and ethanol, have thus been employed to serve as the solvent and reducing agent[95]. Cu, Ni and Ag nanoparticles have been synthesized this way[95].

Sonochemistry, employs ultrasound to create acoustic cavitation (the growth and implosive collapse of bubbles in liquid)[96]. The collapse creates intense heating which produce high temperatures and pressures for a few microseconds[96]. Multiple semiconductor nanocrystals, such as ZnS, $Sb_2S_3$, HgSe, $SnS_2$, CdS, CdSe, PbS, PbSe, PbTe and CuS[97], have been produced using ultrasound. Sonoelectrochemical methods have been used for the synthesis of AgNPs[97]. Zhu et al.[98] were able to synthesise 3 nm gold nanocrystals using ascorbic acid as the reducing agent when sonicated for 1 to 3 hours.

## PHOTOCHEMICAL SYNTHESIS:

Photochemical synthesis of metal nanoparticles is a cost effective and convenient technique that allows controlled reduction of metal ions to be carried out without using excess reducing agents, elimination of adsorbing contamination on the product during the preparation process, absorption of radiation regardless of the presence of light-absorbing solutes and uniform reduction in solution[28]. This method has also been used to synthesise nanorods[29]. UV irradiation has been used to improve the quality of AuNPs and near-IR laser irradiation has led to the enormous growth of thiol stabilized AuNPs[4].

### ELECTROCHEMICAL SYNTHESIS:

The electrochemical process developed by Reetz[30] generally involves five steps: 1) oxidative dissolution of a sacrificial metal bulk anode, 2) migration of metal ions to the cathode, 3) reductive formation of zerovalent metal atom at the cathode, 4) nucleation and growth of metal particles and 5) arresting the growth process and stabilizing the nanoparticles with protecting agents[31]. Electrochemical synthesis avoids the use of toxic reducing agents and the products can easily be isolated from the precipitate[31]. The size of the nanoparticle can easily be tuned by controlling the current density, distance between the electrodes, reaction time, temperature and solvent polarity[31]. An elegant synthesis was performed by Yin et al.[32] in which they produced AgNPs protected by PVP. PVP was found to accelerate silver particle formation and to lower silver deposition on the cathode. Another attractive possibility for using electrochemical procedures is the possibility to form nanorods with specific aspect ratios[33].

### Mechanochemical synthesis:

Conventional nanoparticle syntheses often rely on large amounts of solvents, ligands, reducing agents, auxiliaries, phase transfer agents, and purifications steps[35]. A mechanochemical procedure offers a scalable, low energy and rapid synthesis without the use of solvents and reducing agents[35]. Mechanochemical processes are characterized by the repeated welding, deformation and fracture of the reactants[36]. This has the consequence that reactions that would normally require a heat input can proceed without external heating[36]. Ultra-small AuNPs, 1 to 4 nm in size, have been made under mild mechanochemical milling through a galvanic reduction[35]. The nanoparticles can be stabilised using amine ligands, which provide control over nanoparticle size[35].

### Biological synthesis:

Bio-inspired nanoparticle synthesis has developed as a novel route for sustainable synthesis[39]. Many alternative organisms have been employed, such as yeast, virus, bacteria, fungi, plants, plant extracts and algae [13,39,40]. The use of these organisms has led to the production of low-cost, energy-efficient, and non-toxic metallic nanoparticles while using renewable feedstock, limiting waste production and using safe solvents[39,40]. Biological methods can also be complemented by the application of microwave, sonication and visible-light irradiation[13]. According to Iravani[41], three main rules should be followed for successful biological synthesis of nanoparticles.

1. Selection of the best organism: Focus should be put on the important intrinsic properties of the organism such as enzyme activity and biochemical pathways. For examples, plants that have the potential to accumulate and detoxify metals are good candidates.
2. Optimal conditions for cell growth and enzyme activity: For optimal conditions, the nutrients, inoculum size, light, temperature, pH, mixing speed and buffer strength should be adjusted for the best cell growth.

3. Optimal reaction conditions: To obtain the best nanoparticle yield, the bioreduction conditions must be optimized. The substrate concentration, the bio-catalyst concentration and the electron-donor concentration, as well as the pH, temperature, exposure time, buffer strength, mixing speed and light, must be adjusted.

### *YEAST:*

Yeast are very common eukaryotic microorganisms. They are chemoorganisms in that they use organic compounds as food and do not require sunlight to grow. Certain yeast species exhibit strong detoxification processes which lead to the formation of nanoparticles[42]. Yeast has mainly been employed in the synthesis of semiconductors[43], such as reported by Dameron et al.[42], who demonstrated that when *Candida glabrata* and *Schizosaccharomyces pombe* yeast were challenged with toxic metals they produced extracellular cadmium sulfide quantum dots. There are few examples of the use of yeast for the synthesis of metal nanoparticles, however several groups have demonstrated its feasibility[13]. Kowshik et al.[44] have performed the synthesis of 2-5 nm silver AgNPs using the silver-tolerant yeast strain MKY3. Agnihotri et al.[45] employed the yeast *Yarrowia lipolytica*, due to its biological features required for interactions with metals, to intracellular synthesis of 15 nm AuNPs.

### *VIRUS:*

Viruses are small infectious agents that can be employed as templates for nanoparticle synthesis. Tobacco mosaic virus (TMV) has often been employed as a template in light-harvesting systems[46], metamaterials (negative index of refraction)[47] and nanowires[48]. TMV has been shown to successfully direct the mineralization of PbS and CdS crystalline nanowires and the formation of Pt, Au and Ag nanoparticles[40,48,49]. However very little has been reported on the synthesis of nanoparticles from viruses.

### *BACTERIA:*

Bacteria produce inorganic materials either intra or extracellularly, in the nanoscale dimension, due to their chemical detoxification of most toxic heavy metals[43]. The detoxification results in a reduction or precipitation of the metal ion into insoluble non-toxic metal nanoclusters[43]. Intracellular production of nanoparticles poses the extra challenge of extracting the nanoparticles, for which ultrasound or detergent treatments are required[43]. Extracellular synthesis occurs when cell wall reductive enzymes or soluble enzymes secreted by the microorganism are involved in metal reduction[43]. Extracellular production has been found to be readily applicable in many different applications, such as optoelectronics, electronics, bioimaging and in sensor technology[43].

Slawson et al.[50] have demonstrated that *Pseudomas stutzeri* AG259, a bacterial strain isolated from silver mines, synthesised 35 to 46 nm AgNPs in its periplasmic space. This was a rather surprising result as silver has often been considered to be an antimicrobial agent[51, 52]. However many other groups[53-56] have found that microorganisms can effectively be used for metal nanoparticle synthesis. Bacteria such as *Morganella* sp. RP-42[53], *Lactobacillus*[54], *Brevibacterium casei*[55], *Shewanella algae*[13] and even cyanobacteria such as *Plectonema boryanum* UTEX 485[57] have been used to synthesise Ag, Au, Pt and Au/Ag nanoparticles. *Escherichia coli* DH5α[58] has also been found to mediate intracellular bioreduction of auric acid to $Au^0$ nanoparticles. *Rhodopseudomonas capsulata*[59], a photosynthetic bacterium produced extracellular AuNPs with size and shape varying according to the pH. At pH 7 10 to 20 nm spherical nanoparticles were produced while at pH 4 a mixture of 50 to 400 nm triangular nanoparticles and 10 to 50 spherical nanoparticles.

**Table 1: Biological Synthesis of Metal Nanoparticles**

| Microorganism or plant | Nanoparticle | Size (nm) | Intra or extracelluar | Reference |
|---|---|---|---|---|
| **Yeast** | | | | |
| MKY3 | Ag | 2 to 5 | Extra | 44 |
| *Yarrowia lipolytica* | Au | 15 | Intra | 45 |
| **Bacteria** | | | | |
| *Pseudomas stutzeri* AG259 | Ag | 35 to 36 | Intra | 50 |
| *Morganella* sp. RP-42 | Ag | 15 to 25 | Extra | 53 |
| *Lactobacillus* | Au | 20 to 50 | Intra | 54 |
| | Ag | 15 to 500 | Intra | 54 |
| *Brevibacterium casei* | Au | 10 to 50 | | 55 |
| | Ag | 10 to 50 | | 55 |
| *Shewanella algae* | Au | 9.6 | Intra | 13 |
| | Pt | 5 | Intra | 13 |
| *Plectonema boryanum* UTEX 485 | Ag | Up to 200 | Intra extra | 57 |
| *Escherichia coli* DH5α | Au | 17 to 33 | Intra | 58 |
| *Rhodopseudomonas capsulate* | Au | 10 to 20 (pH 7) | | 59 |
| *Thermonospora* sp | Au | 8 | Extra | 60 |
| *Klebsiella pneumonia* | Ag | 28.2 to 122 | | 56 |
| **Fungi** | | | | |
| *Verticillium* | Ag | 13 to 37 | Intra | 61 |
| *Aspergillus fumigatus* | Ag | 5 to 25 | Extra | 62 |
| *Trichoderna asperellum* | Ag | 13 to 18 | Extra | 63 |
| *Verticillium luteoalbum* | Au | <10 | Intra | 64 |
| *Colletotrichum* sp | Au | 8 to 40 | Extra | 65 |
| **Plants and plant extracts** | | | | |
| *Pelargonium graveolens* | Ag | 16 to 40 | | 66 |
| *Coffee extracts* | Ag, | 20 to 60 | | 19 |
| | Ag | 20 to 30 | | 67 |
| | Pd | 20 to 60 | | 19 |
| *Tea extracts* | Ag, | 20 to 60 | | 19 |
| | Ag | 20 to 90 | | 68 |
| | Pd | 20 to 60 | | 19 |
| | Au | 200 to 500 | | 69 |
| *Cymbopogon flexuosus* | Ag | 10 to 35 | | 70 |
| *Citrus sinensis* | Ag, Au | - | | 71 |
| *Swietenia mahogany JACQ* | Au | 14 | | 72 |
| *Hibiscus rosa sinensis* | Ag | 13 | | 72 |
| | Au | 6.5 to 17 | | 73 |
| *Anacardium occidental* | Ag | 15.5 | | 73 |
| | Pd | 2.5 to 4.5 | | 74 |
| | Ag | 4 to 30 | | 75 |
| *Ocinum sanctum* | Au | 12 to 38 | | 76 |
| *Morinda citrifolia* | Ag | 50 to 80 | | 77 |
| *Nyctanthes arbor-tristis* | | | | |
| **Algae** | | | | |
| *Spirulina platensis* | Ag | 7 to 16 | | 78 |
| | Au | 5 to 10 | | 79 |
| *Eolimna minima* | Au | 5 to 80 | | 80 |

One of the main issues with such syntheses is high polydispersity. Ahmad et al.[60] have demonstrated that *Thermonospora* sp, an extremophilic actinomycete, can yield extracellular monodispersed 8 nm AuNPs. These syntheses have been found to be rather slow, a strong barrier to industrial applications. Shahverdi et al.[56], in order to solve this problem, employed *Klebsiella pneumonia*, *Escherichia coli* and *Enterobacter cloacae*. They reported that within 5 minutes of silver ion coming in contact with the cell filtrate, AgNPs were formed employing MW irradiation. In order for bacteria to be readily implemented in large scale production, the speed and polydispersity both have to be accounted for. This lack of control makes these types of synthesis much less attractive for particular applications where the shape and size have to be controlled with high precision.

*FUNGI:*

Fungi have many advantages for metal nanoparticle synthesis compared to other microorganisms due the presence of enzymes, proteins and reducing components on the cell surface[13]. In addition, fungi are fastidious to grow, easy to handle and easy for fabrication, and the nanoparticle precipitated outside the cell is devoid of unnecessary cellular components[43]. They are taking center stage for biological nanoparticle synthesis due to their tolerance and metal bioaccumaulation capabilities[40]. *Verticillium* has been used by

Mukherjee et al.[61] for the synthesis of 25±12 nm AgNPs. Fungi such as *Aspergillus fumigatus*[62] and *Trichoderna asperellum*[63] have been used to synthesize AgNPs. *Verticillium luteoalbum*[64] produced <10nm AuNPs at pH 3 and a mix of spheres and rods at higher pH in 24h while *Colletotrichum* sp[65] produced 8 to 40 nm AuNPs.

*Plants and plant extracts:*

Plants have shown great potential in heavy metal accumulation and detoxification[13]. Numerous plants and fruits have been shown to reduce and stabilize both single and multi-metal nanoparticles in one-pot photosynthesis[13]. This method has found great use due to the rapid formation of nanoparticles compared to other bioinspired methods. Geranium leaves (*Pelargonium graveolens*) has been shown to produce 16 to 40 nm AgNPs in only 9h compared to the 24 to 124 hours required when using fungi or bacteria[40,66]. Varma et al.[19] have reported the synthesis of Ag and Pd nanoparticles at room temperature using coffee and tea extracts. For coffee extracts, Dhand et al.[67] also performed the synthesis of 20 to 30 nm AgNPs and for tea leaf extract, Sun et al.[68] also performed the synthesis of 20 to 90 nm AgNPs. This method required no usage of a capping agent, is environmentally friendly and can be extended to Au and Pt nanoparticles[19]. Lemongrass, *Cymbopogon flexuosus*[69], was used in a single step procedure at room temperature to synthesize triangular gold nanoprisms. *Citrus sinensis* peel[70] was employed to prepare AgNPs at room temperature and 60°C. At room temperature, the nanoparticles were approximately 35 nm while at 60°C they were approximately 10 nm. Therefore size control can be achieved by varying the temperature. Other extracts such as mahogany leaves (*Swietenia mahogany JACQ*)[71], *Hibiscus rosa sinensis*[72], *Anacardium occidental*[73,74] and Tulsi leaf (*Ocinum sanctum*)[75] have been used to synthesize Ag, Au, Pd and Au/Ag nanoparticles. Roots extracts have also been used. A simple, economic, non-toxic and efficient synthesis was performed by Suman et al.[76], using *Morinda citrifolia* they obtained 12 to 38 nm AuNPs. 50 to 80 nm AgNPs were synthesised with seed extracts of *Nyctanthes arbor-tristis* (night jasmin)[77]. This synthesis employed mild conditions and was completed within 20 minutes.

*ALGAE:*

There are few reports on the use of algae to prepare metal nanoparticles, however *Spirulina platensis*[78,79] has been used to synthesise 7 to 16 nm AgNPs and 5 to 10 nm AuNPs for 120h at 37°. *Eolimna minima*[80], an aquatic microalgae diatom, was successfully seen to naturally produce AuNPs due to its effective detoxification properties.

*CARBOHYDRATES AND VITAMINS:*

Carbohydrates, the most abundant class of organic compounds in living organisms, are composed of sugars starches, cellulose, *etc*[13]. In a very interesting synthesis, Philip et al.[81] demonstrated that honey can be used to synthesise AgNPs. This reaction is pH dependant, at pH 8.5 it was found that monodispersed, nearly spherical 4 nm AgNPs were obtained. Vitamins B, C, D and E can be used to manufacture highly stable and efficient metal nanoparticles[13].

The combination of green chemistry and nanoscience will have a significant impact on future products and processes[99]. In order for nanotechnology to be responsibly developed, new processes have to be developed and made known in order to influence the industry[99]. Metal nanoparticles, being centre pieces in the nanorevolution, have therefore been the focus of a greening process in which benign solvents, reducing and protecting agents have been employed. Much progress has been made in perfecting solution-based synthesis by using sugars or plant extracts as reducing and protecting agents. Electrochemical and mechanochemical processes offer a wide range of advantages, such as the absence of a reducing agent and scalability. Most of the research, however, has gone into the very promising field of bioinspired synthesis of metal nanoparticles. This method employs the intrinsic properties of bacteria, yeast, virus, fungi, *etc.* to advantage to synthesise nanoparticles in a wide range of size and shapes. Much work has to be done to obtain monodispersion and better kinetics but this method should be regarded as a very good alternative for the near future.

## AUTHOR INFORMATION

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## ABBREVIATIONS

AuNPs: Gold nanoparticles; OLA: oleyamine; 4-MBA: 4-mercaptobenzoic acid; CTAB; Cetylmethylammonium bromide; CMC: Carboxymethyl cellulose; MW: Microwave; AgNPs: Silver nanoparticles; VOC: volatile organic compound; PVP: Polyvinylpyrrolidone; ILs: Ionic liquids; AILs: Alcohol ionic liquids; SCF: Super critical fluids; TMV: Tobacco mosaic virus

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# Current Developments in Green Chemical Extraction Techniques of Lignocellulosic Materials: Implications to Next-Generation Biorefineries

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*KEYWORDS: Green Chemistry, Biorefineries, Biomass, Extraction Techniques, Ionic Liquids, Supercritical $CO_2$*

**ABSTRACT:** Biomass offers one of few sustainable alternatives to fossil fuels as a source of renewable carbon. In light of growing concerns by society on the negative impacts of fossil fuels on the environment, and their inevitable depletion, research into the development of chemical technologies to harness biomass (i.e. the biorefinery concept) has been extensive. It is important, however, to realize that biorefineries are not *inherently* green – as outlined by the 12 Principles of Green Chemistry by Paul Anastas and John Warner. The initial processing steps of many next-generation biorefineries will involve the extraction of natural polymers and other valuable materials from lignocellulosic biomass. At the moment, conventional means of dissolving and extracting cellulose from lignocellulosic materials involve very harsh solvents and reagents that are toxic and harmful to the environment. This review focuses on current developments of two alternative green chemical extraction techniques that have garnered significant attention in recent years: the use of ionic liquids and supercritical carbon dioxide. The applicability of these methods to future next-generation biorefineries are discussed and current progress, challenges and future goals are highlighted.

## INTRODUCTION

In light of substantial data that has accumulated in the literature in recent years concerning the contribution of fossil fuels to climate change[1-3], and the rapid depletion of the world's accessible fossil reserves[2,4], we can no longer be ignorant of the growing unsustainability of a primarily fossil-dependent society. Currently, fossil-based energy resources constitute about three-quarters of the world's primary energy consumption.[4] To add to this problem, crude oil has become important feedstocks in the manufacture of many consumer products including: plastics, fertilizers, clothing, cosmetics and building materials.[1,5] In the years to come, the transition from a fossil-dependent society will be achieved in two steps: 1. radical reform in the management of existing fossil fuel-based systems[6]; and 2. the development of technologies to utilize renewable energy resources.[5] To this end, the refinery of biomass (i.e. biorefinery concept) have been predicted by many to be the eventual successor to fossil fuels and oil-based refineries.[5,7-9] Biomass is abundant, renewable (i.e. with cycle times on the order of years) and is a sustainable source of carbon.[7] Many proponents of biomass have also claimed that the use of biofuels is *carbon-neutral* as the carbon dioxide generated in the energy conversion will be sequestered back into biomass in the biogeochemical cycling of carbon.[4]

It is important to realize however that biorefineries are not *inherently* green. The incorporation of green chemistry principles to the development of next-generation biorefineries will be pivotal in the realization of a truly sustainable alternative to conventional fossil-based supply chains. These principles include: maximum utilization of the feedstock mass in the final product (i.e. atom economy), minimized energy demands, utilization of safer processes and materials and the generation of products that are non-toxic and totally biodegradable.[7] Thus, it is imperative that we extend beyond simply the use of renewable feedstocks in any discussion concerning the development of green and sustainable biorefineries.

Figure 1 depicts an outline of some important extractives, and their downstream chemicals, that can be obtained from biomass.[7]

The operation of the idealized biorefinery can be divided into two parts: 1. production of high-value low-volume (HVLV) extractives; and 2. The conversion of low-value high-volume (LVHV) intermediates into energy and fuel products.[8] As shown by figure 1, the extraction of natural polymers from biomass will constitute the initial processing steps of many next-generation biorefineries.[7-10] Thus, the development of efficient and environmentally benign extraction techniques will be an area of research with important implications to the development of green biorefineries in the years to come.

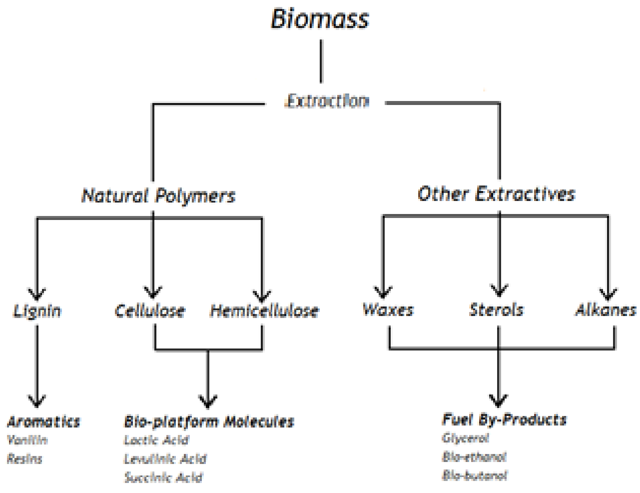

**Figure 1.** Simplified biorefinery flowchart including some of the extractives and downstream chemicals to be discussed in this report.

A significant challenge to the development of extraction techniques for next-generation biorefineries involve the vast array of different biomass feedstocks that will be utilized by future supply chains. These feedstocks include: low-value plants such as trees, grasses and heathers; byproducts from energy and food crops; and marine resource and food wastes.[9] This review will focus on the development of two solvent-based green chemical extraction techniques that have garnered a lot of interest in the literature in recent years; namely, the use of ionic liquids[7,12] and supercritical $CO_2$ ($scCO_2$) [9,10] for the treatment of lignocellulosic (i.e. plant-based) feedstocks. These methods will be assessed according to the twelve principles of green chemistry – as defined by Paul Anastas and John Warner – and their current progress and challenges will be outlined, as well as future goals for implementation in next-generation biorefineries.

## CELLULOSE FROM LIGNOCELLULOSIC BIOMASS: CURRENT DEVELOPMENTS

Lignocellulose is the principal component of plant cell walls.[13] It is mainly composed of cellulose, hemicellulose and lignin, as well as smaller amounts of pectin, proteins, ash, and other valuable extractives (e.g. nonstructural sugars, nitrogenous materials, chlorophyll and waxes).[13] The exact composition of plant biomass can vary significantly from one species to another, with important implications to the properties of the plant material.[7,13] For instance, hardwood contains greater amounts of cellulose, whereas wheat straw contains more hemicellulose.[13] The relative amounts of cellulose, hemicellulose and lignin of some common plant feedstocks are given in table 1 (adapted from Kumar et al.).[13]

Cellulose is an important precursor for the generation of many useful bio-platform molecules, such as lactic acid, levulinic acid and succinic acid.[7] However, the large majority of cellulose in lignocellulosic materials remain inactive, or unavailable for direct modification from unmodified biomass.[13,14] Thus, the pretreatment of plant biomass to separate, or expose cellulose in lignocellulosic materials is an important step that can greatly improve the efficiency and costs associated with the manufacture of chemical products derived from plant biomass.[7,13] Traditional methods of cellulose extraction involve the utilization of acid hydrolysis processes[13] or the treatment of cellulose with carbon disulfide in alkali conditions to prepare cellulose xanthate (viscose).[7,14] However, these techniques suffer from several drawbacks, including high energy demands, harsh reaction conditions and significant solvent wastes.[7,13,15]

Table 1. Relative Amounts of Cellulose, Hemicellulose and Lignin in Some Common Plant-Derived Feedstocks[13]

| Lignocellulosic Material | Cellulose (%) | Hemicellulose (%) | Lignin (%) |
|---|---|---|---|
| Hardwood | 40-55 | 24-40 | 18-25 |
| Softwood | 45-50 | 25-35 | 25-35 |
| Nut Shells | 25-30 | 25-30 | 30-40 |
| Corn Cobs | 45 | 35 | 15 |
| Grasses | 25-40 | 35-50 | 10-30 |
| Wheat Straw | 30 | 50 | 15 |

| | | | |
|---|---|---|---|
| **Waste Papers from Chemical Pulps** | 60-70 | 10-20 | 5-10 |
| **Solid Cattle Manure** | 1.6-4.7 | 1.4-3.3 | 2.7-5.7 |

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### Ionic Liquids

Ionic liquids (ILs) refer to a class of organic salts that exist in the liquid state at relatively low temperatures (< 100 °C).[15] In recent years, there has been significant interest in the use of ionic liquids as environmentally-friendly alternatives to conventional industrial solvents, such as volatile organic compounds (VOCs).[17] Some of the advantages to ionic liquids in the context of green chemistry are as follows: 1. ionic liquids are non-volatile, and therefore do not contribute to the pollution of VOCs into the atmosphere[17,18]; 2. they possess very good solubilities for a wide range of inorganic and organic materials, thus requiring less volumes of solvent[18]; and 3. they can be designed to be environmentally benign.[17] Furthermore, the fine-tuning capabilities of ionic liquid solvents are extensive, allowing for the optimization of reactions (i.e. yield and selectivity) through the utilization and design of ionic liquid solvents.[18]

The development of ionic liquids to dissolve cellulose has been significantly advanced by the work of Rogers et al. in recent years.[16] In particular, solubilities of up to 25 wt % were achieved by the Rogers group (2002) using ionic liquids, containing 1-butyl-3-methylimidazolium cations ($[C_4mim]^+$) and chloride anions, with pulsed microwave heating.[16] This was in comparison to typical solubilities around 10 wt % using dimethylacetamide (DMAC)/LiCl binary solvent systems that have also been explored extensively in the literature for the environmentally-friendly, and non-derivitizing extraction of cellulose from biomass.[16,19] The solubility of cellulose is primarily dependent on the ability of the solvent molecules to disrupt and penetrate the robust, intramolecular hydrogen-bond network of supramolecular cellulose structures.[16,19] It is believed that the solubilizing power of these solvents is directly related to the activity of the chloride ions in these solvent systems – and in particular, the mobilization and interaction of these chloride ions with the cellulose hydroxyl groups.[16,20] Thus, ionic liquids present an intrinsic advantage over conventional solvent systems, such as DMAC/LiCl, in that: 1. the effective concentration of $Cl^-$ ions is not limited by the solubility of the salt in the case of ILs; and 2. the fine-tuning capabilities of the ion constituents in ILs provide significantly more control over the activity and mobilization of the active ions (i.e. $Cl^-$).[20]

There has been substantial progress in the development of new IL systems for the dissolution of cellulose.[20] In general, IL systems with cations based on methylimidazolium (MIM) and methylpyridinium (MPy) cores have been found to yield the greatest success.[20] Furthermore, small anions (i.e. hydrogen bond acceptors), and chlorides in particular, have been shown to be most effective for cellulose dissolution.[16,20] For a full comprehensive table of current results achieved for the solubility of cellulose in various IL solvents, the reader is directed to a review by Marsh et al. (2009).[20]

A major limitation to ILs is often related to compromises between its rheological properties and solubilizing power when designing ILs for industrial applications.[16] Furthermore, the solubility of cellulose in ILs was found to be highly sensitive to water impurities.[16] In particular, significant impairment to the solvent properties of ILs was observed for concentrations of water as low as 1 wt %.[16] There have also been some disagreements in the literature[21-23] as to whether ionic liquids are really "green", owing to the toxicological properties and environmental impacts associated with some IL solvents. Additionally, the large-scale use of microwave heating in industrial applications have been the subject of some scrutiny in the green chemistry community based on the sixth principle of green chemistry, concerning the energy efficiency of microwave-assisted methods.[24]

## FRACTIONATION OF SECONDARY METABOLITES FROM WHEAT STRAW

### Supercritical $CO_2$

Wheat straw is a LVHV agricultural byproduct with important uses to next-generation biorefineries as a source of hemicellulose[13], and other valuable secondary metabolites such as waxes.[9] Natural waxes exist as complex mixtures of long fatty acids and alcohols, sterols and alkanes.[25] They have a wide range of industrial applications, including: cosmetics, polishes and coatings.[25] Conventionally, the extraction of these waxes involve harsh volatile organic solvents including: hexane, chloroform, dichloromethane and benzene.[25] In addition to the environmental and toxicological concerns associated with these solvents, these methods are often highly unselective, resulting in the co-extraction of many unwanted compounds (i.e. < 50% of wax present in total extract for most organic solvents).[25] Thus, there is a need for alternative environmentally-friendly, non-toxic and selective extraction methods for waxes from bulk lignocellulosic materials.[25]

The use of supercritical fluids (SCF), and in particular, supercritical $CO_2$ (sc$CO_2$), for the extraction and fractionation of waxes from wheat straw has been explored extensively in the literature.[9-10,25] Supercritical fluids refer to substances that are taken above its critical temperature and pressure.[26] At this state, a single homogeneous fluid is formed with both gas- and liquid-like properties. Table 2 summarizes the general differences in the densities, viscosities and diffusivities of gases, liquids and SCFs (data from report by Baiker).[27]

**Table 2. Comparison of Some Physical Properties of Gases, Liquids and SCFs in the near critical region (data taken from ref 27).**

| State | Density $[kg\cdot m^{-3}]$ | Dynamic Viscosity [mPa s] | Diffusion Coefficient $[10^6\ m^2\ s^{-1}]$ |
|---|---|---|---|
| **Gas** | 0.6-2 | 0.01-0.3 | 10-40 |
| **SCF** | 200-500 | 0.01-0.03 | 0.07 |
| **Liquid** | 600-1600 | 0.2-3 | 0.0002-0.002 |

SCF systems for extraction often employ sc$CO_2$ due to its relatively low critical parameters (i.e. 31.1 °C and 73.8 bar), low cost and non-toxicity.[26] The main advantages to sc$CO_2$

extraction methods include: 1. the properties of $scCO_2$ are highly tunable by adjusting the extraction parameters (i.e. temperature, pressure, flow rate, etc.)[9,25]; 2. very good control over the selectivity of wax products that are dissolved[25], allowing for systematic fractionation of the various wax components; and 3. SCF extraction often leaves the structure of the bulk material unchanged, allowing for easy integration into next-generation biorefineries.[9,25]

Results by Clark et al. (2005) on the extraction and fractionation of wax products from wheat straw using $scCO_2$ yielded an optimum extraction time (*extrapolated*) of *ca.* 100 min for the recovery of 99.9% of total extractable wax products through first order factorial design analysis.[25] Compositions of extracts were evaluated by analysis of GC-MS chromatograms of the wax-enriched, supercritical $CO_2$ mixture under various conditions. They were able to show that selective extraction towards alkanes or fatty alcohols was possible by carrying out the experiment with low pressure (60 bar) or high (300 bar) pressures, respectively.[25] The method reported by Clark et al. is currently patented and shows great promise for integration in biorefineries. Most importantly, they have been able to successfully collaborate with Botanix Ltd to scale up the extractions to yields over 75 kg.[25]

However, there are some challenges to SCF extractions that still remain. While much progress has been made in terms of the development of optimal extraction parameters (i.e. temperature, pressure, etc.)[25,28], there is still much room for improvement, including the fractionation of other secondary metabolites from a wider range of lignocellulosic feedstocks. Furthermore, the costs associated with SCF extraction methods may also be a significant barrier in some industrial applications.[26]

## CONCLUSION

The development of green and sustainable biorefineries will be important in the years to come as we slowly transition away from crude oil and petroleum. This review focused on the importance of green chemical extraction techniques in particular, which will form the initial processing steps of many next-generation biorefineries. These methods will need to be adaptable to a wider range of feedstocks and produce good separation of natural polymers and secondary metabolites from the bulk lignocellulosic material for further modification into fuel and valuable consumer products. Recent advances to ionic liquids[16] and $scCO_2$[25] for the treatment of lignocellulosic biomass have been promising and show potential for considerable tunability for application in diverse feedstocks with ever improving yields. However, for integration into future biorefineries, there is still much room for improvement. For ionic liquids, these include: improvements to the rheological properties of ILs without compromise to its solubilizing power[16], robustness of ILs in the presence of water impurities[16] and further improvements to yield and energy-efficiency.[24] For $scCO_2$, the high costs associated with its implementation to industrial scales will be its biggest obstacle.[26]

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# Endangered Element: A review on palladium

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*KEYWORDS: Catalysis, Palladium, Endangered, Depletion*

ABSTRACT: Platinum group elements have found increasing uses as catalysts yet they are quickly becoming excessively expensive and scarce. Palladium's main uses are in automotive catalysis and as a catalyst in the chemical industry. This review investigates the causes for resource depletion and provides alternatives to replace palladium with greener and more sustainable solutions. Fuel cells for catalytic converters and biocatalysis for catalytic reactions are promising options in both fields, however both come with their own downsides.

## INTRODUCTION

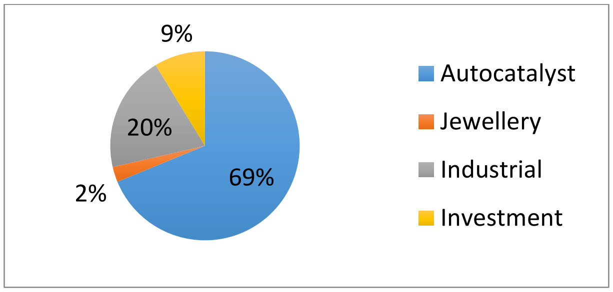
We all recognize the value and benefits to mankind that chemistry has given us, however we often take for granted how these precious metals are extracted and produced. The expectations of modern society for improved safety, lower environmental impact, more sustainable practices and lower energy use at a fair cost place tremendous demands and responsibility on us as scientists. The complex task of the chemical industry is to balance current knowledge with the robustness and durability of chemical processes used with these regulatory pressures and escalating costs. This review will examine the difficulties faced when balancing technological advancements, environmental concerns and scarce resources by assessing palladium's use in modern society.

Palladium's discovery was made public in 1805 when William H. Wollaston spoke in front of the Royal Society of London and declared he had obtained a novel metal through dissolving residues left from platinum in aqua regia, which is a concentrated solution of hydrochloric and nitric acids [1]. Wollaston, who had discovered rhodium in the same year [2], had discovered palladium two years before this however he explained he had remained anonymous so that he would have time to understand and explain all of the metal's properties before putting his name to account [3]. Palladium is part of the platinum group elements (PGE) along with iridium, osmium, ruthenium, rhodium and platinum. Palladium has a shiny, lustrous, silvery-white appearance. At ordinary temperatures it is strongly resistant to corrosion in air and to the action of acids [4], it has the ability to diffuse large amounts of hydrogen [5], it has good electrical and optical conductivity [6], and it can form alloys to improve ductility [7] and durability [8]. Palladium's unique properties have allowed it to find many uses in modern technologies, especially by replacing other PGE's in catalysis because of comparatively reduced toxicity [9], cost and improvements in efficiency. Nevertheless, palladium is still considered acutely toxic [10], its price has tripled in the last five years and concerns over scarcity are now emerging.

## USES

Palladium has been used in jewelry, dental fillings [11], computers, mobile phones, televisions, alloys for electrical contacts and ceramic capacitors [12]. However, palladium's principal use is in catalysis, especially automotive catalysis. As cars have become more common in society and our awareness of climate change has increased, demand for catalytic converters has increased with it. Catalytic converters are estimated to use 80% of all palladium used in 2015 [13].

Chart 1: Breakdown of global palladium use in different sectors for 2014



| Supply | 2011 | 2012 | 2013 | 2014 | 2015 |
|---|---|---|---|---|---|
| South Africa | 2,560 | 2,320 | 2,464 | 2,125 | 2,480 |
| Russia | 3,480 | 2,890 | 2,610 | 2,628 | 2,600 |
| Others | 1,320 | 1,320 | 1,300 | 1,351 | 1,323 |
| Total Supply | 7,360 | 6,530 | 6,374 | 6,104 | 6,403 |
| Gross Demand | | | | | |
| Autocatalyst | 6,155 | 6,705 | 6,958 | 7,351 | 7,457 |
| Jewellery | 505 | 445 | 355 | 279 | 245 |
| Industrial | 2,465 | 2,350 | 2,192 | 2,125 | 2,074 |
| Investment | -565 | 470 | -8 | 932 | -400 |
| Total Gross Demand | 8,560 | 9,970 | 9,497 | 10,687 | 9,376 |
| Recycling | -2,385 | -2,290 | -2,525 | -2,750 | -2,873 |
| Total Net Demand | 6,175 | 7,680 | 6,972 | 7,937 | 6,503 |

| | | | | | |
|---|---|---|---|---|---|
| Difference | 1,185 | -1,150 | -598 | -1,833 | -100 |

Table 1: A summary of global demand & supply for palladium over the last 5 years

Coupling reactions in the chemical sector have benefitted hugely from palladium, from the Suzuki reaction of aryl halides and boronic acids [14] to the first discovered palladium-catalyzed coupling reaction between a Grignard reagent and an organic halide [15], they have become quintessential in organic synthesis. Coupling reactions provide useful ways to form C-C, C-N and C-O bonds between different hydrocarbon fragments, they have been used extensively in the pharmaceutical, fine chemical and agrochemical industries [16]. Many pharmaceutical companies have used coupling reactions as key steps in synthesis involving palladium as a catalyst [17].

Estimates of palladium abundance in the earth's crust vary from 0.015-0.0063 ppm [18], this places it as one of the rarest metals on earth [19]. The 'Chemistry Innovation Knowledge Transfer Network' has signaled a warning because of the limited availability of palladium and the increased demand in recent years. The price of palladium saw a ten-fold spike in 5 years between 1996 and 2001 due to uncertain global supplies and increased demand, it has since decreased to 547 USD/ozt (correct as of 16/11/2015) however the historic trend has been one of steady increase. As is illustrated in Table 1, global demand has outstripped supply for four years running, despite increases in recycling, and the trend is set to continue in the coming decade as emerging economies develop and demand for cars increases. Recent reports by Johnson & Matthey's have pointed to Russia's decreased supply as a sign that stockpiles may be close to exhaustion. Geopolitical instabilities in South Africa and Russia, the largest extractors of palladium, may also cause decreases in supply and price fluctuations.

Palladium is becoming an endangered element; its current use is unsustainable. This, however, does not mean that we will run out of palladium. Instead, mining will become prohibitively expensive and companies will no longer be able to profit. This will in turn force car manufacturers, technology companies and industrial chemists to find alternatives. By applying the '12 Principles of Green Chemistry' [20] (PGC) to current chemical processes in the two largest sectors where palladium is used. This review will aim to provide an insight into the current advancements being made to tackle the problem of depleting palladium. "A raw material of feedstock should be renewable rather than depleting whenever technically and economically practicable" [20] (PGC – 7).

## CATALYTIC CONVERTERS

A multitude of different catalytic converters have been developed, most modern automobiles use a three-way catalytic converter composed of rhodium, platinum and palladium in differing ratios depending on the type of engine, stabilized by cerium and zirconium. They are used to convert carbon monoxide (CO) and unburnt hydrocarbons (HC) to carbon dioxide (CO2) and water (H2O), while also reducing oxides of nitrogen (NOx) to nitrogen (N2) and oxygen (O2) [21]. Catalytic converters have been hailed as great tools for fighting climate change, however they have many limitations in terms of functionality.

Due to scarce natural occurrence of PGE's, several environmental impacts are accrued in the process of mining and extraction, which must be taken into account when examining the environmental impact of modern catalytic converters. A life cycle assessment (LCA) of a catalytic converter for passenger cars found that the electrical consumption during mining and extraction needed to produce one catalytic converter is 110 MJ. Electricity production in South Africa is mainly based on coal-fired power stations; thus, it contributes significantly to a substantial amount of coal use corresponding to 11kg/catalytic converter [22]. Enforcing stricter emissions control may also be counterintuitive, as car manufacturers are forced to advance catalyst technology. The solution may be concluded with a higher use of PGE's. The benefits accrued from reduced emissions may be outweighed by environmental impacts of the mining and extraction of PGE's. For instance, a fuel cell vehicle under current development as an alternative for zero car exhaust emissions requires at least 10 grams of PGEs, significantly more than that of a car installed with a catalytic converter [22]. Another LCA study concluded that the second greatest environmental burden of catalytic converters after CO2 emissions is due to the chemical constituents of the catalyst, almost solely based on the addition of palladium [23].

Studies performed on airborne particulate matter and road dust found increased levels of palladium in urban areas compared to rural areas due to automotive catalysts [24]. As a metal, palladium will bio-accumulate in the environment and once a certain concentration is reached, 10 ppm according to the European Medicines Agency (EMA) [25], negative health effects from palladium exposure will start to be seen; dermatitis, stomatitis, skin irritation and cancer. "Chemical products should be designed so that so that at the end of their function they do not persist in the environment and break down into innocuous degradation products" [20] (PGC-10).

Current advancements in catalytic converters are diverse; increasing efficiency of key catalytic reactions [26], synthesis of 'bio-palladium' based catalysts [27], improved recyclability of catalytic converters in diesel cars through acid washing [28] and novel catalytic systems such as PremAir® which directly reduce ground level ozone to oxygen [29]. This is great chemistry in itself, but it has misunderstood the true meaning of green chemistry. Instead of trying to improve the efficiency of catalytic converters we should be looking to eliminate the need for them at all. In turn reducing the need for palladium and its consequential environmental implications.

Fuel cells, especially polymer electrolyte fuel cells (PEFC's), appear to be a good alternative however the need for larger amounts of PGE in the catalyst, due to low temperatures (80°), high acidity and a difference in kinetics between reactions at the anode and cathode side [30], has held fuel cells back. Fe- and Co-based electrocatalysts for this reaction have been studied for over 50 years, but they were insufficiently active for the high efficiency and power density needed for transportation fuel cells. PEFC catalysts have also suffered from fast degradation rates [30]. Recent developments in PFEC technology has allowed non-precious metal catalysts (NPMC's) to be used for oxygen reduction; cyanamide- [31] and polyaniline- derived [32] NPMC's have been established. Studies into degradation rates have found there to be a trade-off between lifetime of catalyst and activity [33], but further work needs be performed on optimizing the relationship. However we must not forget that the sustainability of PEFC's will invariably depend on the production, storage and transportation of hydrogen. No matter how many improvements we make to the catalytic activity of fuel cells, the majority of environmental pollution will occur prior to the usage of the fuel.

## CHEMICAL INDUSTRY

Palladium's principal use in industry is to catalyse coupling reactions; from bulk chemicals to pharmaceutical syntheses it is almost indispensable. "Catalytic reagents are superior to stoichiometric reagents" [20] (PGC – 9), while catalysts provide improvements in atom economy and energy efficiency they still hold some of the limitations of stoichiometric reactions such as solvent use, by-product formation, toxicity, high costs and non-renewable precious metals.

There are many ways to optimise palladium-catalysed coupling reactions by increasing efficiency in all areas; room temperature Suzuki coupling [34], using ionic liquids to improve recyclability of the catalyst [35], using microwaves to reduce energy use [36] and performing reactions in water instead of organic solvents [37]. Recyclability, solvent use and energy efficiency may be improved yet once again this does not solve the main issues. We are still left with high costs, toxicity, bioaccumulation and depletion of scarce resources. We cannot eliminate the need for catalysts, but we can replace palladium with more sustainable and less toxic metals. Copper [38] and nickel have been used in coupling reactions [39], where both of which are less expensive and less toxic than palladium. Although this is an improvement we must remember that copper and nickel are both toxic, will accumulate in the environment and are finite resources. The relatively new field of mechanochemistry has also provided benefits. The process of milling and grinding is more energy efficient [40*] than microwave or common hot-plates and has also been used in Suzuki coupling reactions [41][42]. However both syntheses still use palladium as a catalyst.

Biocatalysis, which is the act of performing catalytic reactions in living organisms, is uniquely suited to the development of green chemistry routes for complex molecules. High selectivity, mild conditions [43], low cost, no risk of bioaccumulation and use of renewable feedstock makes enzymatic catalysis a good candidate to replace palladium-based catalysts. Biocatalysis has been applied to pharmaceutical syntheses [44] at the industrial scale and is gaining momentum as a viable alternative to metal-based catalysts. On the other hand, enzymes will require solvents to function.

## CONCLUSION

In this review data has been presented to show the various uses of palladium contributing to its current increase in demand, which will soon make it prohibitively expensive to mine forcing different industries to look for alternatives. The focus was on the largest contributors to palladium demand: automotive catalysis and the chemical industry. Modern palladium based catalytic converters posed many environmental issues including toxicity of palladium, waste produced during extraction of palladium and low recyclability. Advancements in efficiency are not enough; eliminating the need for catalytic converters by using PEFC's may be a good solution, however even they do not come without difficulties. Palladium-based catalysts have been excellent for coupling reactions used everywhere from pharmaceutical synthesis to bulk chemical reactions, although with recent price hikes alternative shave been considered such as using less expensive metals and biocatalsysts. All alternatives will have downsides and upsides however the difficulty is in deciding which green chemistry principles to value more on. No future solution will be green; it will be merely greener than its predecessor.

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# Visibly green chemistry: in favour of polyhydroxyalkanoates (PHAs) to replace conventional petroleum-based polymers

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*KEYWORDS. PHA, biopolymers, green polymers, petroleum replacements.*

**ABSTRACT:** Given the difficult problems facing traditional petroleum-based polymers, a replacement that is sustainable, biodegradable, comparable, and economical is desired. There is mounting evidence and considerable research in favour of adopting polyhydroxyalkanoates, PHAs, as the biopolymer of choice. Recent advances in this technology support the argument in favour of a transition away from conventional plastics. Taken together, the sustainable production, biodegradability, compatibility, and nontoxicity of PHAs makes for a compelling case toward their adoption. In the near future, improvements in economic competitiveness will further enhance the long-term relevance of PHAs.

## INTRODUCTION

Plastics and polymers are ubiquitous in the world today. These materials are used in applications as diverse as water bottles and biologic stents. As synthetic compounds, they are preferred because they can be structurally modified to have diverse physical properties [1]. Unfortunately, the vast majority of these materials are synthesized from polluting petroleum sources, and stalwarts such as polyethylene and polypropylene exhibit minimal biodegradation when they reach their end of life. Plastics production exceeds 75 billion pounds every year, of which at least 40% ends up in landfills, causing an important accumulation of waste worldwide [2]. Even if much effort is invested in recycling those materials, the challenges of sorting the used material and structural weakening limit its viability [3]. While there is significant research in the field of remediation, considerable effort is necessary to limit the negative consequences of these petroleum-based polymers. The principles of green chemistry can be applied to this endeavour, and one of the most privileged solutions is the development of new classes of polymers. These should be made from renewable resources and biodegrade in ambient conditions while retaining the most desired qualities of traditional polymers [4].

Polyhydroxyalkanoates, or PHAs, are one such group of materials. These biopolymers possess diverse and easily variable physical properties that allow them to directly compete with synthetic plastics [5]. Perhaps the most popular is poly(3-hydroxybutyrate), or PHB, and it is this variety that was first discovered by Maurice Lemoigne nearly a century ago [4]. PHB is itself a member of a class of PHAs called short chain length PHAs, or scl-PHAs, which contain up to five carbon atoms per unit monomer [4]. Larger examples are called medium chain length PHAs, or mcl-PHAs, and contain up to fourteen carbon atoms [4].

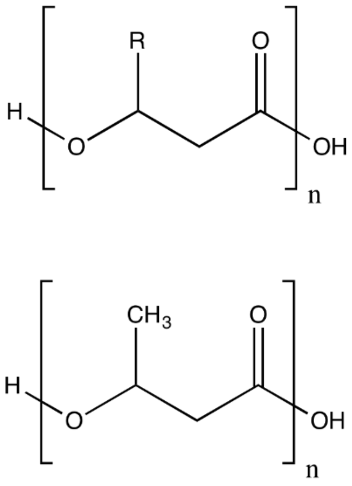

**Figure 1.** Chemical structure of polyhydroxyalkanoates. Top: General structure of PHAs. Bottom: Structure of PHB

Regardless of their size, PHAs are synthesized by self-sufficient organisms, among which are over 300 species of bacteria [4]. They are made via biosynthetic pathways involving a chain of enzymatic reactions, but unsurprisingly, the pathway differs for each producer and polymer [6]. For example, PHB is synthesized in three steps: a condensation of acetyl co-enzyme A (acetyl-CoA) molecules, followed by their reduction, and finishing with polymerization [6]. In an alternative route, PHAs can be synthesized by metabolism of fatty acids [7]. All of these naturally occurring syntheses involve aqueous processing environments and generate only nontoxic wastes [5]. When this process is translated to commercial production, PHA manufacture requires just two simple stages [8].

In recent years, PHAs have become the subject of considerable research and development. Clear advantages have been elucidated, among which are paths to sustainable sourcing and production, evident biodegradability and nontoxicity, competitive physical properties, and economic feasibility. Given these stellar properties, there is great incentive to migrate to these biopolymers in the near future. Consumers and industry alike should therefore closely examine such a transition.

## SUSTAINABLE SOURCING AND PRODUCTION

The design of better, greener polymers, such as PHAs, starts at the cradle. As with any other product technology, it is of great importance to avoid the pitfall of shifting environmental burdens elsewhere in the life cycle [9]. To solve the plastics problem, this idea must be a priority; thus, the best solution produces no material waste that nature cannot handle [2]. Fortunately, PHAs fulfill this criterion. They are produced from an array of renewable sources, such as sucrose, starch, and even carbon dioxide [2]. In fact, it is possible to produce PHA by taking advantage of precursors found in existing waste streams. This reduces the impact of the waste. Some of these sources include dairy byproducts [10], raw sewage [9], fermented paper mill wastewater [11], and even discarded fruit [12]. By leveraging these novel sources, it is possible to sustainably source the materials needed to synthesize PHAs.

Sustainability considerations do not end at the sourcing of feedstocks. The production process itself must also strive to abide by the principles of green chemistry. Unfortunately, some current commercial PHA production procedures exhibit higher fossil fuel demands and carbon emissions than conventional plastics manufacturing. This results from poor choices for feedstock [9]. The use of non-renewable feedstocks accounts for up to a third of the total energy requirements of PHA production, and the use of inefficient bioreactors can add 30% or more on top of that proportion [9]! Fortunately, by using creative and inexpensive precursor sources, such as the ones previously mentioned, the feedstock expense can be drastically reduced [13].

As research progresses, the goal of an entirely sustainable manufacturing process becomes possible. This is expected because PHAs are synthesized as a store of energy and nutrients [4]. In fact common strains of bacteria such as *A. eutrophus*, *A. latus*, or recombinant *E. coli* synthesize most varieties of PHAs [14]. These bacteria naturally produce PHAs when exposed to an environment abundant in carbon, but limited in another nutrient, such as nitrogen or phosphorous [4].

The capability to biologically synthesize PHAs is not limited to bacteria. Many other organisms can be genetically modified to produce polymers. As long as a PHA synthase gene is transferred, a synthase protein is activated, and substrates can be reliably provided, many organisms can produce PHAs [15]. Since the genes required for PHA production are easily isolated, plants may be adapted to produce large quantities of these polymers [16]. With oil-producing plants, this process is particularly efficient [2].

The final step of PHA manufacturing is isolation and extraction of the polymer. Traditionally, this task employs organic solvents such as toluene and chloroform. While this achieves PHAs of high purity, these chemicals are toxic and harmful to the environment. Fortunately, recent developments have ascertained the viability of replacing these solvents with milder ammonium hydroxide and sodium hydroxide solutions at concentrations as low as 0.2 M [17]. This substitution yields only a slightly impure product, not below 94 percent purity [17]. Streamlining of the entire process means that PHA production will soon be a sustainable and environmentally friendly process.

## BIODEGRADABILITY AND NONTOXICITY

Given their origin, it is not surprising that PHAs are highly biodegradable under ambient conditions. The degradation process simply reflects the natural purpose of PHA as a source of nutrients for microorganisms. As such, these organisms break down the polymer to derive energy [18]. Studies illustrate these polymers completely degrade in aerobic conditions after short periods of time; observed half-lives are as short as seventeen days [19]. This timescale is remarkable even compared to those of other biopolymers such as poly(lactic acid), which has significant difficulty degrading outside controlled conditions [20]. Even when disposed in aquatic environments, PHAs manage to degrade completely within nine months, with ambient water temperatures not exceeding six degrees [3]. In freshwater lakes, the degree of degradation reaches 100% within eight weeks [21]. Overall, complete biodegradability has been observed under various conditions, a remarkable feat for such useful materials [17].

The speed of biodegradation is as remarkable as the products the process yields. Under aerobic conditions, the only products are water and carbon dioxide [5]. Under anaerobic conditions, the products are carbon dioxide and methane gas [2]. None of these products are particularly dangerous, and all can be reused in various industrial and practical applications. When PHB is degraded, the chief product is 3-hydroxybutyric acid, which is a naturally occurring and innocuous component of blood plasma [5]. Thus, PHB is particularly well suited to medical use. The implications of these properties are significant. With PHAs, it is possible to realistically imagine a world where carelessly littered bottles and bags can safely disappear into the ground, and where plastic rings no longer pose a significant threat to marine wildlife.

**Table 1. Comparison of key physical properties of selected polymers [5].** Reproduced with permission.

| Polymer | Melting Point (ºC) | Young's Modulus (GPa) | Tensile Strength (MPa) |
|---|---|---|---|
| **P(3HB) or PHB** | 180 | 3.5 | 40 |
| **P(4HB)** | 53 | 149 | 104 |
| **Polypropylene** | 176 | 1.7 | 34.5 |
| **Polystyrene** | 240 | 3.1 | 50 |

**Table 2. General comparison of polymer properties [5].** Reproduced with permission.

| Property | scl-PHAs | mcl-PHAs | Polypropylene |
|---|---|---|---|
| **Crystallinity (%)** | 40-80 | 20-40 | 70 |
| **Density (g cm$^{-3}$)** | 1.25 | 1.05 | 0.91 |
| **Tensile strength (MPa)** | 4 – 43 | 20 | 34 |
| **Glass transition (ºC)** | -148 – 4 | -40 – 150 | -10 |
| **Extension to break (%)** | 6-1000 | 300-450 | 400 |
| **UV resistance** | Good | Good | Poor |
| **Solvent resistance** | Poor | Poor | Good |
| **Biodegradability** | Good | Good | None |

## COMPATIBILITY AND COMPETITIVENESS

In spite of their low environmental impact, PHAs are functionally comparable to conventional petroleum-based polymers. Bacterial PHAs have sufficient molecular mass to have polymer characteristics similar to polypropylene and others [1]. Since dozens of bacterial strains produce polymers of varying structures, PHAs can largely match the diversity of synthetic polymers. In addition, PHA exhibits diverse physical properties with modifications to the length of the chain and the presence of functional groups [5].

As a result, for almost every physical property that distinguishes synthetic polymers, there is a comparable analogue in the PHA family. For example, scl-PHAs are crystalline, brittle, and stiff with high melting points and low glass transition temperatures [5]. PHB melts at 180 ºC and breaks with less than ten percent elongation. Both properties make them excellent choices for packaging applications [22]. On the other hand, mcl-PHAs are thermoplastic with low melting points [5]. They are capable of stretching long distances without breaking, which make them well suited for making films and adhesives [5]. In addition, almost all PHAs have a high degree of polymerization, are insoluble in water, and are UV-resistant [2]. Table 1 compares some of the most important properties of common PHAs and petroleum-based polymers.

It is a valid question to ask why competing biopolymers, such as PLAs, are not preferable compared to PHAs. To answer this argument, it must be noted that the competing polymers lack structure variability and material properties PHAs possess, thus limiting their practical use [4]. For instance, most PLAs have softening points of around 60 ºC, a temperature low enough to cause their deformation under sunlight or while holding a hot beverage [20]. With great diversity, different PHAs can replace many conventional polymers for all sorts of uses without the limits of narrow, specific applications [5].

## ECONOMICS AND YIELD

No matter the benefits, the paramount concern of adopting any new technology or product is price, and biopolymers are no exception. Fortunately, the competitiveness of PHAs with petroleum-based polymers extends to price. While previous methods produced PHAs at costs exceeding those of traditional plastics by factors of 20, recent improvements and sensible design considerations reduce the cost to much more competitive levels [5]. To attain this goal, two primary routes are necessary. First, improvements to the production process increase the quality, quantity, and value of PHAs. Secondly, the valorization of existing waste streams spawns opportunities to produce PHAs at minimal cost, thereby lowering the price for everyone.

As an example, improvements in the efficiency of PHA synthetic processes reduce the cost by increasing the yield per unit of input. For some time, bacterial PHA production was quite inefficient, posting yields below 25%. Recently however, procedures using cheap recombinant *E. coli* specimens have resulted in yields exceeding 75%, and this percentage is expected to rise [17]. In the recombination exercise, a gene that encodes for a degradation enzyme can be inactivated, resulting in an increased yield [23]. Additionally, immediate cost reductions can be realized by reducing the cost of feedstock, since that component alone constitutes half of the total expense [24]. Costs can also be minimized at the recovery process, where a considerable proportion of total cost originates [25]. Clearly, these innovative approaches to PHA production significantly reduce its price.

On the same token, turning waste streams into PHA production pathways can result in a cost reduction of 40% to 50% while remaining practical and free from significant capital expense [24]. The procedure involving the use of fermented paper mill wastewater posted PHA yields of 77% [11]. Likewise, production from municipal sewage has yielded PHA approaching 25% by weight [9]. In both instances, no investment was needed outside the repurposing of existing facilities and equipment. Improvements like these are critical to expanding the reach of PHA. Even with current technologies, PHA is within reach of most companies.

These active changes have had noticeable effects on the economics of PHA, and their price has steadily declined. While hovering around $16 per kilogram only a few years ago, the end price in recent years has dropped by three-quarters to stabilize at around $3 to $5 per kilogram [2]. This price is competitive with other biopolymers such as PLA. However, as mentioned earlier, PHAs have superior physical properties, making them the best choice for companies seeking a sustainable polymer.

Nonetheless, the price is still falling. As plant production is refined, the price of PHA is expected to drop below a dollar per kilogram in the near future [2]. Here, the focus shifts to green engineering, wherein the design of pathways becomes important. Providing PHA synthase enzymes at consistent concentrations to suitable substrates can result in significant economic improvements [15]. Additionally, as productivity increases, the fixed costs of equipment and overhead significantly decrease [17]. At those prices, PHAs become directly competitive with conventional polymers, and will likely have a large impact on their adoption.

## CONCLUSION

Green chemistry is concerned with improving the environment and fostering sustainable development. It seeks to provide solutions to the problems traditional chemistry face. One of the most challenging problems facing the world today is that of polymer use and buildup. As PHAs have shown, research and development in chemistry can have far-reaching effects toward solving this quandary. Chemistry has made adopting these biopolymers one of the most solidly sustainable choices ordinary consumers can make. It is up to firms to wholeheartedly begin the transition away from polluting petrochemical polymers and embrace a new generation of sustainable, biodegradable, competitive, and economical ones. PHAs are helping make the world we live in more sustainable and less hazardous. The economic barrier to their adoption is being surmounted, and consumers and firms alike are taking note. With such clear progress being made, everyone can benefit from this true example of green chemistry at work.

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## ABBREVIATIONS

PHA, polyhydroxyalkanoate; PHB, polyhydroxybutyrate; PLA, poly(lactic acid).

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# The Ugliness of the Personal Care Industry: The harmful environmental effects of ingredients used in personal care products and the use of green chemistry for sustainable development

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*KEYWORDS:* Sustainable development; Personal Care products; Green chemistry; Environmental Impacts; UV filters; Aquatic biota; Pollutant

**ABSTRACT:** Everyday, millions of people use personal care products (PCPs) and often times are unknowing that these products are inflicting harm to the environment. With the growth expecting to reach $265 billion, it is of dire importance to address the ramifications these products have to the environment. Owing to the fact that consumers drive the market, scientific knowledge regarding the implications of commonly used ingredients commonly, could help mitigate the associated negative impacts. This review underscores the harmful effects of current ingredients in PCPS, more specifically; ingredients used in oral, hair and skin care products. With sustainable development in mind, the alternative ingredients suggested by researchers and industry are evaluated with the green chemistry principles in mind. Moreover, the question put forth is whether the alternatives are green. Through awareness, public sentiments could help steer research efforts to safer, and greener solutions.

## 1. INTRODUCTION

The personal care product industry currently stands at $200 billion[1] and is predominately driven by diversity and innovation because we demand it. In detail, the industry develops and manufactures cosmetics products which is defined by the *Food and Drugs Act* as "Any substance, or mixture of substances, manufactured, sold or represented for use in cleansing, improving or altering the complexion, skin or teeth and includes deodorants and perfumes" [14]. Everyday many of us use one of the personal care products (PCPs) and unknowingly expose the environment and ourselves needlessly to harm. Elimination of these products entirely is ideal but grossly unrealistic. In particular, the current forecast for the personal care industry shows an upward trend which is a result of an improvement in the economy and no proof of slowing down.[16] with the rise of disposal income expected in the approaching years, consumers are more likely to try and look for products that promise multiple benefits. With this knowledge, it is imperative to know when it comes to your PCPs, what the ingredients and the company's values are. Moreover, are the ingredients harmful and is the company concerned with green practices.

With the ubiquitous use of these products, the risks posed by these to our environment need to better understood. Many personal care products contain several chemicals used to achieve various functions or provide a specific benefit. Studies have provided proof that the chemicals currently used in personal care products have a negative effect and pose a risk to the environment. Identifying the problems can help steer a more focused research in the direction of tackling these issues.

Currently, a globally overarching goal, is to achieve sustainable development, defined as "development that meets the needs of the present without compromising the ability of future generations to meet their needs" [2] Along with the market forecast for this industry, the most viable option for obtaining sustainable development, is by means of green chemistry, a pivotal element to accomplishing this goal. Before delving into some of the impacts of personal care products it is essential to have a firm handle of what is green chemistry

Essentially, it is the practice of implementing 12 principles, first introduced in 1998 by Paul Anastas and John Warner [30]

1. *Prevention* : prioritize preventing waste as much as possible rather than clean or treat created waste
2. *Atom Economy* : Attempt to utilize all materials used in the process
3. *Less Hazardous Chemical Synthesis*: chemical products are designed to achieve their desired function but with minimal toxicity
4. *Designing Safer Chemicals*: minimize toxicity of the molecule
5. *Safer solvents and Auxiliaries:* The use of solvents or separation agents should be used as little as possible or not at all
6. *Design for Energy Efficiency* : Energy requirements should be assessed and minimized and if possible reactions should be conducted under ambient temperature and pressure
7. *Use of renewable Feed-stocks* : The raw material or feedstock should be renewable
8. *Reduce Derivatives:* Unnecessary derivatives should be avoided or minimized
9. *Catalysis*: Catalysts are to be used to increase selectivity reduce waste and reaction time
10. *Design for Degradation:* Chemical products should be designed in a way that they can break down and not persist in the environment
11. *Real Time Analysis of Pollution Prevention* : Analytical methods need to be developed in a way to allow for real-time, in-process monitoring and control in order to ensure hazardous substances are not made
12. *Inherently Safer Chemistry for Accident Prevention:* choose and develop procedures that inherently minimize the risks for accidents

Along with these green chemistry principles, Jessop *et al*[1] suggested cost-effectiveness and the carcinogenicity of ingredients needs to also be considered.

The objective of this paper is to review some of the current ingredients used in personal care products and the problems that arise, hindering a sustainable development. The focus will mainly be on commonly used ingredients in oral, skin and hair products and their environmental impacts. Through the implementation of some of the green chemistry principles, progress has been made in offering alternatives to toxic chemicals. Of the 12 Green Chemistry Principles the main focus will be geared towards prevention, design for safer chemicals, use of renewable feedstocks, and design for degradation.

## 2. ORAL

The quest for healthier teeth and gums has been endless with chemistry playing a crucial role in the improvement of overall oral health. Some of the ingredients used in these oral products have proven to be an environmental problem. Moreover, triclosan [ 5-chloro-2(2, 4-dichlorophenocy)phenol; TSC; see structure Figure 1] a halogenated phenol[3], has been used in oral products more specifically, as an antibacterial in mouthwash and toothpaste. [4] Additionally, research has shown their effectiveness in killing several types of bacteria, some fungi and are a primary player in the prevention of bacterial growth. [3,4] Recently, studies have exhibited the health implications of TSC[5] including being a liver tumor promoter. Along with the health concerns there is strong evidence to suggest that TSCs pose a threat the environment. No known natural sources of TSC exist with this it can be concluded that its presence in the environment is due to human activity.[6]

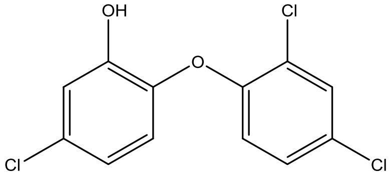


**Figure 1.** Triclosan (TSC) is commonly used as antimicrobial disinfectant in PCPs.

### 2.1 ENVIRONMENTAL IMPACTS

Toothpaste, which employs triclosan, is released down the drain, discharged into sewers and carried to Waste Water Treatment Plants (WWTPs). Figure 2 depicts the possible pathways for release of TSC to the environment.

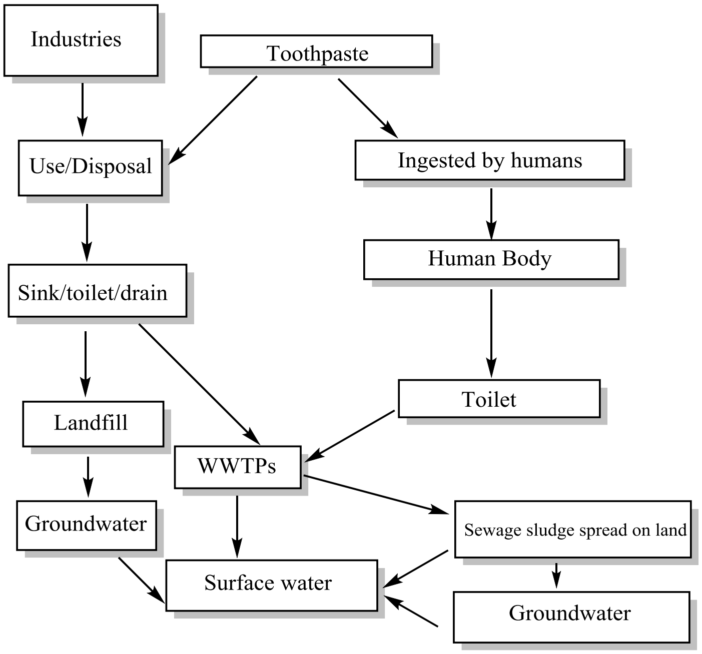


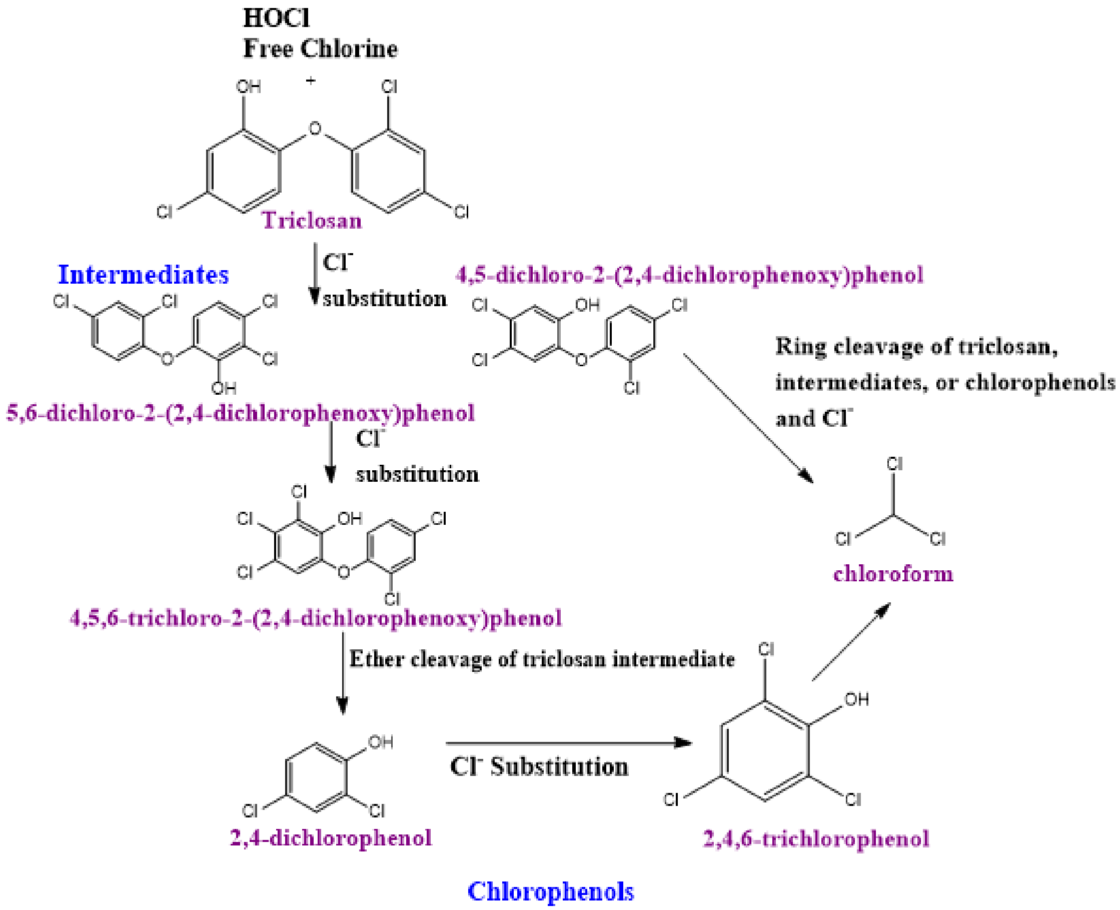
**Figure 2.** Possible pathways for releases of TSC to the environment. Modified from Health Canada[6].

### 2.1.1 Aquatic environment

A range of problems arise due to the use and presence of TCS in the environment. Moreover, the impact of triclosan to the aquatic environment has been explored extensively. The analysis of the eco-toxicological studies have demonstrated that triclosans are toxic to bacteria and can bio-accumulate. [4] TCS is ubiquitous and found in various environmental settings(Figure 2).[7]

With the release of TCS in WWTPs, often times free chlorine is also available as it is commonly used during wastewater treatments. Moreover, when a free chlorine, which is employed during wastewater treatment, reacts with phenol, 2-chlorophenol and 4-chlorophenol are the initial products. These are further chlorinated to form 2,3-dichlorophenol and 2,6-dichlorophenol to produce 2,4,6 TCP, full depiction is present in Scheme 1[8]. Additionally TCSs can react with free chlorines to produce chloroform.

Additionally, it has been suggested that the complex matrix of wastewater could react with triclosan and the extent of the environmental implications, which are not fully understood.



**Scheme 1. Reaction scheme showing reaction mechanisms and chemical structures for triclosan and its decay products**

## 2.2 ALTERNATIVES

Ideally, it is best to prevent the formation of waste rather than clean it up. While TCS has been shown to be removed from water using reverse osmosis, this process has its drawbacks such as fouling [9], finding a way to eliminate the need for water remediation is more beneficial. This could be done by replacing TCS with an ingredient that does not persist in the environment and is inherently safer. Chalcones (see structure Figure 3) a flavonoid and a renewable resource, has shown promise to replace these TCS and provide antimicrobial resistance[10]. In particular, it was shown to inhibit some strains of bacteria that TCS inhibits as well, in particular, *Streptococus mutans*, bacteria known to contribute to human dental decay.

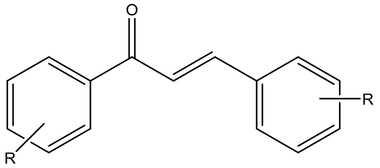


**Figure 3.** Basic 1,3-diphenyl-2-propen-1-one framework of flavonoid natural product, chalcone, suggested as a replacement for triclosan in toothpaste products

The chalcone and TSC are similar in that they contain aromatic rings, however, chalcone is found in nature.

Chalcone synthesis can be accomplished solvent-free, meeting number five of green chemistry principle, *Safer solvents and Auxiliaries*. More specifically, Saini *et al*[11] showed that chalcones were obtained in high yield and high purity by grinding piperanal and the acteophenone in the presence of solid sodium hydroxide, a general depiction is shown in scheme 2 . Additionally, its potential to replace TSC is exhibited, as it proved to have good activity against gram-positive and gram-negative bacteria *viz staphylococcus aureux*, *Escherichia coli*, *Steptococcus viridiaus* and *K.Salmonilla.* [11] Additionally, Chalcones[12] were shown to improve the efficacy of anti-microbrial agents to treat oral conditions such as gingivitis, and plague just to name a few.

$$\mathrm{RCOCH_3 + R'CHO} \xrightarrow[\text{Grinding}]{\text{NaOH}} \mathrm{RCHOCH{=}CHR'}$$

**Scheme 2.** [13] [14] Method reported for the synthesis of chalcones

Making the connection to the green chemistry principles, Scheme 2 depicts this a reaction that is void of solvents and proceeds at ambient temperature and pressure and is derived from a natural feedstock. The persistence of chalcone in the environment is not a problem however this aspect hasn't been fully researched.

## 3. HAIR

Many of us use shampoo which serve to cleanse the hair and scalp in addition to enhancing the hair compatibility and appearance. The main ingredients used in shampoo are surfactants which are mainly responsible for cleaning.[15] They are effective cleaning agents because of the nature of its structure; its hydrophobicity and hydrophilicity. The hydrophobic side interacts with the dirt of the hair while the hydrophilic suspends the surfactant and bounds dirt to water. In many shampoos, sodium laureth sulfate (SLES, see structure Figure 3), is used as the main active surfactant.[16] It has several desirable characteristics such as its solubility in water, and its insensitive to water hardness.

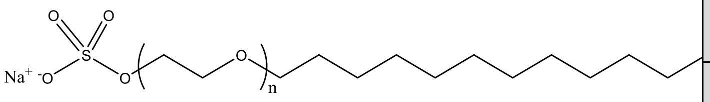


**Figure 4.** Sodium Laureth Sulfate (SLES), a chemical surfactant responsible for the foaming action of shampoo and toothpaste. [18]

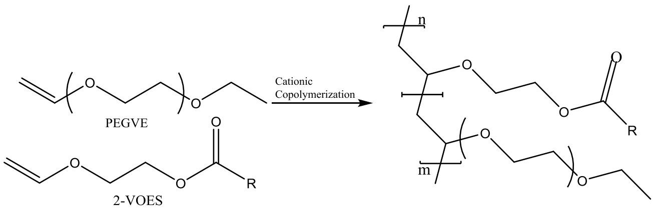
### 3.1 ENVIRONMENTAL IMPACTS

The surfactants pose a problem to the environment. For instance, while SLES is derived from a natural source - coconut and/or palm oil, it is manufactured via a chemical process. Moreover, the nature of this process, ethoxylation, is known to result in contamination with 1,4 dioxane, a carcinogen.[17] While a product may be marketed as natural this does not mean it is green nor does it mean that it is clear of any pollutants.

### 3.2 ALTERNATIVES

#### 3.2.1 Naturally- derived surfactants

A novel soybean oil-based polymeric surfactant (SBPS) demonstrated its ability to meet major requirement of shampoo while being non-toxic, environmentally friendly and derived from renewable sources, meeting many of the green chemistry principles aforementioned. [15] The hydrophobic ends of the macromolecules were derived from soybean oil and the hydrophilic portions were based on ethylene glycol units. Additionally, the physicochemical properties were studied along with their cleaning ability, foaming characteristics, and viscosity in order to study the utility of this novel surfactant in shampoo. Popadyuk *et al* evaluated the novel SBPS along with commercial shampoo and was able to conclude that soybean is a viable replacement. Scheme 3 depicts the facile synthesis of this copolymer.



R= -$C_{18}H_{33}$(linoleate), -$C_{18}H_{35}$(oleate),- $C_{16}H_{33}$(palmitate)

**Scheme 3. Synthesis of the SBPS copolymer, where R is soybean fatty acid component. Adapted from Popadyuk *et al*[15]**

Another green surfactant is alkyl polyglycoside (APG). It is manufactured from renewable resources, are readily biodegradable and are low in toxicity .They contain a large sugar-based hydrophilic head (i.e glucose, galactose, maltose, etc.) and hydrophobic hydrocarbon tail (cite analysis of the influence of alkl). The problem with pure APG is it is too expensive to be used in an industrial application. Surfactant blends have offered a solution to reducing the cost of pure green surfactants, some are found in table 2.

**Table 2. Naturally derived surfactant examples.[18]**

| Name | Natural source | Benefit |
|---|---|---|
| Disodium cocoyl glutamate | Coconut fatty acids | High foaming |
| Sodium coco-glucoside tartrate | Coconut and amino acid from fermented sugar | Non-drying with skin and hair conditioning properties |

Saponins[19] have been explored for their potential as surfactants. It occurs in different tissues of a large number of plant species and are predominately glycosides possessing one, or more sugar chains attached to the aglycone, the nonpolar parts of the molecule. Saponins are obtained from oleochemical feedstocks and an important source of these saponins is the *Yucca Schidigera* plant. However, the supply from plant sources has been limited making the products less available and resulting in a high cost. Additionally, the saponins make a good lather but have low cleansing properties making its use in industrial application unlikely.

#### 3.2.2 Surfactants from Waste Biomass[20]

Recently, microbes were studied for their potential to degrade waste biomass to produce useful bio-surfactants. Based on the fact that humic acids are capable of reducing the surface tension of water, and solubilizing hydrophobic compounds.[20] An alkaline treatment was used to convert comport to surfactant-like material, figure 7. The potential to commercialize the product was not assessed.

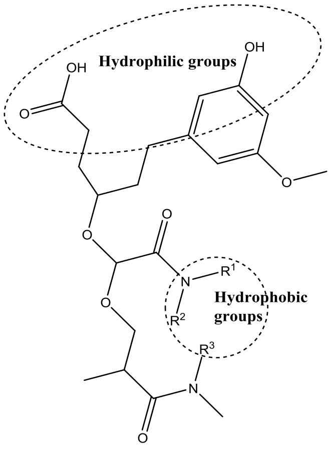


**Figure 7.** Structure for surfactant-like humic material extracted from compost.

## 4. SKIN

With the growing recognition of the harmful effects of ultraviolet (UV) radiation this has lead to the development of chemicals, more specifically, UV filters to mitigate the effects. These filters have become popular because of their protective role in reducing skin damage which has shown to eventually lead to premature skin aging [21] They work to absorb UV radiation and mitigate the negative effects of sunlight exposure and protect skin. Some common UV filters include, oxybenzone, avobenzone, methoxycinnamate and Benzophenone-2 (BP-2).[6]

### 4.1 ENVIRONMENTAL IMPACTS

These UV filters are meant to be applied externally to the outermost layer of the skin, however, concerns have risen with regard to their ramifications to the environment. UV filters approved for use have been detected in surface water, and drinking water.[22] Nowadays, UV filters are considered emerging contaminants due to their widespread presence in the environment and because of the unknown risks associated with their presence.[22] UV filters can enter the environment in various ways, for instance, directly from recreational activities when they are washed off from the skin as a result of swimming. The UV filters are lipophilic and end up accumulating in sediments and biota[16] proving to be a problem.

### 4.2 ALTERNATIVES

In addition to meeting as many of the 12 principles of Green Chemistry as possible, desirable alternatives to these UV filters would need to be characterized as readily biodegradable, low toxicity to aquatic organisms, non-sensitizing, non-irritating and pose little to none toxicological problems to humans.

Gelatin, produced by the partial hydrolysis of collagen, is a natural biopolymer widely used due to its biocompatibility, biodegradability, and low cost and have been employed in various cosmetic products.[23] Additionally, it does not produce harmful byproducts upon enzymatic degradation. Recently, rutin-entrapped gelatin nanoparticles (GNPs) were designed and associated with ethylhexyl dimethyl PABA (EHDP), ethylhexyl methoxycinnamate (CHMC) an alternative to synthetic-based sunscreen. Encapsulation of natural ingredients such as rutin, can offer improvements in sun protection effectiveness by reducing the amount of UV filters in sunscreens[24]. This leads to the prevention and inherently safer chemistry.

Some plant oils have been shown to possess some natural sunscreen abilities. For example, sesame oil resists 30% of UV rays. Additionally, the active ingredient, epigallocatechin-3-gallate (EGCG), a phytochemical found in green tea has shown to work as sunscreen. [25] However, they cannot be used as a sole sunscreen ingredient and must be used along with current UV filters. The benefit with using the plant extracts or biopolymers is this minimizes the need for UV filters despite not completely replacing them.

Additionally, green coffee oil[26], and extracts of carica papaya[27] , natural products, have undergone cytotoxicity assay and are safe for use as additives to personal care products which would lead to a reduction of commercial UV filters.

Lignin [28], one of the most abundant biopolymers on earth[29] Recently, Qian et al[28], studied the effectiveness of lignin addition to pure suncreams via magnetic stirring. They demonstrated that the commercial sun protection factor (SPF) 15 sun lotions saw an enhancement, in fact with the addition of lignin the SPF could reach up to 30. This nature-inspired lignin system provides an alternative to replace some synthetic chemicals.

The use of microbial 'sunscreen' compounds has been growing as they have shown to provide a photoprotective mechanism. Scytonemin, a cyanobacterial, is a lipid-soluble and stable pigment. Under UV light it was seen to be effective in acting as a shield for the cells. Melanin, known from fungi and bacteria. These have shown resistance to UV light and could potentially be employed in personal care products.

## 5. ISSUES WITH GREEN INGREDIENTS

Achieving high performing products with more green alternatives is the biggest challenge faced and the performance does not yet match that of conventional ingredients. A suggested alternative blending ingredients could reduce harmful ingredients as was the case with some of the proposed green alternatives for surfactants and UV filters. Additionally, problems can occur when trying to scale up from laboratory to manufacturing which could mean a less controlled environment. Moreover, natural ingredients tend to be more susceptible to bacteria as it finds it more nutritious. [18]

## 6.CONCLUSION

Eliminating current toxic chemicals in personal care products (PCPs) needs to be addressed. With the current forecast of the PCP, the need to replace toxic chemicals is needed. With some of the green chemistry principles viable alternatives can be found and success can be made. Efforts need to be focused on understanding the full implications of the PCP ingredients as there is a lack of information regarding this. Looking at improving the biodegradability of ingredients, the reduction of harmful chemicals either by completely replacing the toxic chemicals or by finding ways to reduce the need of the harmful chemicals through blending them with natural products. Lastly, biodiversity needs to be considered when trying to find 'green' alternatives, it is important not to jeopardize the system.

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## ABBREVIATIONS

TCS, Triclosan; SLS, Sodium Lauryl Sulfate ; PCPs, personal care products; , EGCG; epigallocatechin-3-gallate; GNP, gelatin nanoparticles; EHDP, ethylhexyl dimethyl PABA; CHMC, ethylhexyl methoxycinnamate; 2,4 DCP, (dichlorophenol); 2,4,6 TCP(trichlorophenol); UV ultra violet.

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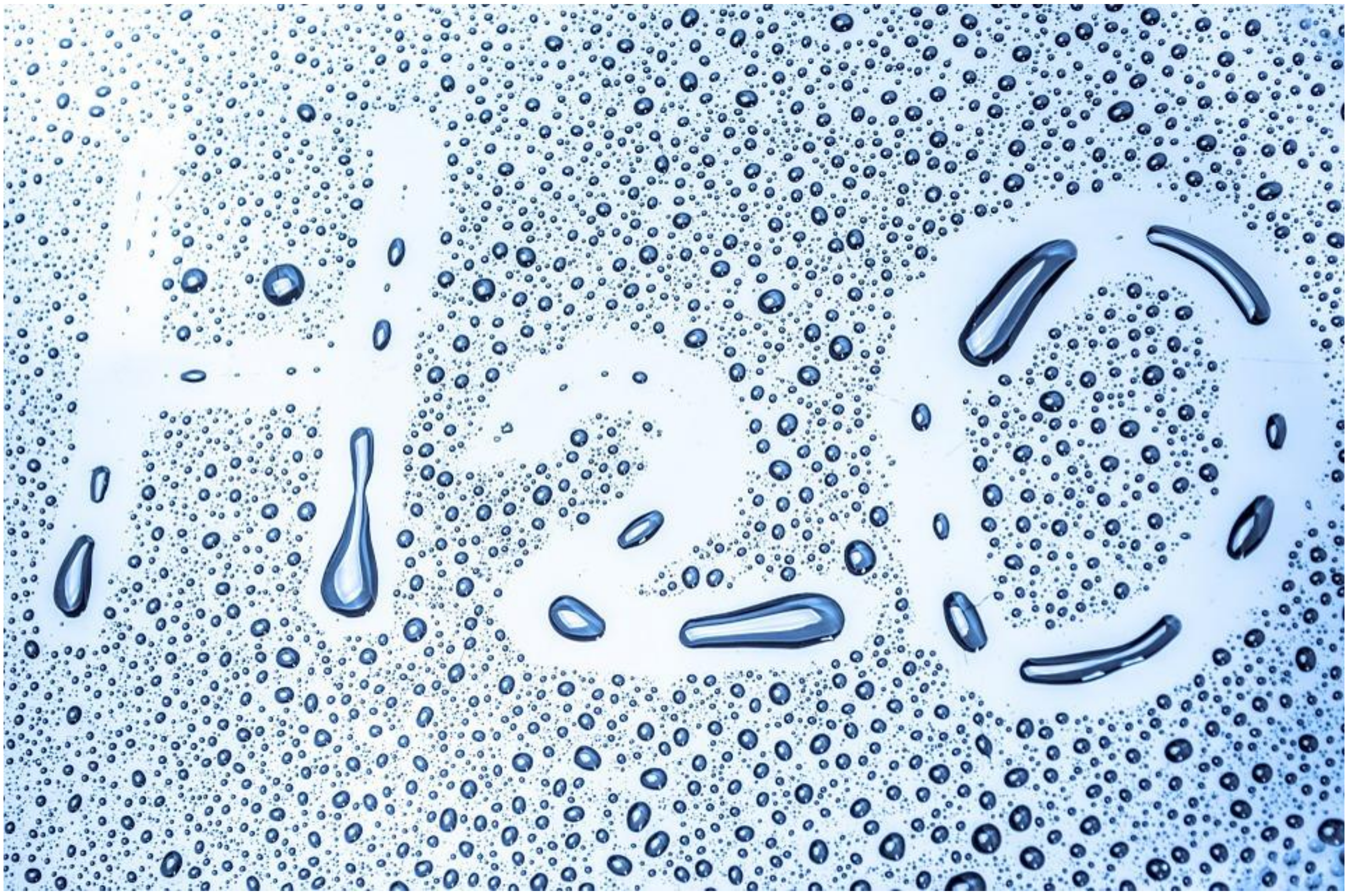

# Sustainable Water-Splitting Methods to Produce Hydrogen

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*KEYWORDS:* Water-splitting, Electrolysis, Photoelectrolysis, Photoelectrochemical, Thermochemistry, Hydrogen fuel

**ABSTRACT:** Hydrogen is primarily used in the chemical industry, but with the depletion of fossil fuels, hydrogen fuels are becoming an attractive alternative especially because the only by-product is water. This article reviews the technologies related to hydrogen production by water-splitting methods. These methods include electrolysis, photoelectrolysis or photoelectrochemical processes and thermochemistry with solar powered energy. The efficiencies of each method were compared as well their realistic use for the future. It was found that the amount of water it takes to produce hydrogen is not a critical problem in comparison to the production of gasoline. Although great aspects come from these methods, more research will be needed to have better and consistent efficiencies.

## 1. INTRODUCTION

The urgency in finding an alternative to the world's diminishing fossil fuels have never been greater than today. Today, the increase in greenhouse gas emissions due to carbon dioxide has been the main culprit of global warming and climate change. The global economy and energy supply depends largely on fossil fuels. This has led to the hyper-consumption of these non-renewable resources, which in turn has resulted in the escalating atmospheric carbon dioxide concentration and the rapid depletion of fossil fuel resources [1]. Scientists have become more and more interested in the production of hydrogen fuels. Currently, however, 95% of commercialized hydrogen is produced from fossil fuels by steam reforming and coal gasification [1]. In the long run, it is not sustainable to produce hydrogen from non-renewable hydrocarbon sources. For cleaner processes of hydrogen production, one possible solution to help mitigate global warming is to explore renewable energy sources that replace fossil fuels, such as hydrogen [2]. Hydrogen could be the ideal fuel, as it possesses very high energy density and the only byproduct is water; there is no climate-altering carbon dioxide released from hydrogen during combustion [3]. As Leonardo Di

Vinci once said, “Water is the driving force in nature;” pun intended in this case.

However, there most definitely are problems or disadvantages of renewable primary energy since energy sources such as solar energy, wind energy and ocean energy are regionalism, intermittence and unstorability, which will result in instability of power source [4].

Apart from its use as a clean energy resource, hydrogen can be used for various other purposes in chemical process industries. It can be used to crack hydrocarbons, saturate compounds or remove sulphur and nitrogen compounds [5], as well as it is used as a reactant hydrogenation process to produce lower molecular weight compounds [6]. Hydrogen is well known in manufacturing ammonia, methanol and synthesis gas [7] as well as a good oxygen scavenger and can therefore be used to remove traces of oxygen to prevent oxidative corrosion [8]. The future widespread use of hydrogen is likely to be in the transportation sector, where it will help reduce pollution. Aside from the uses of hydrogen, the main concern today is the production of hydrogen itself. Currently, however, are these new methods really reliable? How much water will be used if these processes were to be commercialized? This review will go through a variety of renewable hydrogen production technologies with the emphasis on their applications in the world by looking at water-splitting methods and their energy efficiencies. There has been a great deal of research in splitting water to make hydrogen and oxygen. Water splitting can be divided into three categories: (2) electrolysis, (3) photoelectrolysis or photoelectrochemical processes, (4) thermochemistry.

## 2. ELECTROLYSIS

Water electrolysis for hydrogen production has many advantages such as high purity and simple process by passing electricity through two electrodes in water. The water molecule is split and produces oxygen at the anode and hydrogen at the cathode [9]. Hydrogen produced by water electrolysis is considered as the best energy carrier to adjust the balance between the generations of power source by renewable primary energy and energy demand for end-use [4]. Although the prospect of the sustainable energy route is inspiring, the problems are low gas evolution rate and high energy consumption of water electrolysis. Generally, energy requirement is up to 4.5 -5.0 kWh $m^{-3}$ $H_2$ in conventional industrial electrolyzers [4].

Today, some industrial electrolyzers involve an aqueous solution of potassium hydroxide (KOH) (due to its high conductivity) and are referred to as alkaline electrolyzers [10]. Recent studies have also tried ionic liquids for conventional water electrolysis as well as more developing types like proton exchange membrane (PEM) electrolysis and Solid oxide electrolysis cells (SOEC) [11-14,45].

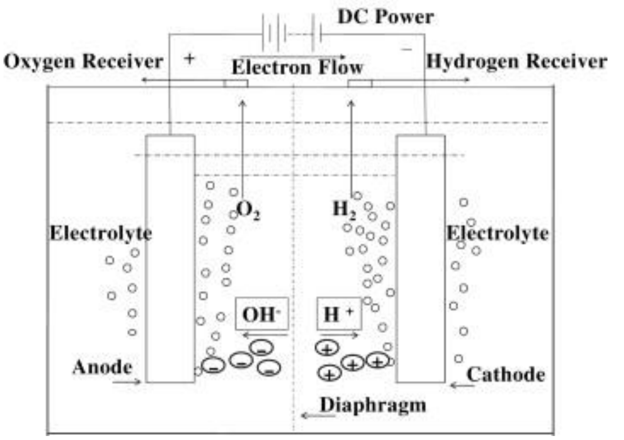

**Figure 1.** A schematic illustration of a basic water electrolysis system [15]

### 2.1 New electrolyte composition and system for water electrolysis

**2.1.1 Ionic liquid/Water electrolyte** exhibits good conductivity and is chemically inert to metal electrodes [4]. In conventional water electrolysis, corrosive reagents such as NaOH, KOH and $H_2SO_4$, are usually used as conductive salts, however these cause serious destruction in the corrosive electrolyte and lose catalytic activity for the catalyst in the metal electrodes. Therefore, low stability of metal electrodes is another major problem of water electrolysis.

In 2006, Souza et al. [11] used $BMIFB_4$ as conductive electrolyte for hydrogen production by water electrolysis that resulted in no effect on the catalytic process of electrodes. This mechanism was consistent with a variety of metals such as gold, molybdenum, nickel, titanium and platinum electrodes [4]. Furthermore, this lead to maximum optimization for the following: electrode materials, type of ionic liquid and concentration in water. “The best efficiency of about 99% was obtained in the solution of 10 vol% $BMIMF_4$ and 90 vol%” [11]. In more recent studies, such as in 2012, Pool et al. [16] designed a molecular electrocatalyst $\{[Ni(P_2N_2)_2](BF_4)_2\}$ as medium in highly acidic ionic liquid/water electrolyte to promote the reduction of protons to $H_2$. This was inspired by the fact that the Molybdenum electrode was a great substitute to Platinum electrode as it had better efficiency, cost and stability of hydrogen production. “However, the viscosity of ionic liquid is large, which affects negatively the transportation rate of ions. Current density, i.e. hydrogen production rate, is also low in ionic liquid/water system.” [16]

**2.1.2 Alkaline electrolyzers** are typically composed of electrodes, a microporous separator and an aqueous alkaline electrolyte of approximately 30 wt.% KOH or NaOH [17]. In alkaline electrolyzers nickel with a catalytic coating such as platinum, is the most common cathode material [18]. For the anode, nickel or copper metals coated with metal oxides, such as manganese, tungsten or ruthenium, are used [18]. Platinum, in most cases however is known to be very expensive. Recent studies show that the aim of presented work is lowering the cost and the energy consumption of the conventional alkaline water electrolyzer by raising its efficiency using combinations of d-metals from different parts of transition series as activating compounds [19]. “Such combination metals like cobalt and tungsten based ionic activators are added directly into the electrolyte during the electrolysis process and concluded to be extremely active and reduces the energy per mass unit of hydrogen produced" [19].

Firstly, in the alkaline cell, the decomposition of hydrogen and $OH^-$ occurs when water is introduced in the cathode [20, 45]. Then, $O_2$ is formed when the $OH^-$ travels through the electrolytic material to the anode and the hydrogen gets left behind in the alkaline solution [20]. Outside the electrolyzer, the hydrogen is then separated from the water in a gas liquid separation and typically achieves efficiencies of 59-70% based on the lower heating value of hydrogen [20, 45]. The overall reactions at the anode and cathode are [20, 45]:

Anode:

$$4OH^- \rightarrow O_2 + 2H_2O \qquad (1)$$

Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

Overall:

$$H_2O \rightarrow H_2 + \left(\frac{1}{2}\right) O_2, \Delta H = -288 kJmol^{-1} \qquad (3)$$

### 2.1.3 Proton exchange membrane (PEM) electrolysis

PEM electrolyzers build upon the recent advanced PEM fuel cell technology [21]. This perfluorosulfonic acid polymer (also known as Nafion) has ben used in chlor-alkaline electrolysis and also in fuel cells. PEM electrolysis is a process just reverse of a PEM fuel cell (Figure 2). Water is split into oxygen, protons and electrons on one electrode (anode) by applying a DC voltage higher than a thermoneurtal voltage. Protons pass through the polymer electrolyte membrane and on the cathode combine with electrons to form hydrogen. [22] The $O_2$ gas remains behind with the unreacted water. There is no need for a separations unit. Depending on the purity requirements a drier may be used to remove residual water after a gas/liquid separations unit. PEM electrolyzers have low ionic resistances and therefore high currents of >1600 mA $cm^{-2}$ can be achieved while maintaining high efficiencies of 65-82% [23,45]. The reactions at the anode and cathode are [23,45]:

Anode:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (4)$$

Cathode:

$$4H^+ + 4e^- \rightarrow 2H_2 \qquad (5)$$

Overall is the same as for alkaline electrolyzers:

$$H_2O \rightarrow H_2 + \left(\frac{1}{2}\right) O_2,\ \Delta H = -288 kJmol^{-1} \qquad (6)$$

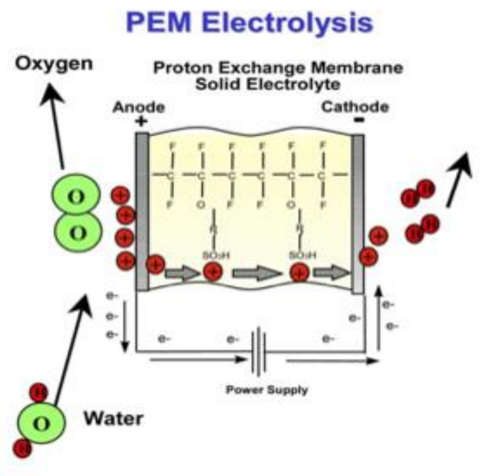

**Figure 2.** Schematic representation of PEM electrolysis [22]

The following table (Table 1) presents a comparison of the two types of commercialized electrolyzers looked at thus far.

**Table 1. A comparison of the two types of commercialized electrolyzer. [15]**

| Parameter | Monopolar alkaline electrolyzer | PEM electrolyzer/cell |
|---|---|---|
| Cell voltage | 1.85 | 2 V |
| Number of cells | N/A | 7-51 |
| Current density | 0.25 $Acm^{-2}$ | 1.075 A $cm^{-2}$ |
| Temperature | 70 ℃ | 65 ℃ (outlet) |
| Current | 10 kA | 1 kA (maximum) |
| Scale | 200 kW | N/A |
| Hydrogen production rate | 42 $m^3\ h^{-1}$ | 0.42 $m^3\ h^{-1}$ |
| Oxygen production rate | 21 $m^3\ h^{-1}$ | 0.21 $m^3\ h^{-1}$ |
| Hydrogen gas purity | $H_2 > 99.5\%$ | $H_2 > 99.995\%$ |
| Oxygen gas purity | $O_2 > 99\%$ | $O_2 > 99\%$ |
| Demineralized water conductivity | N/A | k < 0.25 S $cm^{-1}$ |

### 2.1.4 Solid oxide electrolysis cells (SOEC)

The key components of an SOEC are a dense ionic conducting electrolyte and two porous electrodes. The fundamental mechanisms involved in SOEC operation are shown in Figure 3. [24] Water at the cathode combines with electrons from the external circuit to form hydrogen gas and negatively charged oxygen ions [25]. The oxygen ions pass through the solid ceramic membrane and react at the anode to form oxygen gas and generate electrons for the external circuit. Advantages for high temperature electrolysis with a solid oxide based electrolyzer include: the use of a solid electrolyte, which, unlike KOH for alkaline systems, is non-corrosive and it does not experience any liquid and flow distribution problems [25,45].

Operating at high temperature, the SOEC components must meet certain requirements for efficient and cost-effective hydrogen production such as: (1) "the dense electrolyte should be chemically stable and have good ionic conductivity with low electronic conduction to achieve high energy conversion efficiency because the presence of electronic conduction will lower the ionic conduction of the electrolyte and current efficiencies of the cell." [24] (2) "The dense electrolyte must be gastight to eliminate any possibility of recombination of $H_2$ and $O_2$, but it should be as thin as possible to minimize the ohmic overpotential" [24]. (3) "The thermal expansion coefficients of both electrodes should be close to that of the electrolyte to prevent material failure of the electrolyte due to exceedingly high mechanical stress induced by thermal expansion mismatch." [24] (4) "Interconnect materials are needed in large-scale hydrogen production plant." (5) "The cost of the raw materials and the manufacturing cost should be as low as possible." [24]

High temperature electrolysis efficiency is dependent on the temperature and the thermal source. The efficiency as a function of electrical input alone can be very high with efficiencies 85-90% being report [21]. However, when the thermal source is included the efficiencies can drop significantly (down to about 40-60% efficiency) [25,45].

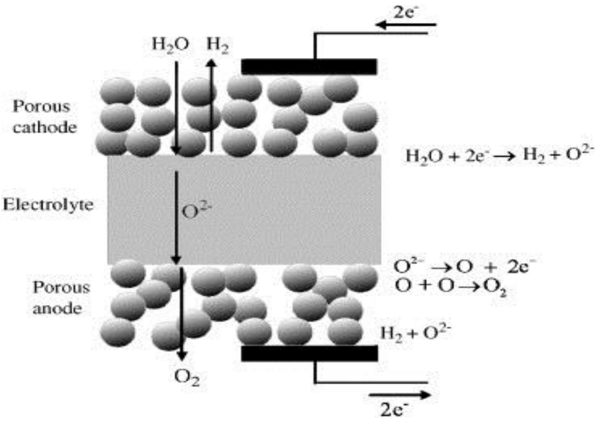

**Figure 3.** Schematics of SOEC hydrogen production [24]

### 2.2 Comparing electrolysis methods

SOEC electrolyzers are the most electrically efficient, but are the least developed of the technologies. SOEC technology has challenges with corrosion, seals, thermal cycling, and chrome migration [26,45]. PEM electrolyzers are more efficient than alkaline, do not have the corrosion and seal issues that SOEC, but cost more than alkaline systems [27,45]. Alkaline systems are the most developed and lowest in capital cost. They have the lowest efficiency so they have the highest electrical energy costs [15]. Adding ionic activators to alkaline electrolytes or using ionic liquid/water electrolyte improve the electrocatalytic activity and stability of electrodes [11]. Electrolyzers are not only capable of producing high purity hydrogen, but recently, high-pressure units are being developed [28]. Currently, electrolysis is more expensive than using large-scale fuel processing techniques to produce hydrogen. And, if non-renewable power generation is used to make the electricity for electrolysis, it actually results in higher emissions compared to natural gas reforming [29]. Several different approaches have been proposed to address these shortcomings. These include renewable sources of energy such as solar, wind, and hydro, to produce the electricity [29,45], or excess power from existing generators to produce hydrogen during off-peak times [30,45], and high temperature electrolysis. There have been several studies on the cost of using renewable energy for electrolysis, all reaching the conclusion that as the cost of natural gas increases renewable energy will become economically competitive at central production facilities as well as at distributed generation points especially if carbon dioxide and other pollutants are included in the analysis [31, 32,45].

**Table 2.** Comparison of different electrolyzer technologies [15]

| Technology | Efficiency | Maturity |
|---|---|---|
| Alkaline electrolyzer | 59-70% | Commercial |
| PEM electrolyzer | 65-82% | Near term |
| Solid oxide electrolysis cells | 85-90% | Mediate term |

### 3. PHOTOELECTROLYSIS AND PHOTOELECTROCHEMICAL (PEC)

In the PEC process, solar energy is converted into chemical energy in the form of hydrogen through photoelectrolysis by using sunlight to directly decompose water into hydrogen and oxygen, and uses semiconductor materials. [33] This is similar to photovoltaics, where two doped semiconductor materials are brought together forming a p-n junction [34] Different semiconductors work at particular wavelengths of light and energies. "PEC is considered to be one of the most promising technologies for hydrogen production as it is based on perpetual solar energy, is environmentally safe and can be used on both large as well as small scales and the technology is uncomplicated" [33]. To capture sufficient solar radiation to generate electric potential, the sunlight absorbing electrode must be arranged to face the sunlight window and wired externally or internally with the counter electrode to form a closed circuit. [35] At the junction, a permanent electric field is formed when the charges in the p- and n-type of material rearrange [24, 36,45]. The reaction mechanism below shows how the usage of electricity splits the water molecule by an imposed electric potential [35]:

$$2H_2O(l) = O_2(g) + 4H^+(aq) + 4e^-, \phi A \qquad (7)$$

$$= 1.23\,V\ on\ surface\ of\ anode\ (oxidation)$$

$$2H^+(aq) + 2e^- = H_2(g), \phi C \qquad (8)$$

$$= 0.00\,V\ on\ surface\ of\ cathode\ (reduction)$$

where 1.23 V is the standard potential of the anode that indicates the theoretical minimum requirement. The sunlight absorbing material has a prominent role in determining the hydrogen production efficiency. The potential created by the electrode material must exceed the bottom theoretical limit of 1.23 eV to split water molecules, plus overcoming the electric resistance of the closed circuit. [35]

"The process can be summarized for a photoanode-based system as follows: (1) a photon with greater energy than the bandgap strikes the anode creating an electron-hole pair. (2) The holes decompose water at the anode's front surface to form hydrogen ions and gaseous oxygen, while the electrons flow through the back of the anode which is electrically connected to the cathode. (3) The hydrogen ions pass through the electrolyte and react with the electrons at the cathode to form hydrogen gas. (4) The oxygen and hydrogen gasses are separated, for example by the use of a semi-permeable membrane, for processing and storage." [24,36,45]

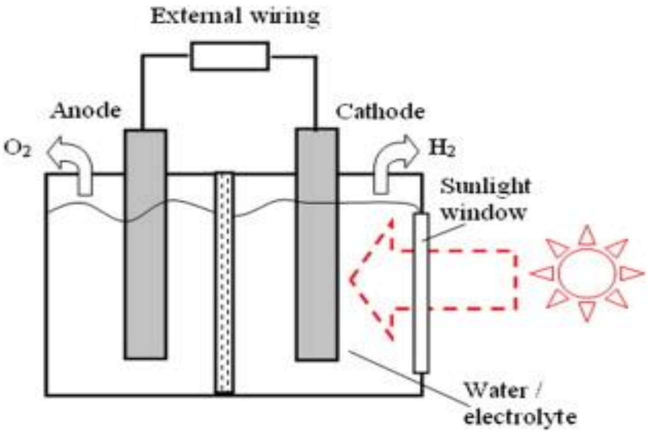

**Figure 4:** Components of a photoelectrolysis or photochemical unit [35]

The hydrogen production efficiency is generally limited by imperfections in the crystalline structure, bulk and surface properties of the photoelectrodes, the material's resistance to corrosion from the aqueous electrolytes, and the ability to drive the water decomposition reactions [37,45].

In order to maximize the efficiency of this process, the energetics of the electrochemical reaction must be harmonized with the solar radiation spectrum, which is a non-trivial problem. A mismatch of the solar radiation and materials can produce photo-generated holes that can cause surface oxidations leading to either a blocking layer on the semiconductor surface or corrosion of the electrode via dissolution [24,36,45]. Current photoelectrodes used in PEC that are stable in aqueous solutions have a low efficiency for using photons to split water to produce hydrogen. The target efficiency is >16% solar energy to hydrogen.

To achieve the highest efficiency possible in a tandem configuration, "current matching" of the photoelectrodes must be done. Electron transfer catalysts and other surface enhancements may be used to increase the efficiency of the system. These enhancements can minimize the surface over-potentials in relationship to the water and facilitate the reaction kinetics, decreasing the electric losses in the system. Fundamental research is ongoing to understand the mechanisms involved and to discover and/develop appropriate candidate surface catalysts for these systems [38,45]. In addition to semiconductor devices for photoelectrolysis, it is possible to use suspended metal complexes in solution as the photochemical catalysts [36,39,45]. Typically, nanoparticles of ZnO, $Nb_2O_5$, and $TiO_2$ (the material of choice) have been used [20,31,45]. Two of the most promising dyes are the N3 dye and the Black dye [39,45]. The advantages of these systems include the use of low cost materials and the potential for high efficiencies [39,45].

In comparison with water electrolysis, the production of hydrogen and oxygen is more challenging for the photoelectrolysis or photochemical processes. It is more difficult for the photochemical unit to efficiently track the sun because of the structure and operating complexity of the equipment. [35] Say if the equipment is tilted, this may affect the efficient sunlight tracking as the contact between an electrode and water may be changed. "The lack of a combination of a stable, efficient light absorption system consisting of suitable photoelectrodes and light windows partly accounts for the low efficiency. [35] Current research involves overcoming the low light absorption and unsatisfactory stability in time for these systems [37,45].

## 5. THERMOCHEMICAL REACTIONS

The thermochemical water splitting processes promise to produce hydrogen and oxygen from water and heat without using electricity. This process is also called high temperature water splitting process where the chemical reactions are driven by high temperature heat in the range of 500-2000 ℃. [33,40]

Carrying the reaction out using a series of chemical transformations can reduce the temperature. The reaction systems are assembled to use water as the only input and have hydrogen as the only output. Ideally, all other chemicals are recycled with minimal loss within the process. The following examples illustrate the principle [41,45]:

Thermolysis:

$$H_2O(g) = H_2(g) + \left(\frac{1}{2}\right) O_2(g), T > 2500\,K \qquad (7)$$

Zinc-zinc oxide:

$$ZnO = Zn + \left(\frac{1}{2}\right) O_2(g),\ T = 2473\,K \qquad (8)$$

$$Zn + H_2O(g) = ZnO + H_2(g),\ T = 900\ K \tag{9}$$

Nickel-manganese ferrite:

$$NiMnFe_4O_6 + 2\mathrm{H}_2O(g) = NiMnFe_4O_8 + 2H_2(g), \\ T = 1073\ K \tag{10}$$

$$NiMnFe_4O_8 + NiMnFe_4O_6 + O_2(g), T = 1273\ K \tag{11}$$

Sulfur-iodine:

$$H_2SO_4(g) = SO_2(g) + H_2O(g) + \left(\frac{1}{2}\right) O_2(g),\ T = 1123 \tag{12}$$

$$2HI(g) = H_2(g) + I_2(g), T = 573\ K \tag{13}$$

$$I_2(aq) + SO_2(g) + 2H_2O = 2HI(aq) + H_2SO_4(aq), \\ T = 373\ K \tag{14}$$

The basis for using multistep closed-cycle chemical processes to reduce the temperature required for thermal water-splitting has been the subject of numerous articles [32,45].

“In choosing the process there are five criteria, which should be met [20]. (1) Within the temperatures considered, the $\boldsymbol{\Delta G}$ of the individual reactions must approach zero. This is the most important criterion. (2) The number of steps should be minimal. (3) Each individual step must have both fast reaction rates and rates which are similar to the other steps in the process. (4) The reaction products cannot result in chemical-by-products, and any separation of the reaction products must

**Table 3.** Summary of the characteristics of various solar-to-hydrogen technologies [24]

| Methods | Water electrolysis | Photoelectrolysis | Photochemical | Thermochemical |
|---|---|---|---|---|
| Reaction mechanism | **Potential** | **Potential** | **Photon-activated electrons** | **Thermal splitting** |
| Form of energy input | **Electricity** | **Electricity** | **Photon** | **Thermal** |
| Whether or not the $H_2$ production unit mist be constructed together with the solar energy capturing device | **No** | **Yes** | **Yes** | **No** |
| External or internal energy supply | **External** | **Internal** | **Internal** | **External** |
| Basic components for engineering apparatus | **2 electrodes and electrolyte** | **2 electrodes and electrolyte, and sunlight window** | **At least 1 sensitizer at least 1 catalyst, and sunlight window** | **More than 3 thermal reactors** |
| $H_2$ and $O_2$ produced separately or in mixture | **Separately** | **Mix** | **Mix** | **Separately** |
| Overall production efficiency | **30%** | **16%** | **10%** | **45%** |
| Suitable for large scale production or fueling stations | **Medium scale and fueling station depends on production scale** | **Fueling station** | **Fueling station** | **Large scale** |
| Additional hydrogen distribution network | **Depends on production scale** | **Not necessarily** | **Not necessarily** | **Needed** |

be minimal in terms of cost and energy consumption. (5) Intermediate products must be easily handled [36].” [45]

There may be processes that meet the five criteria [36,45], however, they are still not competitive with other hydrogen generation technologies in terms of cost and efficiency, which is the major focus of research in those processes [36]. In addition, these processes require large inventories of highly hazardous corrosive materials. The combination of high temperatures, high pressures, and corrosion results in the need for new material.

It is believed that scaling up the processes may lead to improved thermal efficiency overcoming one of the principle challenges faced by this technology [43,45]. However, this might not be economically feasible. In addition, a better understanding of the relationship between capital costs, thermodynamic losses, and process thermal efficiency may lead to decreased hydrogen production costs [43,45]. The current processes all use four or more reactions, and it is believed that an efficient two-reaction process may make this technology viable [43]. Improvements are currently needed for materials, lowering cost and increasing efficiency [43,45]. The current overall efficiencies are believed to be close to 45-50% achievable by using these processes [43,45].

Below in table 3 shows a summary of the characteristics of various solar-to-hydrogen technologies.

## 6. CONCLUSION

In conclusion, hydrogen can be produced from the renewable energy resources and water by a variety of processes (electrolysis, photolysis, photoelectrochemical and thermochemical). Electrolysis of water is the simplest technology for producing hydrogen. The electrolytic technology of hydrogen is currently the only way to produce large quantities of hydrogen without emitting the traditional by-products associated with fossil fuels. Solar energy can be used to produce hydrogen in the form of heat (thermochemical), light (photochemical), or electricity (electrolysis). Solar energy collected as heat, may be the most efficient solar path to hydrogen from water since it does not have the inefficiencies associated with photochemical transformations or the conversion of solar energy to electricity followed by electrolysis. The weaknesses of these economic evaluations are related primarily to the uncertainties in the viable efficiencies and investment costs of the various components due to their early stage of development and their economy of scale. Further development and large-scale demonstration are warranted. For the developed countries the emergence of extra water demand for hydrogen production is unlikely to be critical.

The projected annual demand for hydrogen generation is estimated at 150 Mtonnes/year, which is equivalent to 100 billion gallons of water/year. As domestic water usage in the US is around 4800 billion gallons/year and conventional power generation is 70 trillion, the amount needed for hydrogen generation would not be a significant perturbation [44].

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### ABBREVIATIONS

Proton exchange membrane (PEM) electrolysis, Solid oxide electrolysis cells (SOEC)

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# How current hydrogen producing fuel cells show promise of a green, zero-emission energy generation

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*KEYWORDS: Solar-to-fuel cells, artificial photosynthesis, water splitting, photoelectrochemical cell, hydrogen evolution catalyst, oxygen-evolving complex*

**ABSTRACT:** Society has never been more concerned about our limited fossil fuel reserves. One possible solution is artificial photosynthesis, which has the potential to meet our substantial energy consumption without excessive and unrealistic investment in infrastructure. Most research is devoted to splitting water into hydrogen and oxygen because the only byproduct of hydrogen fuel is water. Artificial photosynthesis is a very active field of research though it is mostly focused on improving particular processes rather than developing fully functioning solar-to-fuel cells. The fuel cells that have been built recently have shown significant promise as they do split water into hydrogen and oxygen effectively, however their efficiency is far too low. Furthermore, once efficient solar-to-fuel cells have been developed, they need to be scaled up and robust enough to be commercially viable which is potentially just as challenging. There is definitely no set time frame for industrial scale fuel cells but it is quite improbable that they will be a reality in the next couple of decades.

## 1. INTRODUCTION

One of the great challenges for our society in the near future is our growing global consumption of energy which has led to global warming and the rapid depletion of unsustainable fuel reserves, namely fossil fuels.[1,2] There are a numerous environmental concerns associated with fossil fuels, chiefly carbon dioxide emissions into the atmosphere, which is widely considered the cause global warming.[3] As a result, there is extensive research dedicated to finding sustainable energy sources.[4] Current renewable sources are hydroelectric, geothermal, wind and solar power which have public opinion divided over their ability to meet our current and future energy demands.[5] The majority of the public do believe that our energy needs can be met by renewable energy sources.[6] The biggest challenge for renewable energy is economic viability with the media highlighting the substantial cost of government subsidies.[7] Another issue is the conflicting estimates and calculation of cost for renewable energy, which kindles existing public doubt.[8]

It is estimated that the annual energy consumption of the global population is equivalent to the energy captured in one hour by biological processes from sunlight.[9] Solar power is the broad term used to describe harnessing this energy. Predominant methods include the use of photovoltaic cells to directly convert sunlight to electricity or solar thermal methods involving focusing large quantities of light on a highly absorptive heat engine. Unfortunately, these methods suffer from low efficiency (<30% for industrial methods),[10] meaning large losses of potentially useful energy. Additionally, there are no suitable methods to store large quantities of electricity, thus far. Ideally, we would produce a fuel so we could easily transport, store and use large quantities of energy.[11] Another proposal is to replace fossil fuels with biofuels, indirectly harnessing the power of the sun through plants. Biofuels were initially viewed as sustainable and environmentally friendly.[12] However, subsequent studies on the environmental consequences of biofuels have altered how they are viewed.[13] Biofuels have been shown to have significant detrimental effects on the environment, such as carbon dioxide emissions and the current limitations of biorefinery.[14] Presently, they are generally considered a good option in the short term to decrease our dependence on fossil fuels but they are not a long-term solution without significant technological advances.

Photosynthesis is the process that nature has been refining over billions of years to harness the power of the sun.[15] The Italian scientist, Giacomo Ciamician, was the first to propose the idea artificial photosynthesis in 1912,[16] foreseeing the energy problems we now face. Without sufficiently advanced chemistry there were no breakthroughs until the discovery of the Honda-Fujishima effect in 1972, providing the first example of water photolysis.[17] But, it is only in the last 5 years that artificial photosynthesis has been researched in ardor.[18]

Natural photosynthesis is the ultimate 'green' energy production method consuming carbon dioxide and producing easily applied energy in the form of sugars. While photosynthesis is the process of converting sunlight, water and carbon dioxide into carbohydrates and oxygen specifically, artificial photosynthesis encompasses any process that uses sunlight to store energy in the chemical bonds of a fuel.[18b,19] There are two different but complementary goals of artificial photosynthesis.[20] The first involves the photolysis of water, the use of light to dissociate water into hydrogen ($H_2$) and oxygen ($O_2$) in a photoelectrochemical cell. Hydrogen is the fuel produced with this method. The other is the photochemical reduction of carbon to produce higher energy carbon-based fuels, generally methanol, ethanol or formic acid. Most research is focused on water splitting since hydrogen is a cleaner fuel than the hydrocarbons, only producing water as a byproduct opposed to carbon dioxide. Additionally, hydrogen fuel is more energy dense than traditional fuels.[21] This means it requires less storage space and is easier to transport.

## 2. NATURAL PHOTOSYNTHESIS

Oxygenic photosynthesis is the most effective known process to convert sunlight into applicable, productive energy. The two most interesting components for the design of 'artificial leaves' are photosystems II and I (PSII & I), shown in figure 1. Photosystems are large pigment proteins that are responsible for the photochemical reactions that drive photosynthesis.[18a] Photosynthesis begins at photosystem II, which absorbs 4 photons of red light with a variety of pigments (mostly chlorophylls) and excites pigments' electrons. The electron energy is passed through to the reaction centre where the charge separation occurs. This leads to the reduction plastoquinone to plastoquinol and the oxidization of water to produce 4 protons and oxygen (scheme 1).[22]

$$2H_2O \xrightarrow{4\mathit{h}\mathrm{u}} O_2 + 4H^+ + 4e^-$$

Scheme 1 – the oxidation water half-reaction

The electrons get transferred through cytochrome $b_6f$ from the plastoquinol to photosystem I where they are excited by another 4 red photons to a higher energy state. The electrons combine with the potential gradient of protons to reduce NADP to NADPH and drive the thylalkoid-bound ATP synthase to chemiosmotically produce ATP.[23] The electron transport chain that the electrons are transferred through is the initiator of the chemiosmotic potential across the thylakoid membrane; it is often called the Z-scheme. NADPH and ATP can then reduce carbon dioxide into carbohydrates in the 'dark' (light independent) reactions of oxygenic photosynthesis (scheme 2).

$$CO_2 + 4H^+ + 4e^- \xrightarrow{4\mathit{h}\mathrm{u}} (H_2CO) + H_2O$$

**Scheme 2 – the reduction of $CO_2$ to carbohydrates half-reaction**

While photosynthesis is a highly intricate and effective process for providing plants with the energy they require, the conversion rates of light to storable energy in the form of sugars is only around 4.5% by most calculations.[24] In fact, it is believed that plants only achieve around 1-2% conversion.[24] The current global energy consumption means that we must build artificial leaves with far better yields in order to support our needs. However, many of the individual reactions in photosynthesis are exceedingly efficient and serve as good models for future photosynthetic devices, especially photosystems I & II.

Both photosystems have a similar structure; they are light-harvesting complexes made up of numerous pigments coupled to a reaction centre where charge separation occurs.[18c,25,26] The charge can then be applied to perform the pertinent oxidations and reductions. It is this arrangement that researchers use as a blueprint in their design of artificial systems. Although considerable research has been done on solar fuel cells, few have ever been constructed. This paper shall give an overview of existing solar fuel cells and the advances made in solar fuel cell technology over the last 30 years.

## 3. COMPLETE SOLAR FUEL CELLS

There have been only a small number of attempts to build complete solar-to-fuel cells. The majority of research is still devoted to improving the individual processes that would be applied in future cells, since they are still considerably short of the standards required to build a commercially viable fuel cell. However, those cells that have been created provide a useful insight into the most pressing processes that need to be improved and illustrate how close we are to constructing fully operational and scalable solar fuel cells.

### 3.1 Inorganic Solar Fuel Cells

Oxygen evolving complexes (OECs) are a key feature required for water splitting in photosynthesis that all artificial systems include. Nocera et al. made a meaningful step towards developing a commercially viable artificial leaf when they discovered that certain artificial oxygen-evolving complexes (OECs) can be self-repairing if they are formed in situ.[27] This imitates the self-repair mechanisms that occurs in natural photosynthetic systems with proteases, which repair and remove the oxidatively damaged constituents of PSII.[28] The first artificial OEC that demonstrated self-repairing behaviour is a $Co^{2+}$ and phosphate aqueous solution. The explanation is that the $Co^{2+}$ and phosphate are in equilibrium so cobaltate ions will reform after it has been oxidized. Cobalt and phosphate are not the only pairing that exhibit this behaviour, another example is nickel-borate.[29] This discovery is important in addressing the photodegradation present in systems using PSII and most other catalysts.[30] Furthermore since the Co-OEC catalyst operates in neutral water, simple hydrogen evolution reaction (HER) catalysts can be used in place of platinum, for example NiMoZn, which can achieve current densities as high as 1000 mA $cm^{-2}$.[31]

Nocera et al. were also involved in the development of the first standalone water splitting cell in 2011 with 3 amorphous silicon solar cells.[32] The solar cells were packed in with a triple junction and interfaced with the Co-OEC and NiMoZn catalyst. The system managed to produce 8mA $cm^{-2}$ with 1.8V under 100 mW $cm^{-2}$ illumination giving an efficiency of 6.2%. Overall solar-to-fuel efficiencies (SFE) of 4.7% were obtained using Si solar cells with 7.7% efficiency. These results compare favourably to Si photovoltaic (PV) cells, which have a 6% SFE. Even, the most efficient (and expensive) PV cells only have solar-to-fuel efficiencies up to 18%[33] and these water-splitting cells have yet to test using more efficient solar cells.

These cells are entirely artificial and inorganic negating the photodegradation concerns of using PSII, however the Co-OEC is not nearly as efficient as PSII. These cells would be a very green way to produce fuel if their efficiencies were competitive with other energy production methods. The most prevalent environmental concern with this set-up is the scarcity of molybdenum, as it is a relatively rare metal.[34] Similarly, zinc could be problematic in the future as well. However, nickel and cobalt are two of the most abundant metals.[34] In comparison to other fuel production methods the environmental cost of these metals is small. Other methods either produce carbon dioxide or require batteries that use far larger quantities of limited and toxic chemicals including metals. Thus, the phosphate and silicon cells can be regarded as ecologically friendly, in relative terms.

*Oxidation of water*

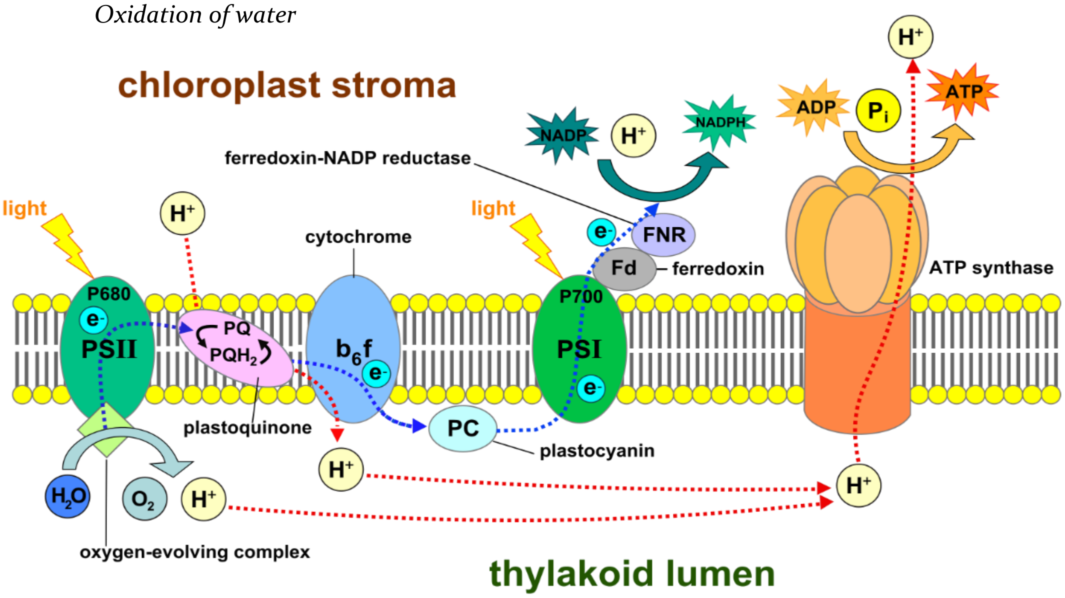

Figure 1 – "*Light-dependent reactions of photosynthesis in the thylakoid membrane of plant cells.*" by somepics is licensed under CC BY 4.0

### 3.2 Biovoltaic Cells

One of the closest attempts to replicating natural photosynthesis is the biovoltaic cell constructed by Kothe et al.[35] The group had previously published papers on the individual half-cells they developed using PSI in the photoanode[36] and PSII in the photocathode.[37] The authors noted that the half-cells had severe deficiencies. The electrons provided by PSII could not be directly applied in $H_2$ evolution as they were insufficiently energized. The photoanode, on the other hand, either needed an external potential to be applied or sacrificial electron donors to be able to reduce the desired electron acceptors. Subsequently, the group managed to couple the half-cells, in doing so, closely replicating the Z-scheme. The semi-artificial photoelectrochemical cell (PEC) operated as a closed system with no sacrificial electron donors or acceptors. This is a very significant step towards sustainable PECs that have a net energetic output. When the cell was exposed to red photons, the PSII oxidized the water to oxygen and simultaneously the PSI reduced the oxygen. PSI cannot reduce oxygen directly so methyl vi0logen (MV) gets reduced by PSI and then regenerates by reducing oxygen. The photocathode has the same half-reaction as scheme 1. The photoanode however, follows reaction scheme 3.

$$MV^{2+} + e^{-} \xrightarrow{hu} MV^{+}\cdot$$

$$MV^{+} + O_2 \longrightarrow O_2^{-}\cdot$$

$$O_2^{-} + 4H^{+} \longrightarrow 2H_2O$$

Scheme 3 – the half-reaction occurring at the photoanode of the biovoltaic cell developed by Kothe et al.[35]

Interestingly, the hydrogels connecting PSI and PSII to their electrodes need different redox potentials in order to follow the Z-scheme.

The electrical power output of the photobiovoltaic cell is very low. The limiting factors are the photocurrent density in the half-cells and the potential between the redox hydrogels. While this PEC is far from the performance required for commercial applications, it is notable for mimicking of the Z-scheme using both photosystems. Additionally, since the half-cells are separate, oxygen-sensitive biocatalysts such as nitrogenase and hydrogenase can feasibly be coupled to PSI, potentially increasing the $H_2$ production immensely. Other plans to improve upon this design are to implement hydrogels with more appropriate potentials in order to increase the power output by raising the cell voltage and current density.

The photobiovoltaic cell is a largely green system since most of thee components are directly extracted from plants themselves; however, there would be the cost of farming the plants from which the photosystems are obtained. But it would be trivial in comparison to the energy gained from a cell that is moderately efficient and robust. Methyl viologen is a toxic chemical, but there should be no human exposure during operation and relatively little methyl viologen is needed since it is a regenerating catalyst.[38] Harmful chemicals including pyridine and chloroform are used in its synthesis and disposal through incineration does lead to gases such as carbon dioxide, nitrogen oxides and hydrogen chloride. This system is far from ideal but in comparison to current and alternative methods it is relatively ecologically friendly. Furthermore, future research could find a much more sustainable catalyst, which could make this method a very 'green' way to generate fuel.

### 3.3 Inorganic Hybrid Cells

Another approach is to use hybrid systems to perform solar overall water splitting (OWS). It is the oxidation of water by PSII that is the truly remarkable activity of natural photosynthesis, reaching a maximum thermodynamic efficiency of 70%.[18a] In consequence, researchers have created solar cells using PSII and artificial photocatalysts to reduce the protons to hydrogen. Wang et al. had significant success in 2014, developing a photosystem that reached activity of about 2,489 mol $H_2$ (mol PSII)$^{-1}$h$^{-1}$ under visible light irradiation.[39] The cell also achieved OWS under solar irradiation outdoors, indicating its potential for future industrial implementation. The basic set-up was PSII absorbed the light and oxidized water. The resulting electrons were shuttled through $Fe(CN)_6^{3-}$/ $Fe(CN)_6^{4-}$ to the artificial photocatalyst in an aqueous solution. Two typical semi-conductors (CdS and $SrTiO_3$:Rh) were used as a basis to prepare the photocatalysts ($Ru_2S_3$/CdS and Ru/$SrTiO_3$:Rh) tested in this study. These were chosen because they possess continuous absorption spectra that are partly complementary to PSII absorption. A self-assembly approach was used in order to link the photosystem and photocatalyst. The $Ru_2S_3$/CdS photocatalyst achieved a OWS activity of 411 mol $H_2$ (mol PSII)$^{-1}$h$^{-1}$, however the maximum OWS activity of Ru/$SrTiO_3$:Rh was 2,489 mol $H_2$ (mol PSII)$^{-1}$h$^{-1}$. Since the $O_2$ evolution activity was much lower for the $Ru_2S_3$/CdS system, it suggests that the difference in OWS activity is due to $Ru_2S_3$/CdS causing conformational changes in PSII. Both reactions had a stoichiometric ratio for $H_2$:$O_2$ of 2:1 indicating that electron transfer through the Fe complex was effective. The high OWS activity of Ru/$SrTiO_3$:Rh is comparable to the estimated turnover of just PSII, around 3,751 mol $H_2$ h$^{-1}$, which suggests that PSII can be stable in a hybrid system. It is worth noting that all the reactions were conducted in mild conditions but the OWS activity for both photocatalysts declined much more quickly over 2 hours when the pH was raised from 6 to 7.

The principal problem with this hybrid system is that it suffers significant deterioration after a few hours of exposure to light. The inorganic photocatalysts are known to be stable over several hours[40] so it must be the PSII that degrades. Investigations are needed to find a method to stabilize PSII, so that it can endure the photo-oxidative stress it faces under irradiation, and suppress singlet oxygen radical side reactions.

Overall, this system is relatively productive and clearly demonstrates the possibility of PSII-inorganic photocatalyst hybrid cells. Problematically it does involve the rare metals: ruthenium, rhodium and cadmium. It could be justifiable since large amounts of $H_2$ would be produced from nanoscopic amounts of metal. Iron is not environmentally benign but the iron can be recycled preventing significant environmental consequence. Cyanide, however, is toxic to humans and, more acutely, to aquatic life.[41] Cyanide is essentially environmentally benign if it disposed of through thermal hydrolysis with the byproduct being formate and ammonia. Of course any spills will still be very harmful to the environmental. PSII again will be extracted from plants but the cost should be worth it provided the PSII does not degrade quickly.

## 4. CONCLUSION

Three fundamentally different types solar-to-fuel cells were examined in this paper, completely artificial, hybrid and biovoltaic. Completely artificial cells are appealing because the issue of photolytic degradation of PS I and II can be avoided. However, there is no known oxygen-evolving complex that can achieve the thermodynamic efficiency of PSII. Nocera et al. did create inorganic cells that produced hydrogen,[32] but its SFE needs to be improved as well as scalability of it. The most biological approach is using the components used in natural photosynthesis using both PS I and II. The principal issue is preventing photodegradation of PS I and II. Kothe et al. did manage to stabilize the photosystems for a couple of hours and use them in a functional cell,[35] of course the lifetime of the photosystems needs to be vastly improved before biovoltaic cells can be considered for industrial use. Finally, hybrid systems try to integrate the most advantageous qualities of both natural and artificial components of solar-to-fuel cells. The challenge is then to interface the two systems in an efficient manner and deal with the respective weaknesses of the components involved. Wang et al. developed functional water splitting systems but there are still numerous issues, predominantly stabilising PSII.[39]

If we make the assumption that these systems are fairly robust and efficient then the biovoltaic cell would be the 'greenest' option because all the necessary reagents are renewable. Methyl viologen can be synthesised from biomass and plenty of plants can be farmed for generating photosystems. Inorganic solar-to-fuel cells are a pretty appealing option, with the limited supplies of molybdenum and zinc the only significant trepidations. The hybrid system does have serious concerns with the various rare metals, however there is promise because the metals could quite possibly be replaced with 'greener' and more abundant options.

## 5. FUTURE OUTLOOK

These cells show a lot of promise but have a lot of hurdles to overcome. Progress has been slow but steady since the discovery of the Honda-Fujishima effect and with society's growing concern for future fuel production the attention and research in the area will only increase.

The most pressing caveat is that these systems are not robust, scalable or sufficiently productive. It is sensible to expect that, in the future, similar systems will be commercially viable. These cells demonstrate that there would relatively little environmental cost compared to the benefits and they will most likely use 'greener' chemicals anyhow. With regards to portable fuel, these processes are dependent on effective and 'green' hydrogen fuel cells being available. However, since current fuel cells are already sufficiently effective to be used commercially, it reasonable to assume that 'green' hydrogen fuel cells will be available afore artificial photosynthesis can produce hydrogen on an industrial scale.

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# A Methanol Economy based on Renewable Resources

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KEYWORDS: Methanol Economy, Methanol, Carbon Dioxide, Electrolysis

**ABSTRACT:** The current world reliance on fossil fuels is unsustainable and poses serious environmental consequences. Renewable energy technologies in the form of wind, solar, hydroelectric, and geothermal have proven to be effective alternatives, yet lack a method of convenient energy storage. Storing this energy in the form of methanol by conversion of $CO_2$ has proven to be commercially viable. Current methods of production of methanol and $CO_2$ capture are outlined and the argument for a methanol economy propounded.

## 1. INTRODUCTION

While great strides in the advancement of human societies have been made possible from the abundance of energy in fossil fuels, the world's dependence on this non-renewable resource is becoming increasingly detrimental. More than 80% of the world's energy consumption comes from fossil fuels, and while recent discovery and exploitation of unconventional resources such as shale gas have lowered the price and extended their foreseeable lifetime, their depletion is inevitable.[1] Besides the finite availability of fossil fuels, there are many other associated issues that arise from their use such as the emission of $SO_2$, $NO_x$, volatile organic compounds (VOCs), carbon monoxide, and particulate matter, each having deleterious environmental effects.[2] The rate at which fossil fuels are being consumed has surpassed the natural carbon cycle, causing an accumulation of $CO_2$ in the atmosphere.[2] This accumulation of a greenhouse gas is widely considered as playing a major part in climate change and global warming.[2] The exploitation of fossil fuels since the Industrial Revolution has allowed the unprecedented development of human society, but it is imperative that we now turn our gaze to more sustainable methods of energy production and lead the way for a Green Revolution.

Many methods currently exist for the production of renewable energy – solar, wind, hydroelectric, geothermal. Primarily these methods are used to generate electricity. A major drawback in this type of energy production is that electric power needs to be scaled to follow the demand on the electrical grid.[3] Furthermore, solar and wind power are highly variable. Regional solar flux, cloudy conditions, and daylight hours are large limitations for solar energy. Variable wind conditions and consistency also pose a problem. Therefore a more convenient way of storing this energy must be realized in order for renewable energy to be viable.

One method of storing this energy would be to convert it to methanol, as proposed by proponents of a Methanol Economy in which this molecule is used for fuel and raw material.[4] In this paper, the argument for such a Methanol Economy is put forth and outlines the methods of converting $CO_2$ to methanol.

## 2. HYDROGEN ECONOMY

One of the proposed methods of storing renewable energy is in the form of hydrogen gas, $H_2$. This would be primarily accomplished through the electrolysis of water to yield oxygen and hydrogen gas. The resulting combustion of $H_2$ would yield water (eqn. (1)).

$$2H_2O \rightarrow 2H_2 + O_2 \qquad (1)$$

This method is attractive in the sense that it is clean, with no production of $CO_2$ or other hazardous compounds[5]. Proponents of this method point to a potential Hydrogen Economy, whereby this process provides energy for transportation and industry.[3-4] However, serious limitations exist with this method. While $H_2$ has one of the highest energy densities per unit mass, its energy per unit volume is very low.[3-5] This poses a problem especially for mobile applications, such as the transportation sector, where the volume must not be exceedingly large. In order for $H_2$ to be feasible as an energy source in vehicles, it must be contained in a small enough volume so as to be practical to be transported. Two methods of accomplishing this, compression and liquefaction, are highly energy intensive, and would cost around 20-40% of the intrinsic energy value of the initial gas, respectively.[3-5] As a gas, high pressures are needed, while very low temperatures are required for liquefaction.[3-5] Furthermore, $H_2$ is inflammable and explosive, further complicating its ability to be safely[3-5]. In addition to these barriers, $H_2$ has the ability to escape through solid metal pipes and embrittle metals.[3-5]

In light of these drawbacks, much effort has been placed into finding alternatives to $H_2$ storage. Among these are material based storage methods such as absorbents and metal hydrides.[6] Among the physical adsorption methods are Metal Organic Frameworks (MOFs), Covalent Organic Frameworks (COFs), Polymers with Intrinsic Microporosity (PIMs), and zeolites.[7] These mediums rely primarily on Van-der-Waals forces for adsorption.[7] While there is potential for these mediums, they are currently limited by low temperatures or high pressures needed for significant adsorption.[6-8] Metal hydrides have been an active area of research for $H_2$ storage. The current challenges facing this medium are due to their weight and low $H_2$ density per unit mass.[6-7] Additional complications exist such as their exothermic absorption process, which would necessitate removal of heat upon refueling, expansion upon refueling creating stress upon the container, long refueling times, and with certain metal hydrides such as $AlH_3$ complicated syntheses.[6-7] Coupled with these challenges is the fact that no infrastructure currently exists for $H_2$, and the cost to develop one would be enormous.[3-4]

Considering the challenges associated with the use of $H_2$ as a fuel - the inherent hazards, physical properties, storage methods, the time and cost of creating an infrastructure and distribution, it would be more practical to use methanol as a storage medium. The potential for $H_2$ as a fuel holds potential, and may be a viable source of energy in the future. However the rate of climate change and global warming demands an immediate solution. Thus it is far more sensible to implement a Methanol Economy, wherein the inherent challenges are not only far less formidable, but has proven to be commercially viable.

## 3. METHANOL ECONOMY

In light of the challenges faced with a Hydrogen Economy, proponents such as Nobel Prize recipient George Olah have advocated a Methanol Economy in its stead.[3-4] Being a stable liquid, methanol would be much more preferable than dealing with the complications of a pressurized gas or super-cooled liquid.[3-4] The existing infrastructure for gasoline would only need to be modified in order to accommodate methanol, as opposed to being built from the ground up.[3-4] While methanol's volumetric energy density is only 50% that of gasoline, it is nearly triple that of $H_2$.[3-5] Additionally, methanol burns cleaner than gasoline, and has lower $CO_2$ emissions.[3-4] The argument for a Methanol Economy is based on its practicality, and its ability to be incorporated on a relatively short timescale. While using $H_2$ as a fuel may be attractive, given the rate of climate change and global warming, it is much more sensible to consider employing a Methanol Economy, at least until the technology and economic feasibility of using $H_2$ improve.

Of particular incentive toward a Methanol Economy is the productions of methanol from renewable feedstocks such as biomass and $CO_2$ capture. These processes have the potential not only to be carbon neutral, but also carbon negative if renewable energy is employed.[3-4, 9-10] The ability of recycling $CO_2$ is potentially limitless, either by direct capture from industrial power plants or by that from atmospheric $CO_2$.[3-4, 11] Many methods in this area are being researched, including absorption into liquids, adsorption onto solids, or by membrane separation.[3,11] The capture of $CO_2$ from sources such as fossil-fuel burning power plants, where high concentrations of $CO_2$ emissions exist, and subsequent recycling into methanol is an attractive option. As technologies for direct air capture of $CO_2$ become more viable, transitioning from its capture from these plants would be an attractive solution to the issue of greenhouse gases.[3-4, 11]

## 4. CARBON CAPTURE

Many options exist and are being developed for the capture of $CO_2$. These are based on processes such as absoption of $CO_2$ into liquids, adsorption onto solids, and separation by membrane.[3-4, 11-16] All of these processes are influenced by the concentration of $CO_2$, temperature and pressure, and impurities present in the gaseous mix.[11-16]

### 4.1 $CO_2$ from Industrial Plants

One method of capturing $CO_2$ is by its direct capture from fossil-fuel burning power plants, petrochemical plants, cement production, and refineries.[3-4, 11-16] This method exploits the high concentration of $CO_2$ generated by these plants.[3-4] While it might seem that the obvious solution would be to capture $CO_2$ from a source with the highest emissions, the partial pressure of $CO_2$ plays a large role in its ease of separation, with higher partial pressures requiring less energy.[16] Additional energy would be required for $CO_2$ separation, as well as compression or liquefaction.[16] Additionally, the presence of impurities in the flue gas would increase the energy needed as well as the cost.[16] In post-combustion capture, $CO_2$ is absorbed into amines, $NH_3$, or alkaline solvents.[3, 16] The $CO_2$ is then released from the solvent by heating or decreasing pressure.[16] This method is relatively easily incorporated into existing plants, however the process can be costly.[16] An alternative is to use $O_2$ in the combustion process instead of air, which could increase the purity of the flue gas, and potentially reduce the amount of energy needed.[3, 16] However, this poses additional problems such as adapting equipment to enable this process, and is costly due to the need for $O_2$ production.[3, 16]

### 4.2 Direct Air Capture

The direct capture of $CO_2$ from the atmosphere is a particularly attractive method. In contrast to capture from point sources, direct air capture (DAC) can be employed without the need for proximity to the emission source.[3-4, 11-16] This is especially useful when considering that direct capture from the transportation sector would be economically prohibitive and impractical.[3]

In contrast to capture from industrial sources, which rely on the combustion of fossil fuels, this process has the potential to solely remove $CO_2$ from the atmosphere if renewable energy is used. However, currently the various methods involved are more energy intensive and costly than capture from industrial sources, ranging approximately 2-4 times the energy needed from this process.[3, 16] Furthermore, the process of capturing $CO_2$ is more complicated due to its lower concentration in the atmosphere, and the difficulty in the separation process between water and $CO_2$.[3, 11-16]

Currently there exists many methods for DAC capture, and the design of novel materials is an active area of research. The types of materials used are very diverse, from solid porous materials, polymers, alkali metals on carbonates, ionic liquids, to name a few.[11-16] The use of solid adsorbents such as zeolites, metal organic frameworks (MOFs), activated carbon for example work primarily by their large surface areas, but tend to have poor selectivity, especially in the presence of water.[3, 11-16] Research into improving these mediums, such as surface modifications, are being developed.[11-16] Ionic liquids have shown to have large capacities for $CO_2$ absorption, although their high viscosity poses a problem for absorption and desorption rates.[16] Consequently, the use of ionic liquids supported by porous membranes such as MOFs are being developed and have shown high potential.[16] The use of strong bases such as KOH and NaOH are effective in CO2 capture, although their corrosiveness and high temperatures (>700 °C) needed for regeneration pose a problem.[3, 16] Materials using amines on solid supports have shown promise, and can be regenerated with much lower temperatures (<110 °C).[3, 16] Finally, given the concern that the aforementioned technologies will carry a considerable cost for large scale use, efforts to develop DAC systems from waste materials, such as nut shells, coffee grounds, industrial silica waste, are being researched.[14]

While DAC faces many technical challenges and is at present far from being realized on a large scale, it should not be dismissed as being unrealistic. Whereas other renewable resources such as fuel crops and biomass are fundamentally limited, this process has the distinct advantage of having a limitless feedstock of atmospheric $CO_2$ while simultaneously solving the problem of elevated levels of this greenhouse gas.[14]

## 5. HYDROGENATION OF $CO_2$ TO METHANOL

There are a number of pathways to produce methanol from $CO_2$. One method is by direct hydrogenation of $CO_2$ by $H_2$.[3-4, 11-17] In order for this process to be carbon neutral, the use of $H_2$ by electrolysis from renewable energy would be required.[3-4]

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad (2)$$

This method typically employs the use of a metal catalyst, such as Cu or Zn based complexes.[3, 11-17] This process is primarily the method of methanol production from syngas in industry.[3-4, 11-17] However, there currently exist plants that make use of $CO_2$ from industrial carbon capture and $H_2$ from electrolysis, such as in Carbon Recycling International's plant in Iceland.[3, 14] This plant has an annual production of 4500 $m^3$ of methanol, capturing $CO_2$ from a neighboring geothermal plant and producing $H_2$ from electrolysis from geothermally produced electricity.[3, 14] The success of this plant has led to plans for construction of another with a ten-fold production capacity.[3] Other companies around the world have similar plants. In Japan, Mitsui Chemicals produces methanol from industrially captured $CO_2$ and $H_2$ produced by photo-electrolysis of water.[3] A similar plant in Canada is being designed by Blue Fuel Energy using hydroelectric and wind power to produce $H_2$.[3]

### 5.2 $CO_2$ to Methanol via electrochemical conversion

An area of development is in the conversion of $CO_2$ to methanol by electrochemical reduction. This process is outlined in the following reaction.

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad (3)$$

The process involves various types of metal electrodes immersed in a solvent, typically water, with $CO_2$ pumped into solution.[14, 18] A voltage is applied, $CO_2$ is reduced and reacts with protons to form methanol.[14, 18] While this process has been performed on a laboratory scale, there exist many barriers before its viability on an industrial scale can be realized.[18] Typically this process is energy intensive, with low efficiencies.[18] Competition for reduction at the cathode between $CO_2$ and $H_2O$ further complicate this, with excess $H_2$ being produced.[18]

### 5.3 $CO_2$ to Methanol via Photocatalysis

The photocatalytic reduction of $CO_2$ to methanol is similar to the electrocatalytic reduction process but uses light energy to drive the reaction. While this process has potential, the issues associated with electrochemical conversion, namely low selectivity, high energy cost and low efficiencies, also apply.[18-21] Additional problems arise with the scattering of light and the photo-efficiencies of the catalysts.[18] Until great advancements in this field are achieved, this technique will not be viable on an industrial scale.

## 6. CONCLUSION

An alternative to the current world reliance on fossil fuels is necessary due to their limited resources and associated negative environmental effects. The development of renewable energy technologies such as wind, solar, geothermal, and hydroelectric have proven to be viable alternatives. However these technologies produce primarily electricity, which is difficult to store. Therefore a method of storing this energy for later use is needed. Among the possible methods for storage, methanol is a particularly suitable medium given its physical properties and synthesis pathways. The ability to produce methanol from $CO_2$ is not only commercially viable, but has the potential to reduce the atmospheric concentration of this greenhouse gas. As the technologies for $CO_2$ capture and conversion continue to be improved, so too will its cost and productivity. If climate change and global warming are to be combatted in the immediate future, a Methanol Economy is worth serious consideration.

## ABBREVIATIONS

VOCs, Volatile Organic Compounds; Covalent Organic Frameworks, COFs; Polymers with Intrinsic Microporosity, PIMs; Direct Air Capture, DAC

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# On the Effectiveness and Sustainability of Large-Scale CdTe Photovoltaic Cell Use

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*KEYWORDS: Photovoltaic Cell, Solar Cell, CdTe, thin-film*

**ABSTRACT:** The environmental damage caused by the use of fossil fuels has created a need to develop alternative energy sources with significantly less harmful environmental impacts. Solar energy is one of the fastest growing energy sources, with many different types of photovoltaic cells being developed. One such technology is thin-film CdTe photovoltaic cells. This review investigated the economic, practical, and environmental consequences of these CdTe devices. Life cycle analyses were used to determine environmental impact. Energy payback time and manufacturing costs were used to examine relative economic and energy efficiency. It was concluded that pursuing this technology and its benefits due to efficiency, cost, and versatility in greater applications would indeed be suitable for large-scale use despite to risk to the environment and human health caused by cadmium toxicity and tellurium scarcity.

## INTRODUCTION

The environmental consequences of energy production and consumption have only recently come to the attention of the public. The vast majority of the world's energy currently comes from fossil fuels, meanwhile, "Most of the observed increase in global average temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic GHG (Green House Gas) concentrations" (IPCC, 2007).

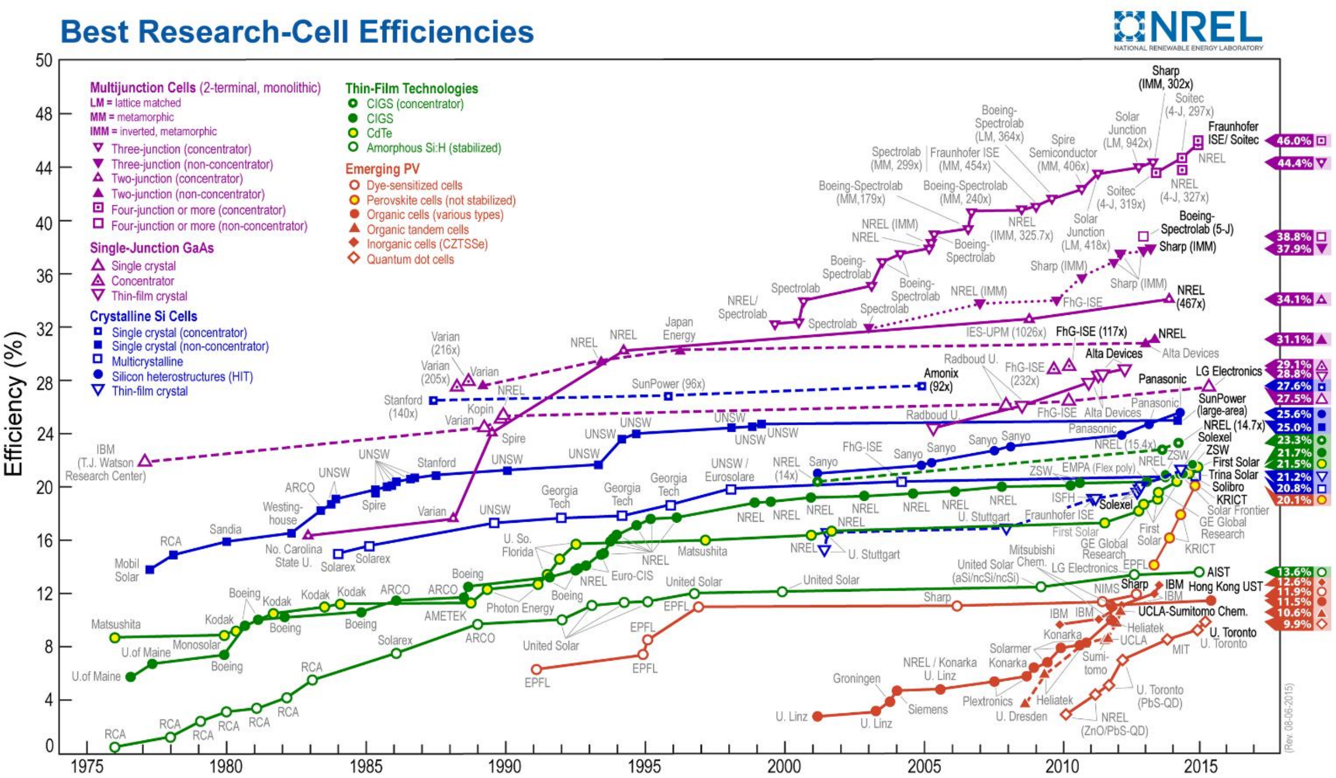

Figure 1: efficiency development of different types of photovoltaic cells over the past 40 years[1].

Our new-found awareness has led to a significant push by governments and citizens alike to discover renewable sources of energy to replace greenhouse-gas emitting fossil fuels. The need for alternative energy from an economic and security perspective was made painfully clear during the oil crisis in the 1970 which displayed the vulnerability of the world's economy to foreign-supplied energy.

Thin-film Cadmium Telluride photovoltaic cells (CdTe PV) are a specific type of PV cell whose characteristics make it a very tempting avenue for further development and large-scale production. In 2013, CdTe PVs accounted for 5.4% of all solar cells. This paper will evaluate the advantages and disadvantages of CdTe photovoltaic production and use, along with its more long-term environmental impacts and sustainability.

## DISCUSSION

Figure 1 shows the efficiency development of photovoltaic cells over the past 40 years. It is clear that CdTe solar cells are not the most efficient cells available. The record efficiency of thin-film CdTe photovoltaic cells is 21.7% as of 2015 while highly complex multijunction cells have reached 46%. Although not the best, they are competitive in terms of efficiency with silicon based PV cells, currently the most common type, and have several other advantages to be discussed later. Many mass-producible solar cells with efficiencies at around 20% are competitive with conventional sources of energy. It is predicted "that solar systems will be at grid parity (production cost of solar=production cost on grid) in up to 80 per cent of the global market within 2 years".

Solar energy has emerged as one of the largest alternative energy sources, accounting for 1% of total global energy production. In 2015, solar PV demand is expected to grow by up to 25%, with double digit growth expected for the rest of the decade. As research and development in this industry progresses, it is important to understand the impacts, advantageous or disadvantageous, of any new technology that is conceived. Every photovoltaic cell has production costs and environmental impacts depending on the type of cell involved. In 2014, investment in solar energy sources reached $150 billion. For governments to develop well informed regulation and policy, the full consequences of whatever technology they incentivize must be known.

Semiconductors are used for photovoltaic cells due to the phenomenon of exciton generation. When a semiconductor absorbs a photon, an electron is promoted from the valence band to the conduction band, above a forbidden region of energies known as the band gap. That electron is now free to flow (hence conduction band) and so is drawn into a metal contact with a galvani potential, creating an electromotive force.

The key, then, is to absorb as much of this light as possible to encourage as much electron excitation as possible. The maximum theoretical efficiency of a solar cell is dependent on the band gap by the Shockley-Queisser limit[2]. The band gap of CdTe is ~1.5eV, very near to the ideal of 1.34eV predicted by the model. This coincidence makes CdTe a near-ideal material for solar light absorption, hence the enthusiasm for its use in solar panels.

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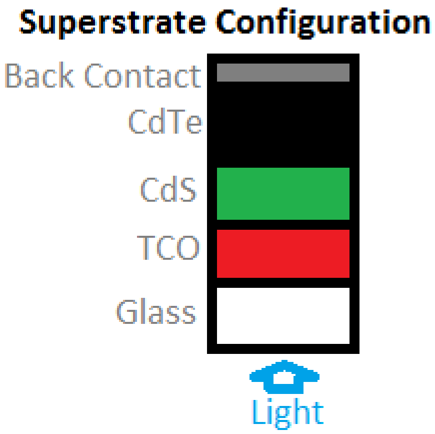

Figure 2: Basic schematic of CdTe Thin Film photovoltaic cell. Design interpreted from Romeo et al. (2004)[3]. (TCO=Transparent Conducting Oxide)

Figure 2 is a simple schematic of the thin-film CdTe photovoltaic devices in question. The very simple construction of these devices along with the low number of materials used heavily contributes towards their low manufacturing costs of thin-film PV cells. Manufacturing costs of CdTe films have reached $0.57/W[4]. The films can be applied to a wide variety of substrates, giving additional freedom to manufacturers to reduce costs[5].

The simplicity of manufacturing is also determined by the material properties of the film itself. Thin films are very flexible; they can be bent and twisted unlike rigid crystalline solar panels. This flexibility allows for installment in more awkward and uneven places such as a curved surface. CdTe films also have a large temperature tolerance, with the ability to sustain significant performance at high temperatures. The combination of these properties has seen CdTe films be the ideal material for use in space[6], as their versatility lends itself to such hostile environments.

Cadmium, the main component of the films, is a widely available and cheap material. It is a significant component of many zinc ores, and so is largely produced as a byproduct of zinc smelting[7]. Cadmium, however, is a highly toxic heavy metal with a very low lethal dose of 135mg[8]. Exposure can lead to kidney failure, liver failure, prostate cancer, and lung cancer. Having cadmium present in high quantities is very dangerous to human life, and it is known to accumulate in plant, animal, and marine life[9].

Tellurium, the other main component of the thin film, is an extremely rare element. It is almost as rare as platinum, with an abundance of only 1 ug/kg[10]. The abundance of tellurium is low enough that production of CdTe thin films would be limited by tellurium production should market share continue to increase at its current rate. With market share of solar energy set to increase to 10% by 2030, tellurium production would have to increase by a factor of 40 to meet such levels of demand[11]. However, it has been shown that modules using 1/30th of the Te can achieve around two thirds normal efficiency[12]. Historical increases in copper production, a major source of tellurium, improved refining techniques as well as discoveries of more tellurium-rich deposits in the ocean provide significant avenues for future Te production[xvi].

CdTe thin films perform remarkably well against other solar cell types in many categories. In terms of energy, a review of photovoltaic LCAs by Bhandari[13] et al showed the energy payback time (EPBT, amount of time to harness as much energy as it took to produce) of CdTe (~0.7 years) is the best of major competing technologies including amorphous Si (~1 year), CIGS (~1.3 years), poly-crystalline Si (~1.6 years), and mono-crystalline Si (~1.7 years).

Another life cycle analysis confirmed CdTe films supremacy in EPBT, and also found CdTe to have the lowest material input per service (kg material/kWh), the lowest global warming potential based on carbon emissions, the lowest ocean acidification potential, and the lowest ecotoxicity potential[14] compared to poly-Si and CIGS. The superiority of CdTe is largely due to the smaller amount of materials needed to produce them, as even though cadmium is highly toxic, other technologies produce much higher volumes of such hazardous waste. Compared to conventional energy sources, CdTe PV cells are greatly superior in terms of emissions of cadmium itself, giving off 0.02-0.3 g Cd/GWh compared to 2-3.1 g Cd/GWh from coal burning power plants. CdTe PVs also gives off less cadmium than mono- and poly-Si, who both had emissions around 0.9g Cd/GWh, triple that of CdTe films (Fthenakis et al., 2008)[15]. The use of CdTe films also led to reduced emissions of arsenic, chromium, lead, mercury, and nickel.

## CONCLUSION

The advantages and disadvantages of thin-film CdTe photovoltaic cells have now been examined. It still remains, however, to see whether this technology can actually be considered a “green” technology.

Thin-film CdTe solar cells are some of the most resource efficient, energy efficient, and waste reducing PV technology on the market. This technology prevents waste cadmium that would be produced should alternative technologies be used. Of competing technologies, CdTe films incorporate far more of its starting materials into the final product. The energy requirements to produce these films are also completely recovered after less than a year.

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CdTe films necessarily produce toxic waste because the central component is a toxic heavy metal. The only way to fix this would be to find an alternative metal to serve in cadmium's place. There are metals that can do this, however, all of them are either rare, toxic or both. Although generated levels are minimized, the persistence of cadmium is a hazard, especially when used over an extended period of time[xiii, xiv]. Because cadmium is a by-product of the smelting of other metals, it is a waste product that must be processed in some regard. Fthenakis et al argue that CdTe PVs are actually one of the most environmentally safe ways to trap and keep cadmium localized compared to other more dispersive methods like its inclusion in fertilizers[16].

The depletion of Tellurium is the major limitation of the application of CdTe films. Tellurium is a very limited and non-renewable feedstock. This can be remediated by either concerted recycling to maximize use of all Te that has been produced. Luckily, recycling programs have been put in place, one in particular by First Solar, the largest producer of thin film CdTe PVs, which is able to recover up to 95% of Cd and Te[17], in addition to developing mobile recycling facilities. They also claim that the CdTe-PV industry can be fully reliant on recycled PV modules by 2038.

In conclusion, thin-film CdTe photovoltaic cells may create toxic waste, but they do so at lower levels than almost all other major forms of photovoltaic energy production, and are one of the best ways to sequester the inevitable wastes of other industries. Improvements in tellurium production and recycling will mitigate supply restrictions on CdTe PV production. This technology is a relatively low-impact, cheap, effective, and so viable long-term energy source.

## AUTHOR INFORMATION

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# Chemical Valorization of Coffee Bean Waste

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*KEYWORDS: Coffee, Waste, Biodiesel, Biorefinery, heavy metal remediation, bio-based plastics,*

**ABSTRACT:** Coffee is a popular beverage consumed by a large proportion of the adult population worldwide. Its production is a key component to the economy of many countries. Because of the large amount of the coffee plant grown, there is a massive amount of agricultural and industrial waste associated with it. This article serves to highlight several proposed uses of various types of coffee waste, and show how they can be beneficial.

## INTRODUCTION

Coffee is one of the most popular beverages in the world and also the 2nd most traded commodity after petroleum[1]. Because of this, there is an astounding amount of solid coffee waste, the covering of the beans known as the husk, or the extracted ground bean, known as spent coffee grounds (SCG). In bulk availability, this waste is mostly from the industrial production of instant (soluble) coffee, though the solid waste from coffee shops and restaurants is still quite significant. There are over 6 million tons of spent coffee waste created every year just from instant coffee production, with most discharged to the environment. This creates issues due to the toxic nature of caffeine and tannins[2], in addition to other bioactive polyphenols, notwithstanding the fact that this waste can ferment and spontaneously combust.

With this much waste created, there is an environmental imperative to utilize it to reduce harm from simply dumping it. At the same time, there is serious economic potential in 6 million tons of organic material full of interesting compounds available at very low costs or for free. One article estimates that there is a potential profit of more than $8 million/year from only Starbucks' waste in the United States[3] being used to make biodiesel and fuel pellets.

As shown in Table 1, spent coffee grounds have a variety of interesting components that are themselves valuable without any processing.

The uses for coffee waste most frequently investigated are production of biodiesel *via* transesterification of extracted oils, use of solid waste as a sorbent or for metal extraction, extraction of small organic molecules such as phenolic compounds, or use as a feedstock in biorefineries. The rest of this paper will focus on modern coffee waste valorization techniques, including those mentioned before.

**Table 1: Spent Coffee Grounds (SCG) Composition[4]**

| Parameter | Content (wt%) |
|---|---|
| Cellulose | 8.6-13.3 |
| Hemicellulose | 30-40 |
| Proteins | 6.7-13.6 |
| Oil | 10-20 |
| Lignin | 25-33 |
| Polyphenols | 2.5 |
| Caffeine | 0.02 |

### Coffee Detoxification

Coffee must be detoxified before it is used in situations where its bioactive components might have detrimental effects[5]. These deleterious effects are primarily due to caffeine and tannins. Caffeine, part of the methylxanthine class, is not particularly harmful to humans[6]. To reach the FDA reported toxic dose of 10 g, more than 50 cups of very strong coffee must be consumed. In other words, one must purposefully try to poison themselves with caffeine. However, plants and many animals are much more susceptible to caffeine toxicity. It is toxic and a teratogen for rats, and also known to be quite toxic to dogs, rabbits, and cows[7]. It is theorized that caffeine is present in plants as a form of "chemical weaponry" to defend young tissue from herbivores and pathogens. Spraying plants with caffeine solutions or engineering them to produce caffeine themselves[8] has been shown to reduce predation[9]. In other words, agricultural coffee waste that will be in contact with plants or animals should have at least some caffeine and other xanthines removed. This is important for its use as a fertilizer, which has been shown to be very beneficial to sandy soils in tropical environments which do not hold water very well[10]. Using a waste product as fertilizer is important, as it disposes of waste, adds value to it, and provides fertilizer for people who cannot afford to buy commercially produced mineral fertilizers. Coffee is often produced and processed in countries with lower buying power, so utilizing a common waste product could be very beneficial to the quality of life for people in these countries.

Coffee waste can be detoxified by a variety of means. One method that has been investigated and shown to be successful is degradation of the pulp or husk by fungi. The husk is the part of the harvest bean removed to yield a usable bean. Using a variety of *Aspergillus* and *Rhizopus* strain fungi, up to 90% of caffeine and 60% of tannins were degraded[11]. This is extremely important for coffee husk use as a feed source for animals, as they can only be used for less than 10% of animal feed without treatment. Coffee husks are rich in nitrogen and a variety of minerals, making them valuable resources.

### Biological Processing

As previously mentioned, fungi can be grown on coffee husk, and it can be used as a growth medium for a variety of different mushrooms. In addition to using fungi for detoxifying SCG, they can be used to produce valuable materials, such as citric acid or gibberellic acid[12], a plant growth hormone. A reaction scheme showing the biosynthesis of gibberellic acids is shown below in figure 1. As coffee husk has a fair amount of fermentable sugars (50% carbohydrates by weight), it can be used as a sugar source for yeast to produce alcohol and a variety of other compounds. Some of the more interesting compounds produced by yeast on coffee husk are flavoring and aroma compounds, including isoamyl acetate and ethyl-3-hexanoate, responsible for the scents commonly associated with bananas, pears, and pineapples.

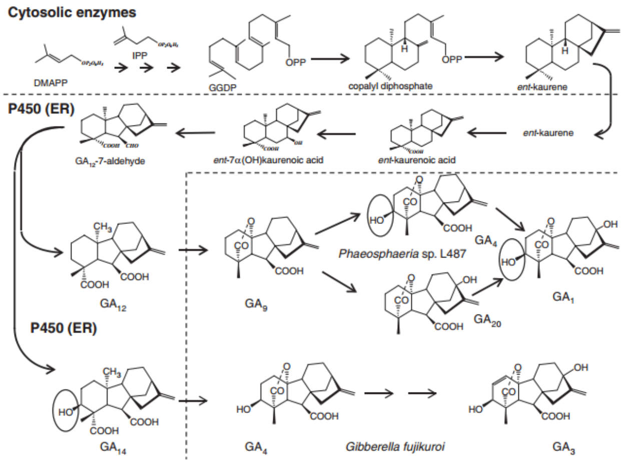

***Figure 1:*** *Biosynthetic Pathway of Gibberellic Acids in Fungi[13]*

Coffee waste can also be used as a feedstock for biogas production, which is mostly methane. This is usually done *via* anaerobic fermentation. A flowchart of this process is shown below in figure 2. It is a particularly good feedstock, producing 730 $m^3$ of biogas per ton, as compared to between 250 and 500 $m^3$ per ton of sugar, agave, or corn waste[14]. It is also shown to be a good plant growth medium, again, making it a good fertilizer.

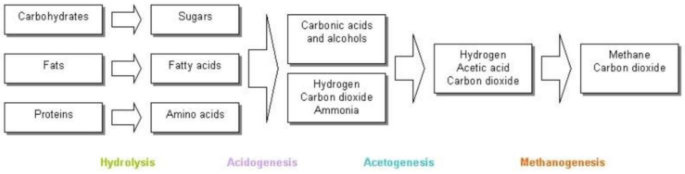

***Figure 2:*** *Stages of Anaerobic Digestion[15]*

### Polyhydroxyalkanoates and Carotenoids

Polyhydroxyalkanoates (PHAs) are biodegradeable and biocompatible polymers similar in properties to polypropylene and polyethylene. They are not currently popular or common because of their high production cost. Polypropylene has a cost of under 1 USD per pound[16], sometimes as low as 65 cents per pound. PHA is priced by Metabolix, the main producer, at between 2.25 and 2.75$ per pound[17] Using a waste material such as SCG would significantly lower this cost, making it competitive with conventional petrol-based plastics. PHAs are themselves promising materials, as there are many types of PHAs that are easily mixable to customize the physical properties of the plastic. The method for producing PHAs is the fermentation of oils with different bacteria[4]. Bacteria produce these polymers as a storage for carbon, and future energy source. As will be mentioned later on, SCG can have a relatively high amount of free fatty acids that can, for example, make it difficult to use as a biodiesel source. However, this free fatty acid content makes it better for PHA production. Some of the compounds found in SCG can have antimicrobial action, like polyphenols. This can be solved by detoxifying the SCG or extracting these compounds.

Carotenoids are another valuable type of compound that can be produced via biotechnological conversion. They are currently used in the food industry, and due to their anti-carcinogenic properties, are expected to be used in or as pharmaceuticals. This makes investigating novel production methods important. Like with PHAs, biotechnological production of carotenoids is expensive due to the cost of the source materials. If waste materials such as SCG can be used, the cost goes down significantly. Carotenogenic yeast can use the SCG solids remaining after oil extraction, allowing for use of the entire waste stream without relying on combustion.

### Biodiesel from Coffee Oils

As shown in table 1, spent coffee grounds have a significant oil content. In an article by the Misra group[3], 15 g of oils could be recovered by refluxing dried coffee grounds for an hour in about 300 ml of a low boiling point organic solvent. After recovery of the oils by rotary evaporation, the solvent can be reused. The free fatty acids were removed by saponification using a basic solution, then rotary evaporation. Less polar solvents extracted a smaller amount of free fatty acids, yielding a better oil mixture for transesterification. With optimized transesterification conditions, 100% yield biodiesel was possible. This biodiesel was of higher quality[19] than that from cooking waste oil in multiple ways, including stability due to antioxidant content, and a pleasant coffee-like odor. With respect to the biodiesel produced, it can be high quality. Data regarding this quality is shown below in table 2. In addition, after extraction of oil, the solid leftover can be used for fuel pellets due to the high concentration of lignocellulosic material. It should be noted that this method of biodiesel production must be altered for a scale up, meaning it might not be industrially feasible.

Considering the world supply of SCG, there is the possibility of producing 340 million gallons of biodiesel per year from coffee waste. This is equivalent to about 8.1 million barrels. Currently, only about 10,000 barrels of biodiesel are produced per day in the United States, compared to almost 5 million barrels of distillates per day, which consists of mostly diesel though includes jet fuel and fuel oil. This means that using SCG as a biodiesel source would make a significant increase in the amount of biodiesel available, adding a production of 22,000 barrels per day.

As is shown in table 2 below, coffee oil based biodiesel can meet industrial requirements and is a potential drop in replacement for diesel in many applications, including vehicular use. However, in a paper by Mata *et al*, the quality of biodiesel produced was insufficient. This seemed to be due to high free fatty acid and moisture content, which are known to lead to poor biodiesel. In this paper, the free fatty acids were esterified as opposed to being saponified, then removed. This may be a simpler process but could be responsible for the lower quality biodiesel that does not meet ASTM standards.

### Adsorbent Qualities and Applications

Solid coffee waste has been shown to have impressive adsorbent characteristics, even without any modifications. An example of this is a paper by Oliveira[20], where completely untreated coffee husks, a residue of coffee production, was shown to remove large amounts of heavy metal ions from aqueous solutions. Due to the carboxylic, lactonic, and phenolic functional groups on the surface of the husks, they are able to bind to or chelate metal ions. Compared to many other popular biosorbents, coffee husks perform very well (~7 mg metal adsorbed / g sorbent). In addition, they are able to adsorb some of the more common heavy metal contaminants such as Cu(II), Zn(II), Cd(II), and Cr(VI). Currently, coffee husks do not have an alternative use besides possibly a biofeedstock as mentioned before, meaning they are a great candidate for biosorbent use in countries that have a large amount due to coffee production. Again, access to a cheap, effective material could be very useful for countries that cannot afford to purchase expensive remediation chemicals or equipment.

**Table 2: Biodiesel Data from Misra Paper[3]**

| Test Name | Test Method | Limit | Results |
|---|---|---|---|
| Free Glycerin (Mass %) | ASTM D 6584 | max 0.020 | 0.006 |
| MG(Mass %) | ASTM D 6584 | N/A | 0.076 |
| DG(Mass %) | ASTM D 6584 | N/A | 0.027 |
| TG(Mass %) | ASTM D 6584 | N/A | 0.000 |
| total glycerin (mass %) | ASTM D 93 | Max 0.240 | 0.109 |
| phosphorus (ppm) | ASTM D 4951 | Max 10 | 2.0 |
| Ca+ Mg (ppm) | EN 14538 | Max 5 | 2.0 |
| Na+ K (ppm) | EN 15438 | Max 5 | 2.0 |
| Viscosity at 40°C | ASTM D 445 | 1.9-6.0 | 5.84 |
| TAN (mg KOH/g) | ASTM D 664 | Max 0.50 | 0.35 |
| oxidation stability by rancimat (h) | EN 14112 | min 3.00 | 3.05 |
| cloud point (°C) | ASTM D 2500 | N/A | 11.0 |
| pour point (°C) | ASTM D 97 | N/A | 2.0 |
| sulfur, by UV (ppm) | ASTM D 5453 | 15 | 8.0 |

In a paper by Boonamnuayvitaya[21], coffee residues (SCG) were pyrolyzed and mixed with clay in a 80:20 ratio to be used as a sorbent. This ratio was chosen due to increasing effectiveness with increased coffee residue content, and the physical property limitations above 80:20. An 80:20 ratio allowed 4 mm granule sizes, typical for a packed-bed adsorbent. For this material, amine, carboxylic, and hydroxyl groups were the main surface functional groups. This led to slightly different adsorption properties and selectivity than with the husks. The sorbent was most effective at capturing Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II). Compared to the coffee residue itself (pyrolyzed or unaltered) or the clay, the sorbent mixture was much more effective. It was shown that these sorbents can be regenerated, with 90% of the metal ions adsorbed being removable by washing with distilled water. After washing, the sorbent was active for more than 5 uses.

### Extraction of Phenolic Compounds

Coffee is a source of a large variety of polyphenol compounds including chlorogenic acids, caffeoylquinic acids, dicaffeoylquinic acids and feruloylquinic acids. These and their metabolites have been shown to be beneficial to the human body[22], and have potential uses as nutritional supplements or pharmaceuticals. One mechanism for their beneficial effect is the chelation of metal ions that can mediate hydroxyl radical formation[23].

Even in SCG, there are phenolic compounds remaining. In work by Lavecchia[1], these were extracted using aqueous ethanol using mild conditions to preserve the activity of the phenolic compounds. The extractable phenolic compound content was high for SCG compared to other commonly investigated materials, such as grape pomace, carrot peel waste, apple peel waste, and kiwi peel waste. In addition, SCG can be used as a fuel source after extraction of phenolic compounds, or have oil extracted, or be used as a feedstock in biorefineries. It should be noted that coffee bean waste from different types of coffee plants have different phenolic compound content, with as much as 20 or 30% difference between Arabica and Robusta.

## CONCLUSION

As can be seen, there are many uses for coffee waste. The applications shown are just scratching the surface. For example, coffee oils and solid waste can be used as feedstocks for many more biorefinery materials than just PHAs or carotenoids. SCG and other solid coffee waste can probably be used as an adsorbent for many other compounds due to their large amount of functional groups on the surface, not just metal ions. As the polyphenols in coffee are more thoroughly investigated, more uses for them will be discovered. As the countries that produce and process coffee continue to develop their scientific resources, they will hopefully allocate more time and money to developing innovative solutions to their unique issues.

The use of waste associated with the coffee industry can be seen as a model for many other systems, for example tea. Waste from manufacture of tea or the tea leaves themselves have many of the same compounds as coffee, including polyphenols, caffeine, and cellulose. There are over 5 million tons of tea leaves produced per year, with this number growing every year, having been at less than 4 million tons in 2006.[24] Many of the solutions to coffee waste issues can be applied to tea waste, and many of the countries that produce tea are developing and could benefit from the use of a waste product.

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## ABBREVIATIONS

SCG, Spent coffee grounds, PHA, polyhydroxyalkanoates

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# How Green is Green? A Critical Analysis of Chemical Processes That Utilize Citrus Waste by Employing the Principles of Green Chemistry

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*KEYWORDS Green Chemistry; Sustainability; Citrus Waste*

**ABSTRACT:** With ever increasing environmental concerns, the chemical industry has begun to look into more sustainable methods for the production of various chemicals. One of the more attractive methods to achieve this is the use of waste byproducts from the processing of other products. These processes are commonly labeled as "green" as they satisfy the principle of using renewable resources, yet fail to address any of the other principles. This paper will review various chemical processes that utilize citrus waste as a feedstock and use the principles of green chemistry to evaluate how sustainable they actually are. The processes will also be compared to either traditional or alternative methods for the same product so as to determine their viability in terms of what's already being used.

## INTRODUCTION

The subject of green chemistry is an ideology which promotes the design of chemical reactions in which environmental impact is minimized, while also being economically viable and feasible on an industrial scale. The concept was made popular in 2000 when the book "Green Chemistry, Theory and Practice" was published which defined green chemistry in detail by setting its standards with the twelve principles of green chemistry[1].

With increasing environmental concerns as well as depleting resources, green chemistry has become more attractive for the chemical industry. The application of the green chemistry principles can be seen as both environmentally friendly as well as a more economically viable solution. By emphasizing the design of more efficient reactions, minimizing power consumption as well as using less toxic compounds, this translates into a reduction of waste management costs and potentially makes accidents significantly less hazardous.

Citrus production has been a major part of the food industry, producing up to 50 million metric tons of citrus product annually[2]. Of this amount, almost half if discarded as waste from the juicing industry in the form of citrus peel, pulp and seeds. This waste is sometimes dried into pellets which can be sold as cattle feed, but since this process tends to yield very little profit, the waste tends to end up in landfill. The waste can accumulate and harm the environment due to its high fermentation ability and its high acidity[3]. As the composition of citrus waste consists mainly of oils, cellulose and various simple sugars such as glucose and fructose, there has been an increasing interest in the use of citrus waste as a renewable feedstock for many different high value compounds. The compounds can either be extracted directly from the peel, as in the case of oils such as limonene, or used directly in synthesis.

Processes that successfully utilize citrus as a feedstock have often been labeled as green as they utilize a renewable feedstock that was originally a waste byproduct, thereby employing one of the principles of green chemistry. This label, however, may be premature as only one principle is considered while the other principles are either overlooked or simply ignored. Potentially this could lead to a false conclusion as the process may still utilize harmful reagents, large quantities of solvent or even be very energy intensive.

This review will consist of analyzing different chemical processes to determine just how sustainable they actually are. This will be established by utilizing the twelve principles of green chemistry, with the greatest emphasis on; solvent usage, energy intensive conditions, reagent toxicity, as well as waste production of the process. These processes will also be compared to alternative methods in order to determine if the utilization of citrus waste is more sustainable than what is currently being done.

## MATERIALS AND METHODS

The chemical processes will be analyzed and compared using criteria similar to what is found in the paper "Green Chemistry Measures for Process Research and Development"[4]. For simplicity, this paper will only focus on the following criteria; the number of chemistry steps, list of process conditions such as heating and high pressure, environmental safety, compound toxicity and the amount of waste produced.

The amount of waste will be calculated two ways. The first will be the E-factor which calculates the amount of waste (in kg) created in order to produce a kilogram of product[5]. The second method which is similar to the first, will exclude the waste originating from the citrus, as it is already considered a waste from a past process and water, as it is the preferred solvent. Gases used for anaerobic conditions, such as carbon dioxide and nitrogen, will be excluded since the amount needed cannot be specified due to its dependence on reservoir size as well as the volume of solution in the tank. This second calculation will determine the actual amount of waste produced from the reaction and if the process is water intensive. Other compounds may also be excluded from the second calculation if the process states that the compound will be recycled. Rather than providing an actual estimation of energy consumed, only the process conditions present will be listed simply due to the lack of data available to provide such a calculation.

## DISCUSSION

**Hydroxymethylfurfural.** Hydroxymethylfurfural (HMF) is a compound that has great potential usage in various fields. The most notable being as a potential source of biodiesel[6], as well as its medical potential as an inhibitor for sickling of red blood cells[7].

The utilization of citrus waste in HMF production, as described by Yi and co-workers[8] is a simple process consisting of the preheating of a mixture containing chromium trifluoride ($CrF_3$)(0.1 g), 1-methyl-3-octylimidazolium chloride ([OMIM]Cl)(4 g), and 0.3M hydrochloric acid (HCl)(5 mL) to 130°C for 15 minutes. The pre-dried citrus peel (0.5 g) and ethyl acetate (1 mL) are then added and left to process at 130°C for 16 hours[8].

Separation and yield quantification incorporated high pressure liquid chromatography (HPLC) with different ratios of water and methanol as the mobile phase. The yield was quantified to be 24.2% weight of the dried citrus peel or 0.121 ± 0.011 g.

The procedure is a simple process consisting of only two steps, yet energy intensive due to the long residence time at the aforementioned temperature. The compounds being used however are of concern with the most notable being the $CrF_3$ catalyst. According to its MSDS, it is a very toxic and a highly corrosive compound that can potentially cause significant environmental damage. The other potential environmental hazard would be the [OMIM]Cl ionic liquid. Ionic liquids are generally favorable alternatives to traditional solvents due to their interesting properties as well as their low volatility. They are also commonly assumed to be non-toxic, which is a false assumption as some are capable of decomposing into harmful compounds[9]. The ionic liquid present in this process is one such case as it has been found to have some short term negative effects on soil microbial populations[10], as well as being toxic to algae populations that live in lower salinity environments[11].

An alternative process to produce HMF described by Hanson and colleagues[12] utilized microwave radiation to heat a solution of 27 wt. % fructose (2.7 mL) and 0.1M HCl (0.3 mL) to 200 °C for about 60 seconds[12]. This solution was also analyzed using HPLC but with a mobile phase of $H_2SO_4$.

The yield is commonly quantified to be approximately 53% which in this case, translates to 0.319 g of HMF.

Comparing the two reactions (Table 1), the alternative microwave synthesis using fructose appears to be beneficial in most aspects. There are no toxic compounds present as well as there being much less waste generated. The added benefit of it being less time consuming can also be noted which can greatly decrease the energy consumption of the reaction. The waste produced is also much lower due to it being much less solvent intensive. Overall, the process utilizing citrus waste does not appear to be sustainable when compared to the alternative method reviewed.

**Table 1. Comparison between HMF processes.**

| | Citrus Waste* | Fructose (Microwave)** |
|---|---|---|
| Number of steps | 2 | 2 |
| Process conditions | 130°C<br>16.25 hours | 200°C<br>1 minute |
| Safety concerns | Crf3, [OMIM]Cl | - |
| E-factor (kg/kg) | 86.2 | 11.1 |
| Modified E-factor (kg/kg) | 41.8 | 1.70 |

* Values generated with data from Yi et al.[8]

**Values generated with data from Hansen et al.[12]

**Xanthan Gum.** Xanthan gum is a polysaccharide that is produced by specific bacteria such as Xanthomonas campestris[13]. It is most commonly used as a thickening agent for various manufactured foods and cosmetic products.

The process consists of a stock culture of xanthan producing bacteria in a medium containing carbohydrates, phosphorus and other nutrients. The carbohydrate source has traditionally been glucose but citrus waste may be a possible alternative due to its high concentration of soluble sugars[14].

The procedure described by Bilanovic and collegues[14] begins with neutralizing dried citrus waste (95 g) with sodium hydroxide (NaOH) to a pH of 7.2. Potassium hydrophosphate trihydrate (K2HPO4*3 $H_2O$)(5 g), yeast (5 g), citrus and magnesium sulfate trihydrate ($MgSO_4$*3$H_2O$)(0.2 g) were then added and diluted with 1 L of water. The stock culture was inoculated at this point and shaken at 220 rev/min at 28 °C and allowed to ferment for 4 days.

The xanthan is extracted from the solution with the slow addition of ethanol (3 L) to induce precipitation. The sample is centrifuged for about 20 minutes and the product dried in an oven at 105°C.

The traditional synthesis utilizes the same procedure in which the citrus waste is replaced with glucose (22.5 g).

The yield was determined to be about 14 g and 10 g for the citrus and traditional processes respectively.

**Table 2. Comparison between the Xanthan Gum processes.**

| | Citrus Waste* | Traditional Glucose* |
|---|---|---|
| Number of steps | 3 | 3 |
| Process conditions | 105°C<br>for drying | 105°C<br>for drying |
| Safety concerns | - | - |
| E-factor (kg/kg) | 247.0 | 339.0 |
| Modified E-factor (kg/kg) | 170.0 | 239.0 |

* Values generated with data from Bilanovic et al.[14]

The results summarized in Table 2 suggest that the reaction is simple in both instances, consisting of only 3 steps including separation. The main issue for both processes is the quantity of solvent required, with the majority being from the utilization of ethanol in the extraction process at an amount that is double the solvent necessary for the actual reaction. Although ethanol is preferable according to its calculated life-cycle assessment[15], it is still known as a VOC and its usage should be minimized. Different extraction processes should be studied in the future in order to find one where the amount of solvent can be significantly reduced or replaced with less volatile solvents that are more easily recycled.

The process however, is more sustainable in comparison to traditional methods which utilize glucose as a feedstock as the procedure is identical and is replaced by a waste. An interesting finding that was observed by Bilanovic and colleagues[14] was that even though the concentration of simple sugars was lower in the citrus medium, the yield was actually larger than that of the glucose medium. This was found to be caused by the bacteria being able to digest other compounds present in the waste such as pectin and hemicellulose.

**Carbon Dots.** The production of carbon quantum dots (CQD) is a somewhat recent topic that has become of great interest to researchers. With interesting properties such as multi-wavelength fluorescence, low toxicity, aqueous solubility and high biocompatibility, they have great potential in bioimaging as well as photocatalysis[16].

The production of CQDs is relatively simple, with most processes being a one-pot synthesis with a single reaction step.

There are currently a large number of different methods in which CQDs can be produced with the most cost effective one being hydrothermal treatment[17].

The process utilizing citrus waste by Prasannan and co-workers[18] begins with a drying step. This dried waste (2g) is washed in 0.1 M sulfuric acid ($H_2SO_4$)(100 mL), rinsed with water and dried again. The waste is then added to 60 mL of sodium hypochlorite for 4 hours and washed. The solids are placed in an autoclave with water (25 mL) for 12 hours at 180 °C and washed with dichloromethane (25 mL). The separation process consists of centrifuging the solution at 5000 rpm for 15 min and then drying the CQDs to acquire a yield of 12.3% (0.246 g)

The reaction does not appear to be very toxic as it uses compounds that have very little impact when properly disposed of. The washing step however, utilizes dichloromethane which is a VOC as well classified as a harmful air pollutant in the US.

Also of note was the inclusion of 3 drying steps which seems inefficient as well as unnecessary. The pretreatment process could probably do away with the drying steps, by simply washing the citrus waste with the sulfuric acid and sodium hypochlorite and of course washing with water in between to prevent the production of sulfur dioxide. The sample drying could simply just be done at the end. Further experimentation should be done in order to confirm if this is possible.

The alternative traditional method[19] consists of heating octadecene (15 mL), 1-hexadecylamine (HAD)(1.5 g) and citric acid (1 g) to 300 °C in an argon atmosphere for about 5 minutes. Purification consisted of precipitating the dots with acetone for filtration yield 0.1 g of CQDs.

The comparison of the two methods (Table 3) suggest that the procedure utilizing citrus waste is less toxic to the environment, with only the dichloromethane used for separation being a concern. The HDA used in traditional synthesis however, is a significant hazard to the aquatic environment being toxic in relatively small amounts according to its MSDS.

There appears to be an apparent trade-off between toxicity and waste/energy consumption. The synthesis utilizing citrus waste is very energy intensive, needing multiple drying stages as well as a 12 hour reaction period at high temperatures. It does appear favorable however, as the synthesis could be altered by reducing the number of drying steps as well as further research to determine if the 12 hour reaction time is actually necessary. It may also be possible to replace dichloromethane with a more environmentally friendly alternative such as ethyl acetate or acetone.

**Table 3. Comparison between the CQD processes.**

| | Citrus Waste* | Alternative** |
|---|---|---|
| Number of steps | 4 | 2 |
| Process conditions | 180°C<br>12 hours,<br>multiple drying steps | 300°C,<br>5 minutes |
| Safety concerns | $CH_2Cl_2$ | HDA |
| E-factor (kg/kg) | 907.4 | 221.4 |
| Modified E-factor (kg/kg) | 34.2 | 221.4 |

* Values generated with data from Prasannan et al.[18]

**Values generated with data from Wang et al.[19]

**Limonene Extraction.** Limonene has widely been used in industry as a solvent as well as a potential use as a biofuel.

Citrus waste is already being used as a source for industrial limonene production with steam distillation as the extraction process. Currently, there are two main procedures being looked into as more sustainable extraction methods. The first pairing the traditional steam distillation with microwave irradiation[21] and the second using supercritical carbon dioxide ($scCO_2$) as an extraction solvent[22].

The procedure utilizing microwave radiation (500 W) places the citrus waste (100 g) into a cartridge and is subjected to microwave radiation while water vapor (14 g/min) is being passed through the cartridge which is then collected via a condenser. The process was done for a period of 6 minutes followed by the drying of the sample. The product was characterized to contain 5.43 g of limonene at 96% purity.

The optimal $scCO_2$ procedure consisted of citrus waste (120 g) at 35°C and 12.5 MPa with a flow rate of 58.3 g/min for 20 minutes yielding about 4.8g and 99.5 % purity.

The process using microwave radiation appears to have been able to acquire higher yields, all while using much less solvent than the process utilizing $scCO_2$ (Table 4). The tradeoff for this is a slightly lower purity of the limonene product which may be a significant factor in certain cases such as if analytical grading is desired. Energy usage consists of a large amount of heating for a small period of time whereas the process using $scCO_2$ requires a longer time with high pressures and thus isn't a good method in comparison.

**Table 4. Comparison between limonene extractions.**

| | Microwave and Steam Distillation* | $scCO_2$** |
|---|---|---|
| Number of steps | 2 | 2 |
| Process conditions | 500W<br>microwave radiation<br>6 minutes | 12.5 MPa<br><br>20 minutes |
| Safety concerns | - | - |
| E-factor (kg./kg) | 32.8 | 267.05 |
| Modified E-Factor (kg/kg) | 0.0 | 242.92 |

* Values generated with data from Sahraoui et al.[21]

**Values generated with data from Mira et al.[22]

**Ethanol Production**. The use of ethanol as a biofuel is currently of great interest to potentially replace traditional fossil fuels. At present the main crop that is used for ethanol production is sugar cane and corn due to their high sugar contents. The direct usage of crops does bring up concerns, mainly potential food shortages as well as land availability if crops are to be used to satisfy both food and fuel demand[23].

The potential use of citrus waste as a feedstock for bioethanol production does not raise these concerns as it is a waste product. The only drawback to citrus waste is from its high limonene content which can be toxic to the bacteria used for fermentation. Because of this, the limonene must be extracted beforehand[24]. This is not that much of a drawback however, as limonene extraction can be incorporated into the process.

Many ethanol designs have already been done, with some being able to produce a wide range of products from the citrus waste including ethanol, methane, pectin and limonene in a single process[24].

The process as described by Lohrasbi et al.[24] begins with the acid hydrolysis of a slurry consisting of fresh citrus waste (1.5 kg), water (0.5 kg) and $H_2SO_4$ (8.5 mL) at 150 °C for 6 minutes. Heating was performed through steam injection. The slurry is then explosively discharged to an expansion tank to cool down and centrifuged for 10 minutes in order to separate the solids which were taken and washed with distilled water (200 mL).

The steam used for hydrolysis was collected and condensed as it contained 99% of the total limonene available.

The supernatant was filtered into a precipitation chamber along with an equal volume of ethanol in order to precipitate the pectin present in solution. The solution was centrifuged for an hour and washed with ethanol and dried with the ethanol being collected and recycled.

The remaining solution is neutralized and fermented with a yeast solution (50 mL) in a fermenter at 30 °C, 200 rpm at a pH of 5 for 24 hours with a steady stream of nitrogen gas (600 mL/min) to ensure anaerobic conditions. The ethanol was boiled off and collected while the remaining solution was placed into a digester with the filtered solids, adding 400 g of inoculum for every 200 g of solution being used as a substrate. The reactor was incubated for 30 days at 55 °C to produce methane.

The paper concluded that an industrial scale process would be capable of producing 39.6 L of ethanol, 8.9 L of limonene, 38.8 kg of pectin and up to 45 000 L of methane for every ton of citrus waste.

As shown in Table 5, the process is quite complex as there are multiple products being manufactured. The process is energy intensive with heating required in almost every step in order to optimize bacterial activity for fermentation. The production of methane required about 20 to 30 days with heating for the entire process for optimal methane yield.

The amount of waste produced was low, with most of it being from the large amounts of inoculum required for the methane fermentation. The nitrogen and CO2 gas were not included as they are only used for anaerobic conditions and thus won't require as much to meet industrial scales in terms of proportions. The chemicals are all relatively safe with the most concerning compound being the sulfuric acid which is easily treatable and used in very small amounts.

The economic viability of similar processes have also been analyzed and it has been found that the use of citrus waste for a source of these compounds could be a profitable strategy for plants that are capable of processing citrus waste on a scale of a hundred tons per year[24].

**Table 5. Environmental Analysis of Ethanol Fermentation.**

| | Citrus Waste* | Corn** |
|---|---|---|
| Number of steps | 9 | 6 |
| Process conditions | 150°C, 6 mins<br>96°C distillation<br>drying steps | Drying step<br>96°C distillation, 3 times |
| Safety concerns | - | - |
| E-factor (kg/kg) | 33.1 | 53.1 |
| Modified E-factor (kg/kg) | 21.7 | 2.4 |

* Values generated with data from Lohrasbi et al.[24]

**Values generated with data from Pimentel et al.[25]

With the overall complexity and wide range of products obtained from this process, there isn't an exact process to which it can be compared. Traditionally, ethanol is fermented from corn in the US[25]. In general, the process consists of adding water (40 L) to finely ground dried corn (2.69 kg), which is fermented with yeast for a certain period of time. The ethanol is then distilled 3 separate times to produce a liter of 95% pure ethanol.

In comparison, the process using corn is much more water intensive, but produces less waste. However, the need for three separate distillations makes it much more energy intensive as well. This process as it is being produced specifically for ethanol fermentation fails to consider the costs related to growing the corn including water, fertilizer and pesticides to mention a few.

Ethanol production using citrus waste is thus more efficient, being able to produce multiple different products as well as not risking any food price increases. Further study however should be examined in order to determine how positive or negative net energy output of this process is.

## CONCLUSION

The usage of a waste byproduct, such as citrus peel, as a feedstock for high value compounds is a meritable goal to aim for. However, it is not adequate to simply settle with satisfying one of the principles of green chemistry in order to label a process sustainable.

The most prominent factors that were noted in this review were the high energy inputs as well as the large amounts of solvent required. Another interesting observation was that a significant portion of these resources were used in the pretreatment of the waste which would have been unnecessary if raw chemicals were used.

The processes mentioned demonstrate that the chemical industry needs to focus on the big picture if they wish to implement green chemistry. Processes need to be analyzed as a whole, and take into account multiple variables, and have set priorities. Some of these citrus waste processes were found to be beneficial when compared to alternative methods such as in the case of xanthan fermentation. Further experimentation should still be done in order to see if the process can be improved.

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## ABBREVIATIONS

HMF, hydroxymethylfurfural; $CrF_3$, chromium trifluoride; [OMIM]Cl, octylimidazolium chloride; HCl, hydrochloric acid; HPLC, high pressure liquid chromatography; NaOH, sodium hydroxide; K2HPO4*3$H_2O$, potassium hydro-phosphate trihydrate; $MgSO_4$*3$H_2O$, magnesium sulfate trihydrate; VOC, volatile organic compound; CQD, carbon quantum dot; $H_2SO_4$, sulfuric acid; sc$CO_2$, HAD, 1-hexadecylamine AD, super critical carbon dioxide.

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# Development in the Commercial Methods of Recycling Poly(Ethylene Terephthalate)

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*KEYWORDS: Polyethylene Terephthalate, PET, Sustainability, Recycling, Green, Solvolysis, Applications*

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**ABSTRACT:** Green chemistry and sustainability are important topics in modern chemistry. The sustainability of the plastics industry therefore, should be of considerable concern. Polyethylene terephthalate (PET) is a common high volume thermoplastic polyester resin, which is used broadly in plastic packaging, textiles and beverage bottles. Development in the commercial methods of recycling PET has therefore been investigated in the context of green chemistry and sustainability. It has been observed that the progress made in the commercial recycling methods of PET has resulted in a not very green and unsustainable system for the production and effective removal of PET from the environment.

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## INTRODUCTION

Sustainability and the term “green” given to certain products and processes are becoming increasingly popular in society and chemistry as the difficulties posed by the finite supply of global resources is becoming more and more apparent. Plastics are a very common material used worldwide, thus their environmental impact and sustainability are becoming important subjects of concern [1]. Due to the broad nature of the subject, focus is made on polyethylene teraphtalate (PET), which is a common, high volume thermoplastic polyester resin [2] and is broadly used in plastic packaging, textiles and most notably, beverage bottles [3]. As a result, over the past three decades, recycling of used plastics across the world has risen greatly [4]. The recycling of plastics has had its difficulties however, where it was expected to be inefficient, impractical and not economically viable [4]. This is due to the low value of recycled PET and its monomers in addition to the costly procedures of recycling. Even so, the relative amount of PET waste occupying landfills has decreased since its use commercially [4]. Therefore, development in the processes of

PET recycling and new applications for recycled PET are suspected to have been developed.

### Methods of Recycling PET

PET is a material that is robust to atmospheric and biological means of degradation [5-7]. Zhang, J., et al. (2004) studied the biodegredation of PET with exposure to microbes and lipase. The conclusion was that there were only cracks on PET fibers after accelerated degredation. Therefore, recycling is the only method to achieve significant PET degradation and reuse. Generally, there are four discernable methods of plastics recycling: direct reuse, chemical reprocessing, mechanical reprocessing, and finally, energetic recovery [4]. Energetic recovery is where the plastic is combusted to yield thermal energy [4]. Due to the reasonable assumptions that reuse and energetic recovery yielded no significant development, where the former offers no potential application of chemistry and that the latter is fundamentally unsustainable, focus is made on developments in chemical and mechanical reprocessing.

### Chemical Reprocessing

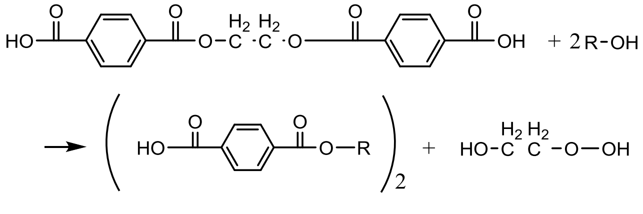
Chemical reprocessing is the most lengthy and expensive form of plastics recycling as it often involves depolymerization and re-polymerization often following purification, which can include distillation, recrystallization and additional chemical reactions [4]. PET belongs to the group of plastics known as polyesters and is commonly synthesized through the polycondensation reaction of terephthalic acid (TPA) or dimethylterephthalate (DMT) and ethylene glycol (EG) [9]. Either pair of reagents first form the monomer bis(hydroxyethyl)terephthalate (BHET). After the addition of certain stabilizers and additives, the pre-polymer (BHET) undergoes polycondensation to form PET and release n-1 moles of EG in the reaction scheme:

**Scheme 1. Polycondentsation of BHET**

$$n\text{BHET} \leftrightarrow \text{PET} + (n-1)\ \text{EG}$$

Depolymerization therefore involves the breaking of the bonds formed in the polycondensation reaction. This is generally accomplished by what us known as by solvolysis [10]. The depolymerization processes that have reached the level of commercial applicability are glycolysis and methanolysis [10-12]. Presumably, glycolysis involves depolymerization in the presence of EG and methanolysis involves depolymerization in the presence of methanol. These two depolymerization processes are fall under the term alcoholysis and progress as follows:

**Scheme 2. Alcoholysis of a Dimer of PET**



Methanolysis is performed in excess methanol at high pressure and temperature (2-4MPa and 453K-553K) along with a transesterification catalyst, which is usually zinc acetate [10]. The products of the methanolysis reaction are DMT and EG.

Glycolysis is similar to methanolysis such that high temperatures and pressures are required (453K-523K, yet the reaction is performed in excess ethylene glycol and methanol is not part of the cycle [10]. In addition, an esterification catalyst is also used and is most commonly zinc acetate [9-10]. An interesting aspect of glycolysis is that partial glycolysis can be performed, resulting in oligomers of lower chain lengths known as glycolyzates [10]. The products of what is known as deep (more complete) glycolysis of PET is BEHT and EG [10]. Much of the research done in chemical processing using glycolysis is not in development of improved methods of chemical processing, rather research in applications of the glycolyzates obtained from glycolysis and many are described in [10]. An unfortunate outcome is this has caused stagnation in the improvement of commercial chemical recycling processes of PET. This is made apparent since glycolysis and methanolysis were proposed as recycling processes since the first commercial uses of PET in the 1950s [10]. Nonetheless, there has been a reported attempt of improving glycolysis methods by Troev, K., et al. (2003), who researched the development of a more effective glycolysis catalyst. They proposed use of titanium (IV) phosphate rather than the commonly used zinc acetate catalyst and proved more rapid depolymerization of PET. A more recent example of improving the chemical recycling of PET was done by Bartolome, Leian et al. (2014), which involves the use of superparamagnetic γ-Fe 2 O 3 nanoparticles as a catalyst, which is easily removed.

Other methods of solvolysis have been considered, such as hydrolysis [3. 10] and aminolysis [15], but have never made it to the commercial scale.

### Mechanical Reprocessing

This method of reprocessing involves actions such as the grinding, melting, reforming and extrusion of PET waste [4, 16]. This process is subject to specific concerns however involving the purity of the recycled PET and its structural integrity [4, 16]. Mechanically recycled PET may include contaminants, making it unsuitable for food containers [17, 18]. In addition, post-consumer PET experiences a loss in inherent viscosity when recycled mechanically due to hydrolysis reactions in the melting process, resulting is shorter chain length [16]. Chain length and inherent viscosity are important parameters in plastic polymers because they are direct measurements of the strength of the polymer. Significant loss in polymer strength may result in the inapplicability of the recycled polymer for its former uses. This is one of the main draw backs of mechanical processing. Recycled PET can be blended with virgin polymer of longer chain length in attempt to prevent this [4], but this reduces the effectives of this recycling process in terms of sustainability.

In attempts to use only recycled PET in mechanical reprocessing, groups such as Awaja, F., et al. (2004) at RMIT university have made processes for chain extension of PET using a “reactive extrusion process”. This process involves the chemical reaction of PET with pyromellitic dianhydride (PMDA), a known chain extending and branching polymer agent [19, 20]. This reaction is perfromed during the extrusion process to afford PET of increased inherent viscocity (increased chain length). The experiment proved that the use of a commercially available extruder with a reactive concentration of PMDA ranging from 0.15-0.31%wt of PET polymer is possible

[16]. Also, the addition of the PMDA during extrusion and the subsequent increase in viscocity of the extruding PET put a pressure on the die of the extruder within standard safety limits and the reaction itself occuring in the extruder was proven to be able to be controlled reasonably [16]. Therefore, using very small amounts of %wt. PMDA, in a processe applicable to existing recycling faclities, recycled PET can maintain its inherent viscocity and thus its chain length resulting in higher tenisle strenght than regular recycled PET. Regular mechanicaly recycled PET exhibits both lower impact and tensile strengtht han virgin PET [16]. Chains extendeded mechnically using recylced PET can thereofore be potentially used for a wider range of applications much like virgin polymer blended recycled PET, whle using a reagent (PMDA) that only consists of leass than 1%wt of the recycled PET polymer.

## Applications of Recycled PET

As stated earlier, chemical reprocessing involving the glycolysis of PET result in what are known as glycolyzates. The majority of the research in chemical reprocessing has gone into applications for these oligomers [10]. For example, their use has been reported many in the production of polyurethanes, by which products such as foams and paints have been produced [10, 21]. Some other applications researched is that of recycled Pet involved in the creation of polymer concrete and polymer mortar using polymer resins derived from recycled PET [10].

## DISCUSSION

Unfortunately, however developed the current commercial mechanical processes become, there will be a point when the recycled PET cannot be reprocessed any further and will once again reoccupy landfills, potentially spliced with many other substances such as chain extenders, plasticizers and other plastics. All of these compounds will potentially persist and harm the environment. However, mechanical processes from a green chemistry perspective are greener than chemical processes since there are no or potentially very minimal stoichiometric reagents (minimal in the case of chain extenders) and they can be performed with or without solvent. Although mechanical processes require considerable energy input as it is a physical conversion, when compared to chemical reprocessing, mechanical reprocessing can be considered roughly on par. This is because of the substantial energy requirements of solvolysis, represented by the high temperature and pressure requirements of the reactions. Not to mention, the energetic and chemical requirements of the purification steps involved in chemical reprocessing. Therefore with regards to green chemistry, mechanical reprocessing can be seen as greener than chemical reprocessing, but its products will end up having a negative environmental impact due to their unsustainability.

Taking into account the direction in the development of commercial chemical recycling methods of PET from a green chemistry and sustainability perspective, the PET industry has taken a wrong turn from the beginning. As stated, the basis of the commercial methods (solvolysis) of chemical reprocessing for PET have remained mostly unchanged since PET started becoming of commercial use. The majority of research and development has gone into potential methods for applications of recycled PET, where the resulting products of these methods are just more polymer resins and other non-biodegradable synthetic products. This research direction is heavily influenced by economic incentive, since the cost and effort of recycling PET will always be greater than the production of virgin PET. In addition, the recycled PET and its monomeric units have a low market value, which is why new high market value recycled PET based products is the desired focus of research. This is detrimental to the sustainability of the PET industry since there is no cyclic nature of the production and recycling of PET. To elaborate, the amount of PET in landfills has been diminishing, but it is simply being transformed into other non-biodegradable materials. Crudely put, this can be seen as just simply spreading the PET waste around, giving it different names and making it look like it is not there. What happens to these new recycled PET derived products after their lifetime? Do they undergo further chemical processing resulting in more waste and energetic burden? Or, do they simply make their way back to landfills? Therefore, the only way for PET to be sustainable is if it were to be chemically recycled and reformed specifically back into PET to be reused. Although this is impossible due to the economic aspects previously mentioned. Moreover, there is the societal responsibility of individuals to properly dispose of their PET waste and provide it recyclers, which is a separate issue entirely in itself.

With regards to green chemistry, the actual commercial chemical processes (solvolysis) involved in chemical reprocessing have elements of greenness, but also possess areas of considerable concern. Inherently, solvolysis reactions can be seen as the reverse of the ester bond formation of the polycondenstaion reaction of PET. This is illustrated nicely in **scheme 2.** if the alcohol were ethylene glycol. It is common fact that reverse reactions often require a lot of energy to proceed and solvolysis is of no exception. As stated both commercial methods (glycolysis and methanolysis) require very high pressure and temperature reaction conditions in order to proceed. This can be seen as not a green aspect of these processes since minimization of energy consumption is important in green chemistry. In addition, glycolysis and methanolysis often leave behind harmful EG residues [5, 9] and the use of solvent (the alcohols) is an innate feature of these reactions. The minimization of toxic byproducts and solvents are also important in green chemistry. Glycolysis and methanolysis however, in terms of the reagents used bear some green aspects. For instance, the alcohol is only partially consumed in the glycolysis reaction, illustrated in scheme 2. This makes PET generally the only fully stoichiometric reagent. Plus, the reaction is mediated by a catalyst. Finally, if the alcoholyzed PET was used to regenerate PET, in the end, PET and the alcohol can be considered as not really stoichiometric reagents, since they are regenerated in the polycondensation reaction. From this perspective of the general overview of the reaction (not considering purification, phase changes etc.), depending on the green aspects of concern, glycolysis and methanolysis can be seen as somewhat green methods of chemical PET reprocessing. Though, the non-green aspects of glycolysis and methanolysis are inherent to the solvolysis reaction and so if commercial chemical reprocessing were to be made greener, then commercially applicable improvements of these methods or potentially new methods of chemically recycling PET would need to be researched. Albeit, this is problematic due to the general focus of previous and more current research. Considering everything learned, it can be concluded that the current commercial methods of PET recycling are in some important aspects not green and do not provide a sustainable system of PET production and removal from the environment.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## ABBREVIATIONS

PET, EG, TPA, DMT, BHET, PMDA.

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# Review of Polychlorinated Biphenyls Treatments in Water and Soils: from Supercritical Fluid Extraction to Rhizoremediation

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*KEYWORDS. PCBs, activated carbon, supercritical fluid extraction, rhizoremediation, aerobic and anaerobic organisms, earthworms*

**ABSTRACT:** After the significant use of polychlorinated biphenyls (PCBs) in the chemical industry between the 1930s and 1970s, the need for treatment has become a relevant research interest. An approach to analyze the overall impacts at a biochemical level, followed by a proposal of solutions to remediate PCBs contamination, is suggested here. The proposed solutions are based on a critical analysis of previous work done on bioremediation processes and chemical treatments for PCBs in soils and water.

## INTRODUCTION

Polychlorinated biphenyls (PCBs) were intensively produced and used from 1960 to 1975. At the time, chemical industries significantly increased their production due to the high demand from the army. Technological advances were critical for many countries during the World War II which justifies for the multiple applications found for PCBs.[2] Because of their numerous physicochemical properties, their industrialization became one of the most developed, especially in the United States.[3] The most common applications for PCBs include hydraulic fluids, plasticizers, adhesives, pesticide and extenders.[4-6]

Although the toxicity of some PCB samples was assessed in 1966 and that it was later confirmed with the Yusho incident in 1968, the production of PCBs is observed to hit its maximum in the 1970s.[7] Records from 1929 until now report about 1.5 million metric tons produced worldwide.[8] It is only until the Stockholm Convention on Persistent Organic Pollutants in 2001 was implemented, that the world-wide production of PCBs started to decrease to reach a less dangerous amount.[9] This reduction correlates with a noticeable decline in the concentration of PCBs found in the environment. The urge to banish such production is supported by the many evidences of high toxicity caused by such chemicals. All high organisms, and indeed the entire population of our biosphere, are greatly affected by long term exposure to PCBs.[10] Health effects such as immune deficiencies, reproductive or nervous system difficulties, and an increased risk of getting cancer were observed in populations subject to continuous exposure to PCBs.[11]

The cessation of the production of PCBs resulted in a significant reduction of its concentration found in fresh water, soils and oceans. Still, the persistence of PCBs, explained by their low water solubility, makes them very hard to completely remove. More importantly, urban areas concentrate the greatest amount of PCBs on the surfaces of buildings and industrial infrastructures. Altogether, the remediation of PCBs in our environment, both natural and anthropological one, represents an important health concern.

Many researchers have looked at the problem and came up with various solutions.[12-14] However, there are two categories standing out overall, namely the chemical direct treatment and the biological indirectly initiated treatment. In this work, the viability of the different techniques reported in both categories is to be evaluated based on the twelve principles of Green Chemistry as defined by Anastas.[15] Eventually, two final preferred techniques are compared on the basis of life cycle assessment to suggest the greenest and most realistic solution for long-term PCB remediation.

**CHEMICAL REMEDIATION.** Thermal desorption represents one of the most efficient methods to decompose PCBs in contaminated soil, at efficiencies exceeding 95% decomposition. Unfortunately, many disadvantages are associated with such a technique. First, it requires very high temperature and therefore a significant amount of energy. Then, in spite of a very high degradation yield, it forms other toxic products known as polychlorinated dibenzofurans (PCDFs). The thermal desorption is found to even increase the toxic equivalency quantities (TEQ) of PCDFs. This technique is not only costly in terms of energy consumption and in financial means, but it also presents dangerous toxicity that doesn't make it a viable technique to pursue in the long term. Furthermore, it has no potential in being performed in situ, which means that it is geographically limited to certain areas such as the Arctic where PCB contamination has dangerous impacts on the fragile and scarce ecosystem. Thermal and chemical oxidation technologies present the same byproducts and inconveniences. The excavation and destruction of PCBs by incineration is another technique that has been extensively used. The summit of Resolution Island, Nunavut, has been successfully decontaminated using this technique by 96%. The PCB removal in this area was especially successful considering that a long term plan was also implemented in order to continue the pollutant control after excavation. A permeable reactive barrier was set up, preventing the remaining contaminated soils from spreading into the ecosystem. Nonetheless, this overall process took about 7 years and cost $20 million. In addition, the removal of PCBs was not absolute and well-controlled over time[16], in spite of the presence of a preventive barrier. In the perspective of making such removal more economic and viable in the long term, the development of an in situ removal process has been studied[17].

**Activated Carbon.** Activated carbon (AC) has long been used to treat waste water, drinking water and ground water by removing organic pollutants. Its high hydrophobicity, high specific surface and microporous surface makes it a good adsorbent for this type of chemical.[18] Its effectiveness, already proven for water treatment, has also been observed in sediments and soils. Experiments have studied the very successful removal of PCBs using activated carbon in Histosol and Alluvial soils, which are organics-rich and sediment-rich soils, respectively. In marine sediments, not only is AC shown to be very effective without being affected over time, but it also maintains an unperturbed system thanks to a stable binding between AC and PCBs. Some studies have evaluated the effectiveness of two types of activated carbon, namely granular activated carbon (GAC) and powdered activated carbon (PAC). The data reported by Vasilyeva et al is presented in Table 1.

**Table 1. GAC and PAC chemical properties (based on data reported by Vasilyeva et al.)** [17]

| Characteristics | GAC | PAC |
|---|---|---|
| Carbon source | Coal | Peat |
| Particle diameter, μm | 400-1500 | 1-100 |
| Elemental carbon, % | 84 | 85.1 |
| Specific surface area, $m^2/g$ | 880 | 1000 |
| Total pore volume, $cm^3/g$ | 0.86 | 0.78 |
| Micropore volume, $cm^3/g$ | 0.36 | 0.43 |
| Fe content, % | 1.4 | 0.65 |

Although no difference of success was reported between the two forms of AC, it was confirmed that PCBs could be successfully removed from historically contaminated soils over a long period of time, down to 95% reduction. [17]

The recovery of PCBs from contaminated soils was reported to be successful, using hexane and acetone. These solvents dissolve AC effectively based on its significant hydrophobicity, predictable from its chemical structure as presented in Figure 1. However, hexane is known to possess adverse health effects. While its effects in the atmosphere are minimal and it is not even considered a greenhouse gas, the presence of hexane in water does have dangerous effects on the ecosystem. Nevertheless, it can be said that well managed and recycled solvents, in spite of their toxicity, represent a negligible risk for the environment and do not go against the twelfth green principle that advocate the preference for safer chemical procedures. [15]

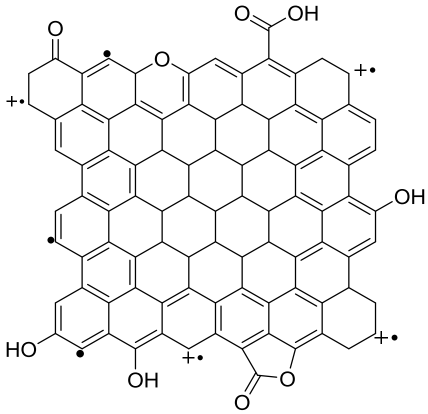
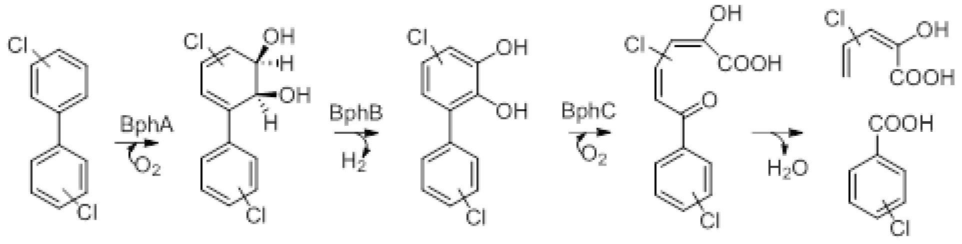


**Figure 1.** AC chemical structure responsible for its hydrophobicity (based on structure as proposed by Mochida) [19]

On the other hand, the carbon source for GAC is more harmful than for PAC as they come from coal and peat, respectively. The production of coal is known to have many



**Scheme 1. Dioxygenase of a PCB by aerobic organisms (as reported by Vrchotová) 1**

polluting impacts on the environment[20]. The air, soil, and water pollution it generates is often poorly controlled and creates many health hazards for populations living nearby. In addition, coal mining results in excavation and destruction of the landscape that are rarely recovered and where vegetation is poorly restored[20]. Similarly, even if peat production is not as harmful as coal industry, it is not totally harmless. It is in fact responsible for a serious upheaval of the environment and more specifically swamp ecosystems[21]. The risk of fire and erosion is significantly increased by the disruption of the hydrology in swamps which is caused by peat extraction. In both cases, the remediation of PCBs, although very efficient, can somehow represent another risk for the environment. As a result, the sources from which GAC and PAC are obtained need to be well-regulated in order to ensure that the environmental improvement they can provide is not counter-balanced by another negative impact.

**Supercritical fluid extraction (SFE).** A study done by Reutergardh et al. reported the use of supercritical carbon to extract three planar PCBs (PCB-77, PCB-159, PCB-126) and three mono-ortho PCBs (PCB-105, PCB-156, PCB-189) from three types of tropical soils. [12] These six PCBs are put under study as they are considered as the most toxic ones of their kind; their structures are given in Figure 2.

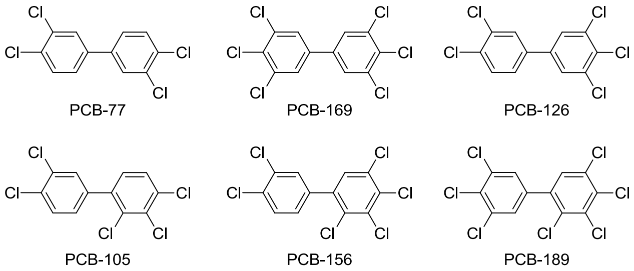


**Figure 2.** Six different PCBs extracted using supercritical carbon

The use of supercritical fluids to extract organic molecules is known to be not only an effective but also a selective extraction method. In this particular case, the use of carbon dioxide ($CO_2$) is one of the most popular green media used in chemical extraction. It has moderate critical pressure, 74 bar, and temperature, 31°C; it is a safe medium to handle as it is neither toxic nor flammable[22]. This study yields good extraction of all types of PCBs from tropical soils. The success of the extraction varied in function of the soils properties but most importantly with the structure of the PCB extracted. Mono-ortho PCBs revealed a more significant extraction yield than their planar congeners. The extraction is found in all cases to be relatively fast, about 40 minutes. Finally, while the moisture of the soils has effects on the final yields, the temperature has little impact on these extractions. [12]

In the same manner as for AC, the isolation and recovery of the extracted PCBs required the use of n-hexane. [12] The same disadvantages associated with this solvent are therefore added to this technique.

**BIOLOGICAL REMEDIATION**. The less harmful way to treat PCBs, that would also require less effort and energy, is to do it in situ. Finding the way to degrade them, where they are found in the environment, consists in the most sustainable way to properly, and eventually completely remove them.

**Rhizoremediation.** The capacity of certain roots to enhance the activity of some pollutant-degrading bacteria is also known as rhizoremediation; this method belongs to phytoremediation which regroups all plants presenting the same ability. All roots do not possess the same rhizoremediation properties, as reported by Slater et al. [13]When evaluating the effect of two plants, Salix alaxensis (willow) and Ricea glauca (spruce), on the reduction of PCBs toxicity in soils, they observed that only willows were rhizoremediating PCBs. More interestingly, the presence and production of salicylate were found to have no effect on PCBs reduction while biphenyls did. Nonetheless, the toxicity associated with biphenyl-treatment was found to be much higher than with willow roots only. Unfortunately, their identity and detailed mechanism of removal have not been reported yet. [23] Nevertheless, a list of biphenyl-utilizing bacteria that could be responsible for such remediation has been proposed and studied by other groups. [24] It is reported that polychlorinated biphenyl is degraded by dioxygenase attack before being metabolized to chlorobenzoic acid. The rough mechanism of a dichloro-PCB is presented in Scheme 1.

The degradation of PCBs is debated to be either due to oxidative degradation by aerobic microbes (grow in oxygen-rich environment) as given in Scheme 1, or to dechlorination by anaerobic ones (grow in deoxygenated environment). These bacteria include multiple gram-negative genera such as Pseudomonas, Alcaligenes, and Acinetobacter, and gram-positive genera such as Rhodococcus, Corynebacterium, and Bacillus. [25-26]

All of the above use biphenyl as a source of carbon and energy, and co-metabolize PCBs with the same enzymes used for biphenyls. This mechanism explains why addition of biphenyl in soils with PCBs yielded an important PCBs removal. Four general concepts were withdrawn from numerous studies on PCBs depletion and are given as reported by Furukawa and Fujihara: (i) the decrease in biodegradability is correlated with an increase in chlorines; (ii) PCBs with only one chloro-substituted phenyl will degrade faster than those with both rings chloro-substituted; (iii) double ortho-substituted PCBs are poorly degraded; (iv) bacterial strains is responsible for the rate of degradation as well as which ring is to be first attacked[27].

In the same range as for willows rhizoremediation, this group reported an effective degradation percentage of about 40% with *Cucurbita* and *Cucumis* species. The list of plants with similar potential goes on and on, all able to perform phytoextraction and rhizoremediation with an efficacy of 30-40%.[28-30] Over about 200 days, soils planted with those species producing the adapted bacteria were observed to present a much lower PCB content and significantly decreased toxicity.

In spite of a longer amount of time to remediate PCBs content, the impact on the environment of these plants is beneficial. It can be debated that the ecosystem in question could be disturbed by the presence of inappropriate species. However, the diversity of plants with the ability of performing rhizoremediation of PCBs has been found to be sufficiently important to find the best-suited plant for a specific biosphere. Finally, such system doesn't require the use of any solvents for further treatment, and would only require manual labor. As in the Nunavut case presented previously, this could represent an employment opportunity to plant and maintain the remediating plants. Although the plants with the highest remediation efficiency haven't been yet determined, an effort in engineering plants generating more efficient PCB degrading enzymes is currently being developed. [30-31]

**Earthworms' contribution.** The efficiency of the phytoremediation performed by the plants presented previously can be further controlled and enhanced in function of the management of the soils. The participation of earthworms in the gas diffusion within soils was proven to contribute in an increase in PCBs bioremediation. Furthermore, the presence of earthworms allowed not only a better removal of PCBs but also a more uniform distribution at all depths. The increase of PCB-degrading bacteria was increased from 39% to 55%. Allowing better aeration and deposition of nutrient rich casts, the presence of earthworms allows a better metabolic activity of the PCB-degrading bacteria. This study raised the importance of parameters such as PCB bio-availability but also conservation of aerobic favored conditions. The selectivity of the enzyme responsible for the degradation of PCBs is not good enough to obtain yields higher than 30-40%. However, the addition of earthworms in the equation increased those yields up to 65%. Once again, this method is harmless to the environment. In addition, introduction and culture of earthworms have been proven to be limited in terms of financial costs.[32]

## CONCLUSION

The principal advantages of the two *in situ* controlled chemical treatments are their high degradation efficacy in addition to relatively fast kinetics. Bioremediation, on the other hand, presents two principal weaknesses, namely slowness and incompleteness. In spite of its great advantages over AC or SFE in terms of cost, bioremediation requires a longer amount of time for a smaller percentage of degradation. Nevertheless, the participation of organisms such as earthworms in the soils under treatment was found to provide significant improvement from 30% to 65% degradation. Unfortunately, location restricts the type of technique usable in addition to the urgency of decision making necessary. In the case of industrial accidents responsible for significant release of dangerous chemicals, immediate actions must be taken, with landfill disposal and excavation followed by incineration representing the first necessary steps. Nevertheless, lands where the use of herbicides containing PCBs was employed represent a less pressing issue. It is suggested that techniques such as AC followed by planting of rhizoremediating plants are considered sufficient interventions for the level of toxicity being faced.

Eventually, the use of rhizoremediating plants in tandem with earthworms would represent the most sustainable and cheapest PCBs remediation. However, in spite of their potential production costs, both GAC and PAC have the capacity to remain efficient over time and do not need to be renewed. The combination of AC and a rhizoremediation-favored environment appears to be the most realistic and flexible application no matter what type of environment is to be treated. This tandem strategy will allow efficient PCBs removal and ensure a reduction in soil toxicity. In contrary, the use of SFE is neither a realistic nor a practical PCBs remediation technique for isolated spaces. Although it is one of the fastest techniques, it requires more labor and expertise when considering larger volume of contaminated soils. An economic analysis was however performed on the use of SFE as a PCB removing technique. It is reported, that with its $170-200 per cubic meter cost, SFE would be economically preferable in comparison with excavation where transportation costs can become significantly excessive.[33] Though SFE can be considered interesting for PCB remediation in urban soils, it still doesn't present a cost-benefit ratio attractive enough when applied to remote and vast areas.

To conclude, because their efficacy does not decrease over time, AC and rhizoremediation ensure the prevention of further pollution of PCBs. Due to their stability in soils, in case of another chemical spill, both bacteria and AC will still have the potential to degrade PCBs. Consequently, industrial areas with chemical risks could plant species with the potential to phytoremediate the dangerous chemicals produced or used by the industry concerned. Although this paper has essentially focused on PCBs, it is interesting to mention that other applications, such as 2,4,6-trinitrotoluene (TNT) could degradation, can be performed using both AC and some phytogenerated bacteria[34]. Further studies on the behavior and chemistry of the enzymes used by PCBs-degrading bacteria could in the future provide a superior and more efficient solution to achieve a 100% degradation of historically PCBs contaminated soils. Overall, the use of a solvent-free and *in situ* remediating technique is preferable.

## ABBREVIATIONS

PCBs, Polychlorinated biphenyls; AC, activated carbon; GAC, granular activated carbon; PAC, powdered activated carbon; PCDFs, Polychlorinated dibenzofuran; TNT, 2,4,6-trinitrotoluene; SFE, Supercritical fluid extraction

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