

GREEN CHEMISTRY: A FOOTSTEP TOWARDS SUSTAINABLE DEVELOPMENT

Abstract

The word *chemical* comes into our mind with something harmful or negative. This aspect is transmitted from our surroundings - deployed from the maltreatment of chemicals. The idea of *green chemistry* has arisen in response to keeping down the harmful impacts of man-made materials. This branch of Chemical Science is usually described by the 12 principles possessing the key elements: minimizing waste reduction, product toxicity, energy consumption, and enhancing the use of renewable and safer resources. This chapter briefly presents the initiatives taken by the government to improve research in the perspective of green chemistry; examples in addition to recent advancements in this area. The considerations in designing novel-safer chemicals and futuristic trends of greener solvents are also introduced here.

Keywords: Green chemistry, safer solvents, polluting chemicals, energy efficiency, biodiesel.

Authors

Sonaxi Kharb

Department of Chemistry
Baba Mastnath University
Rohtak, India.
sonaxikharb@gmail.com

Anshul Singh

Department of Chemistry
Baba Mastnath University
Rohtak, India.
anshul9008@gmail.com



Figure 1: The Diagrammatic Representation of the Twelve Key Principles of Sustainable Chemistry

I. INTRODUCTION

The term “Green Chemistry” corresponds to working out on the designing of chemical products and their production approaches which can eliminate the generation of materials toxic to the ecosystem [1–6]. Green chemistry recapitulates threats, whether physical (flammability, explosivity), toxicologic (carcinogenicity, hormone disruption), or universal (environmental impacts, ozone diminution, atmosphere change) as an in-built trait of a molecule. Therefore, the menace can be taken in hand by designing suitable structures and the physicochemical properties associated with it at the molecular level [7]. In other words, green chemistry also refers to the lowering consumption of nonrenewable resources and various approaches for pollution prevention. The concept of green chemistry is evolved in regulatory communities from pollution prevention initiatives. The upgrade to improve commercial production gave rise to inadvertent harm to our planet and humans. Choked waterways, acid rain, measurable ozone holes, and adverse human and environmental health are some long-term negative effects of these upgrades [8].

The term is similar to sustainable chemistry or circular chemistry [9]. The Organization for Economic Cooperation and Development (OECD) declared in the 1990s that sustainable chemistry is a scientific concept that attempts to promote the use of natural resources in such a manner that human requirement for chemical goods and services may be met [10]. Ecofriendly chemistry deals with making practices that augment product valuation while overlapping the objectives of guarding and enriching the milieu as well as human well-

being [11]. Environmental chemistry meets the consequences of toxic/polluting chemicals on the landscape.

The amount of hazardous household and industrial wastes can be cut down with the help of the reduce, reuse, and recycle model which is the principle of the circular economy - utilizing robust stress on “reduce”. Green chemistry does not adhere to the principle that maintains matters in the current- circular model; even now obliges the procedure of taking up-making- usage- dispose of - linear economy model [9].

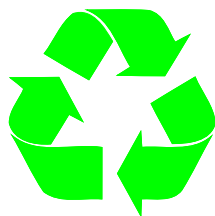


Figure 2: Mobius Symbol for 3R's Principles of Circular Economy

According to the “benign by design” concept, green chemistry bypasses contamination by using environmentally benign processes and designed/innovative products [12].

II. INITIATIVES TO FOSTER STUDY IN GREEN CHEMISTRY

Governments and other officialdoms made an effort to promote the exploration of green chemistry by employing the following initiatives and documents:

1. Competitive award programmes (for example, the 2007 American Chemical Society Award for Affordable Green Chemistry) [13].
2. Project and grant financing programme, the "Presidential Green Chemistry Challenge" from the USA government in 1996 [14].
3. Scientists and researchers are recognised for their contributions to green chemistry. Richard Shrock (USA), Robert Grubbs (USA), and Yves Chauvin (France) were awarded the Nobel Prize in Chemistry in 2005 for developing metathesis [8].
4. Several international organisations highlighted green and sustainable chemistry as part of their strategy. The Organisation for Economic Cooperation and Development, the International Union of Pure and Applied Chemistry, the European Chemical Industry Council, and the Federation of European Chemical Societies are a few examples [15].
5. Pollution Prevention Act (1990) EPA [16, 17]. Pollution prevention (P2) is also known as “source reduction” as presented by the EPA Waste Management Hierarchy. P2 is any practice that prevents pollution at the source level before its creation.
6. In his book Green Chemistry: Theory and Practise, Paul Anastas, the pioneer of green chemistry, outlined the twelve fundamental tenets of green chemistry [3], [18–20]. The US Environmental Protection Agency has now endorsed these principles.

III. PRINCIPLES OF GREEN CHEMISTRY

The concept of green chemistry is comprised of 12 fundamental principles. These are the following:

- 1. Prevent Waste:** Using potent starting material in less amount is more reliable than cleaning after formation.
- 2. Maximize Atom Economy:** Approach synthetic methods that boost whole material utilization furthermore keeping down the byproduct emergence.
- 3. Design Less Perilous Methodologies:** Plan routes of synthesis that employ and produce substances that are less toxic for the upbringing of environs.
- 4. Design Secure Chemicals and Effective Outputs:** Model the substances used in a process to maintain effectuality and have little or no virulency.
- 5. Minimize the Usage of Ancillary Substances:** Make usage of separating agents, solvents and other ancillary chemicals ought to be evaded whenever practicable. If mandatory to use, greener and safer should be used up.
- 6. Increase Energy Efficiency:** Necessities for energy ought to be minimized regarding their impact on the environment and economy, whenever feasible. Chemical reactions need to be completed at room temperature and pressure.
- 7. Utilization of Sustainable Initial Inputs:** Whenever technically and economically possible, starting raw materials should be renewable which is usually obtained from agricultural wastes and products.
- 8. Circumvent Nonessential Derivatization:** Whenever possible, it is best to avoid superfluous modifications like blockage of activated groups, removal of protecting groups, and transient alteration in procedures. Derivatives use extra reagents and create waste.
- 9. Augmenting Catalyst Activity Rather Than Applying Stoichiometric Reagents:** Make use of selective and reusable catalysts instead of stoichiometric reagents as much as possible. Maximize waste reduction efforts by implementing catalytic reactions. Catalytic agents are efficacious in moderate quantities and can be used many times resulting in waste reduction.
- 10. Encourage Biodegradable Chemicals And Products:** Design chemicals that break down into harmless byproducts after use instead of accumulating in the environment.
- 11. Evolve Analytical Methodologies For Real-Time Monitoring:** In advance of harmful product formation, analytical methodologies are developed for real-time monitoring and control during syntheses.

12. Lessen The Potential For Chemical Accidents: Design or select the substances-essential for chemical processes, permeating a lower risk of incidents such as explosions, fires, and environmental releases.

Some of the Well-Known Examples of Green Chemistry are as Follows:

- Double decomposition reaction of natural triglycerides is a catalytic reaction that can be commenced by selecting the materials sourced from sustainable resources e.g. oleochemical feedstocks. Worthful chemical products can be obtained with exceptional selectivity while using gentle conditions either directly or in a few steps [21]. Metathesis of unsaturated fatty ester – oleic acid methyl ester provides a suitable route to unsaturated diesters- dimethyl octadec-9-enedioate and internal alkyne- 9-octadecene provided a suitable catalyst is available. The reaction given below is an example of a 100% atom-efficient process in which only useful products are obtained and no by-products [19].

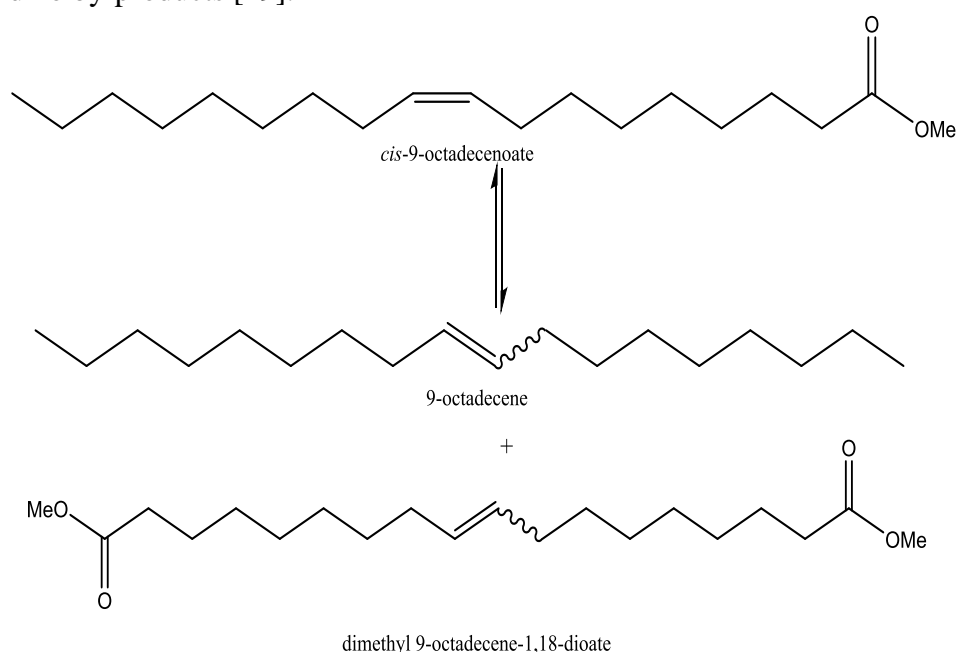


Figure 3: Metathesis of an Unsaturated Ester of Oleic Acid.

- Adipic acid [$\text{HOOC}(\text{CH}_2)_4\text{COOH}$] is used for the production of nylon, lubricants, plasticizers, and polyurethanes. Carcinogenic benzene is used as the standard substrate for the synthesis of this acid. Chemists from the State University of Michigan discovered enzymes in genetically modified bacteria by which glucose-almost inexhaustible, can be converted into adipic acid [22, 23]. Another method of synthesis is- the oxidation of cyclohexene provided hydrogen peroxide as a catalyst. Green chemistry principles - less harmful synthesis, minimal use of organic solvents, better yield, and recyclable compounds, are applicable to this new process [24].

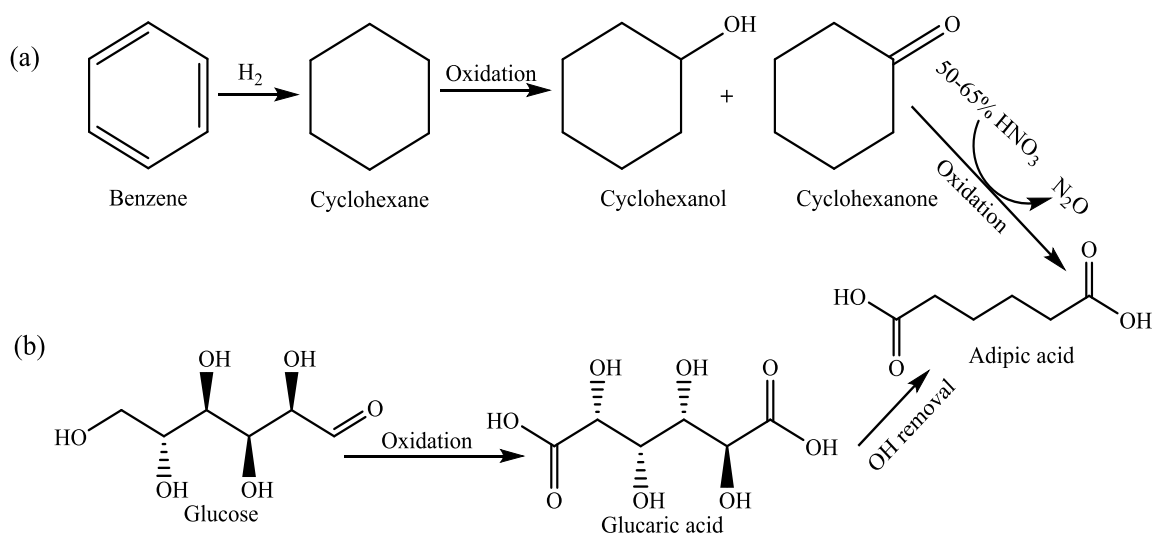


Figure 4: Schematic Representation For Adipic Acid Synthesis (a) Traditional Industrialized Route and (b) Green Route that Relies on Biomass, as Presented by W. Deng and co-workers.

- Biodiesel oil (a mixture of methyl esters and fatty acids) is designed from fats embedded in cultivated plant oils (soya beans) by removing glycerin molecules – a raw material for soap synthesis. Contrary to normal diesel oil, the combustion of biodiesel does not emit harmful sulfur wastes [22, 25].
- Plant oil containing triglyceride + methanol \rightarrow biodiesel + glycerin (in presence of KOH)

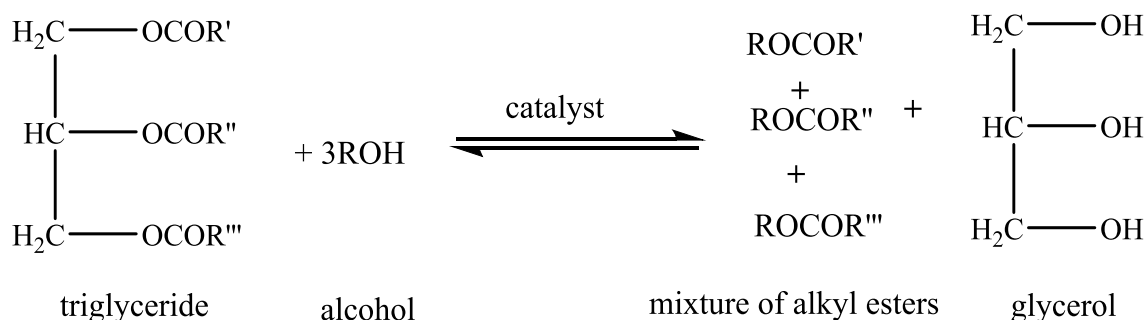


Figure 5: Schematic Representation for Biodiesel Synthesis as Presented by S. M. Ghoreishi and P. Moein.

- Carbon dioxide and water as supercritical fluids (SCFs) are the most frequently used reaction media for fulfilling green chemistry demands. Carbon dioxide as SCF dissolves non-polar compounds and some polar like acetone and methanol. In textile and metal industries, instead of perchloroethylene, liquid carbon dioxide is used for dry cleaning purposes [26, 27]. Trans-critical cycles are thermodynamic cycles in which fluids are used in their supercritical state for heat transport. Compact systems can be framed by the implementation of a single-phase heat transfer method which excludes heating at high temperatures. CO₂ can replace hydrochlorofluorocarbons (HFC) – working fluid in refrigeration systems.

Supercritical CO₂ promotes the segregation of desired compounds from a mixture followed by easy recovery of itself. For crystalline Zn₂SiO₄ formation, the solvent used is supercritical water which is well-suited to the environment. Ionic liquids – SCF is an excellent bi-phasic system for separation and reactions [28].

- Room-temperature ionic liquids (RTILs) behave differently from molecular liquids because of their constitution. Low viscosity and no measurable vapour pressure make RTILs environmentally benign reaction media. β glycosylation of glycosyl bromide and organic acids can be achieved through eco-friendly RTILs-enhanced systems [29].
- Green catalyst: green catalysts/bio-catalysts are safe alternatives for environmentally unsafe reaction mechanisms [30, 31]. Nano-catalysts[32] are a combination of homogeneous and heterogeneous catalysts [33]. Several pharmaceuticals and chemicals are synthesized from highly toxic nitriles that are xenobiotically derived or naturally occurring, by using nitrilase enzyme[34].

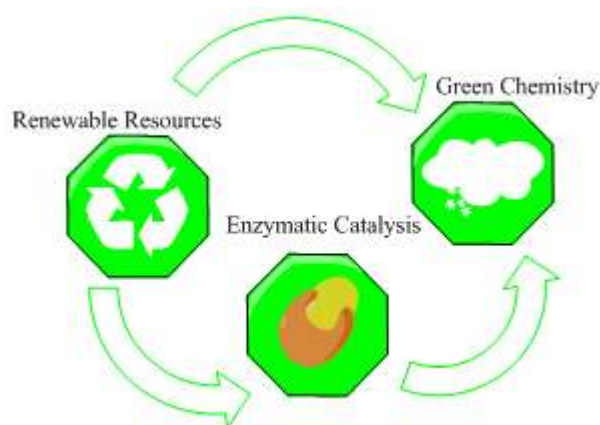


Figure 6: Correlation Between Enzymatic Catalysis and green chemistry

IV. RECENT RESEARCH IN GREEN CHEMISTRY

- 1. Green Ammonia Production:** Manufacturing of chemical fertilizers in industries heavily relies on ammonia production. Haber-Bosch process prerequisite hydrogen for ammonia production which can be generated by the green method i.e. biomass gasification as well as water electrolysis. Water electrolysis is powered by renewable sources [35]. Biomass gasification is an effective process for the conversion of several types of biomasses (renewable feedstock) into biofuels such as syngas (a mixture of CO and H₂) [36]. By this method, greenhouse gas emissions can be controlled at a very low cost.
- 2. Bio-based Polymers:** The utilization of renewable biomass alternatives instead of unsustainable fossil resources (starting materials for commodity material and fuel manufacturing) is what the word bio-based deals with. Polyhydroxyalkanoates (PHAs) are bio-based polymers [37] engendered due to the zymolysis of wastewater from papermaking industries, discarded polystyrene, and metropolitan wastewater [38–40]. Depending upon structural variations PHAs have various properties and

applications. Some physical properties of PHAs make them appropriate for one-time usage products. The PHA was produced from the fermentation of biogas from landfills and the air was successfully converted into a thermoplastic called 'Air Carbon' by Newlight Technologies [41].

- 3. Development in the manufacturing process of lactic acid:** Lactic acid has growing applications as its polymers and esters in industries for packaging, pharmaceuticals, and medical because of its biodegradable and biocompatible properties [42]. Utilizing farming waste like cereals haulm, Indian bean remnants, factorial leftovers of paper as well as pulp industries, indeed domestic refuse as substrates is a worthwhile option for lactic acid production. The conversion of abundantly available feedstock- starch and lignocellulose materials is tedious and cost-oriented hence genetic engineering is very helpful for economical production processes [43–45].
- 4. Biodiesel:** Bio-diesel is an alternative diesel fuel extracted from renewable resources. The calcium oxide nano-catalyst doped with zinc is a promising and affordable solution for creating eco-friendly, sustainable, and profitable biodiesel made by using castor oil [46]. Outili and coworkers stated that the utmost biodiesel transformation can be obtained by using 2% (weight by weight) potassium hydroxide as a catalyst and methanol-oil in a 4:73 ratio at 45°C and outputs satisfying the green chemistry balance [47]. The microwave and ultrasonic radiations were applied by Gude *et al.* to generate biodiesel from spare cooking oil with less energy consumption and by-products [48].
- 5. Plant-Mediated Synthesis of Metal Nanoparticles:** The metal nanoparticles have found applications in enzyme electrode design, medicine, ecology, analytical methods, and surface-enhanced Raman Spectroscopy (SERS). Plant-mediated creation of nanoparticles is an environmentally conscious alternative to chemical approaches as it uses plant or plant extracts, is cost-effective, and avoids the use of toxic chemicals [49]. Silver nanoparticles (AgNPs) [50] and gold nanoparticles (AuNPs) are being studied for their antimicrobial and antibacterial properties [51]. There is a growing trend in the synthesis of NPs by applying eco-friendly techniques.

V. DESIGNING SAFER CHEMICALS

Although all the 12 principles are evenhandedly imperative at this juncture, we will highlight the fourth principle i.e. designing safer chemicals and products/Generating effective but non-toxic products.

The fourth principle is indispensable for all of us, as any chemicals we use today have both a present and future impact. The ACS explicates that the planning of synthesis of chemical compounds is expected to maintain the potency although limiting noxiousness [52]. Prior to manufacturing usable items at the industrial level, most of these chemicals were made from daily-life organic ingredients after a few modifications. Complex chemicals were invented to get stronger, more durable products but with complex degradation. This affects the environment and life quality of people who are using and synthesizing these chemicals.

One of the substantial challenges for green chemistry is designing potent chemicals as acknowledged by the American Chemical Society because we still need these modified

products in everyday life but their eco-friendly and greener version to make breathing our children a sound environment.

1. The Concept of Designing Secure and Sound Chemicals: As defined in (DeVito and Garret; Designing Safer Chemicals), the concept of designing secure chemicals is to attain the most favourable connection among neurotoxic endpoints and productiveness of deliberate usage by implementing the structure-activity relationships and slight machination on molecular level [53–56].

The data supplied by the United States (U.S.) Environmental Protection Agency's (EPA's) Toxics Release Inventory (TRI): the U.S. pollutant release and transfer registry (PRTR) may be used to prioritize the commercial chemicals that need to be replaced.

2. Steps - Considered in Designing Safer Chemicals

- **Step 1: Need to know: safe or not?**

Some fundamental questions arise during the initial phase of designing a new chemical. How do we know whether synthesized compounds are safer or not?

Characteristics of the “Ideal Chemical” are [54, 56]

- Because of its good usage potency, less quantity is required to get the job done; hence lesser units need to be manufactured thus in turn less raw material and fewer byproducts.
- Better use efficacy.
- Can be manufactured greenly.
- Has minimal hazards to the ecosystem and global environment as possesses less toxicity, is non-explosive, and is non-flammable [57].
- Readily degrades to environment-friendly products.
- Does not cause biomagnification.
- **“Its Application Does Not Demand the Concurrent Usage of Other Chemicals that is Noxious.”**

- **Step 2: Procedure/protocol for replacement of compound**

U.S. EPA classified the chemicals as “existing” which were already in the marketplace in 1976 when TSCA (Toxic Substances Control Act) was passed and the chemicals that must pass premanufacture review for safety and compliance, were listed on TSCA Inventory. EPA classified the substances as “new” which were not on the TSCA Inventory and planned to be used in trade. The new chemical is obliged to register with EPA under section 5 of TSCA before starting its manufacturing. When the EPA supervises its review and supposes the substance appropriate, it will be added to the TSCA Inventory as an existing substance. [58].

In European Union, European Chemicals Agency normalized the chemicals under REACH (*i.e.* Registration, Evaluation, Authorization, and Restriction of Chemicals). This normalization standard identifies biological effects and risks linked to chemicals to maintain human health and environmental safety.

The Databank of Toxic Release Inventory (TRI) of the U.S. EPA helps to know whether a chemical is toxic or not. Emergency Planning and Community Right-

to-know Act (EPCRA) was passed by U.S. Congress under Section 313 which created TRI [59].

For future research in green design, the probabilistic diagram is a good approach to minimize the chances of being cytotoxic for a newly synthesized chemical. This is an extension of the chemical architecture method in which toxicity is measured in a lucrative rapid way with nominal use of animals using high-throughput *in vitro* cytotoxicity assays [60].

• **Step 3 : Prepare Hybrid Chemist also named a “toxicological chemist”**

To design safer chemicals, scientists should have integrated knowledge of toxicology, biochemistry, environmental science, and the relationship of pharmacological properties and toxicity with chemical structure. An individual having combined knowledge of all these disciplines is described as a “toxicological chemist” [56, 61]. Concerns in scheming harmless and tame substances imaginably assigned as external – the particulars which are outlying the organisms and internal – approaches that may get access to these organisms.

VI. FUTURISTIC SCOPE OF DESIGNING SAFER CHEMICALS

Green chemistry incorporates all attributes and varieties of chemical operations which could lower adverse impressions on social well-being besides the ecological unit relative to contemporary state-of-the-art attempts.

1. Mohammed and co-workers [62] reviewed the substitution of starting material in the polycarbamates (PC) synthesis procedure. The production of PC was done with ethylene oxide, carbon dioxide, and bisphenol-A instead of phosgene and solvent DCM. The alternative synthetic path with ethylene oxide and carbon dioxide was found safer because

- It replaces both phosgene and DCM.
- By-product is ethylene glycol resulting in less burden of waste treatment [63, 64].

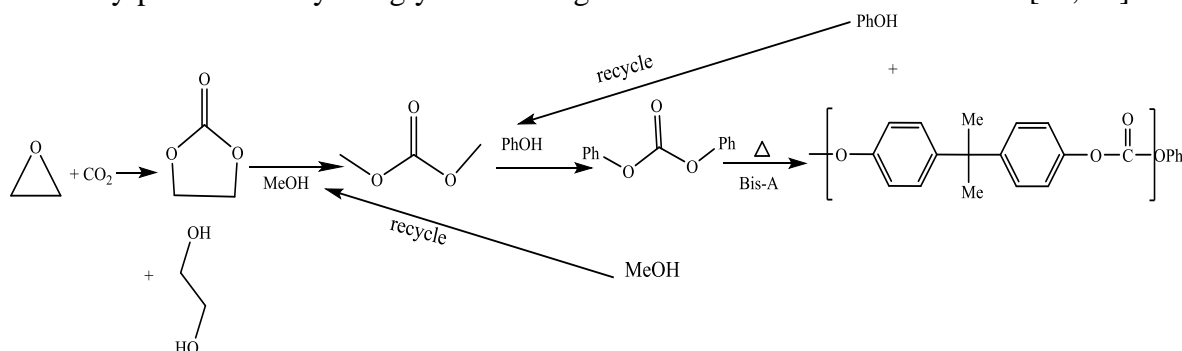
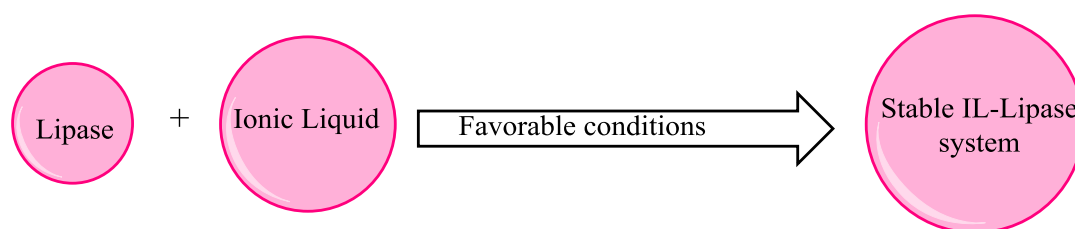


Figure 6: Schematic representation for synthesis of polycarbamates in a greener way as presented by W. Mohammed and Errayes Asma.

2. An environment-friendly approach to building molecular complexity, is a one-pot process. Roberta A. Kehoe and co-workers revealed the creation of multicyclic alkylated heteroarenes through a process that does not require phosphine and an inorganic base.

The process includes multiple steps - Mizoroki-Heck olefination, carbon-hydrogen stimulation, and hydrogenation in one-pot reaction sequences. A green agenda is motivated to avoid problematic additives and solvents and this avoidance might improve productivity and minimize risks in one-pot procedures by mitigating detrimental elements [65].

3. Stable Ionic liquids (ILs)-Lipase-based system can be used as an alternative to biofuel productions and other ester synthesis reactions. ILs increase the potential of reusing the catalyst and lower the risk of adverse environmental impacts. Further research work can be performed to improve the viability of the system[66–68].



4. Safer solvents designed to replace dichloromethane (DCM) for Chromatography Applications: DCM has become a broadly consumed solvent owing to its lower boiling point, expenditure, and ability to solvate heterocyclic compounds but it is carcinogenic and neurotoxic. A. Sharma et al. conducted research on three active pharmaceutical ingredients (API): (C₈H₉NO₂) 4-acetamidophenol, acetylsalicylic acid, and C₁₃H₁₈O₂ (pain-reliever). Thin-layer Chromatography, Hansen Solubility Parameter (HSP) theory, and dissolution analysis – these approaches were adopted to identify the possible substitute for dichloromethane solvent in pharmaceuticals. The down-selected solvents were further analyzed to find the best-fitting less hazardous substituent. This type of study can be applied to replace solvents [69].
5. Researchers reported a distinctive three-reaction process that yielded a series of benzochromenes in good quantities. The example shown below highlights the effectiveness of auto-tandem catalysis and its potential for further advancements in green chemistry [65].

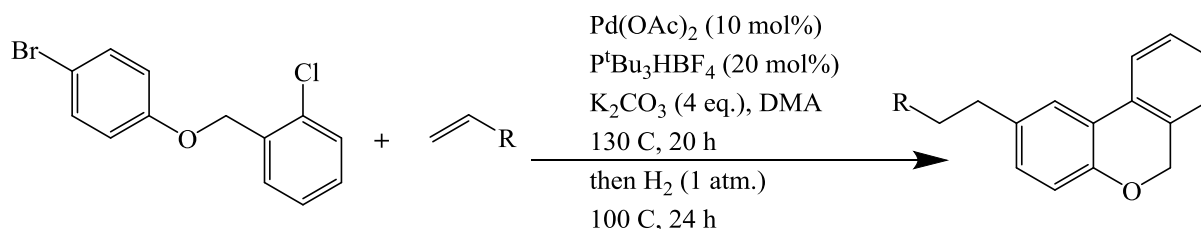


Figure 7: Schematic Presentation for Synthesis of Benzochromene Using Phosgene (toxic) along with other Reagents as Presented by R. A. Kehoe and co-workers.

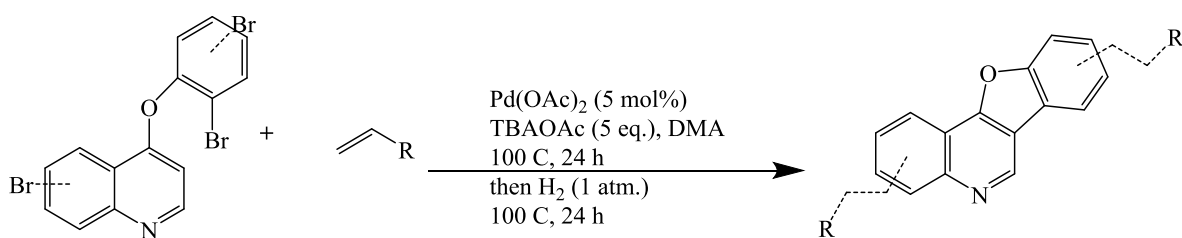


Figure 8: Schematic presentation for synthesis of benzochromene without phosgene derivative still gives better yield as presented by R. A. Kehoe and co-workers.

Part of the text is devoted to outlining the fourth principle viz. proposing harmless and greener solvents. Immense efforts are still being commenced to promote alternative synthetic pathways.

The Major Challenge of Green Chemistry is to apply its Own Principles

VII. CONCLUSION

Green chemistry is used as a sister term for sustainable or circular chemistry. The political involvement helped to launch the Green Chemistry term and implement initiatives to minimize environmental and human health hazards. Recent advancements in the production of eco-friendly chemicals by using renewable resources and alternative pathways can lead to a dazzling future in this field. The chapter focuses on the concept of designing safe and sound chemicals with alternate solvents and catalysts. A little modification in “existing” chemicals and processes may lead to a better or greener one.

REFERENCES

- [1] “United States Environmental Protection Agency,” Green Chemistry, Jun. 2023.
- [2] J. Isac-García, J. A. Dobado, F. G. Calvo-Flores, and H. Martínez-García, “Green Chemistry,” in *Experimental Organic Chemistry*, Elsevier, 2016, pp. 409–415. doi 10.1016/B978-0-12-803893-2.50012-7.
- [3] J. C. Anastas, P. T.; Warner, “Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998,” *Encyclopedia of Toxicology*, no. February 1998.
- [4] P. T. Anastas and R. L. Lankey, “Life cycle assessment and green chemistry: The yin and yang of industrial ecology,” *Green Chemistry*, vol. 2, no. 6, pp. 289–295, 2000, doi: 10.1039/b005650m.
- [5] R. L. Lankey and P. T. Anastas, “Life-cycle approaches for assessing green chemistry technologies,” *Ind Eng Chem Res*, vol. 41, no. 18, pp. 4498–4502, Sep. 2002, doi: 10.1021/ie0108191.
- [6] P. T. Anastas, M. M. Kirchhoff, and T. C. Williamson, “Catalysis as a foundational pillar of green chemistry,” 2001.
- [7] P. T. Anastas and J. B. Zimmerman, “Design through the 12 principles of green engineering,” *Environmental Science and Technology*, vol. 37, no. 5. 2003.
- [8] “What is Green Chemistry?” ACS - Chemistry for life.
- [9] H. Mutlu and L. Barner, “Getting the Terms Right: Green, Sustainable, or Circular Chemistry?” *Macromol Chem Phys*, vol. 223, no. 13, Jul. 2022, doi: 10.1002/macp.202200111.
- [10] “CHEMICAL SAFETY AND BIOSAFETY OECD WORK ON CHEMICAL SAFETY AND BIOSAFETY,” 2019.
- [11] R. A. Sheldon, “Green and sustainable manufacture of chemicals from biomass: State of the art,” *Green Chemistry*, vol. 16, no. 3. Royal Society of Chemistry, pp. 950–963, 2014. doi 10.1039/c3gc41935e.
- [12] Mahmoud Nasrollahzadeh, “Biopolymer-Based Metal Nanoparticle Chemistry for Sustainable Applications,” in *Classification, Properties and Synthesis.*, 1st ed. Elsevier, 2021.
- [13] T. A. Lewandowski, “Green Chemistry,” in *Encyclopedia of Toxicology: Third Edition*, Elsevier, 2014, pp. 798–799. doi 10.1016/B978-0-12-386454-3.01020-4.

- [14] J. A. Gladysz, "Award-winning green organometallic chemistry: The presidential green chemistry challenge," *Organometallics*, vol. 30, no. 22, p. 6059, Nov. 28, 2011. doi: 10.1021/om201014t.
- [15] M. Doble and A. K. Kruthiventi, *Green chemistry and processes*. Elsevier Academic Press, 2007. Accessed: Jul. 22, 2023. [Online]. Available: <https://cir.nii.ac.jp/crid/1130282273167814784.bib?lang=en>
- [16] US EPA, "Summary of the Pollution Prevention Act," Environmental Protection Agency, 2020.
- [17] S. Bayrakal, "The U.S. Pollution Prevention Act: A policy implementation analysis," *The Social Science Journal*, vol. 43, 2006, doi: 10.1016/j.soscij.2005.12.012.
- [18] J. A. Linthorst, "An overview: Origins and development of green chemistry," *Found Chem*, vol. 12, no. 1, 2010, doi: 10.1007/s10698-009-9079-4.
- [19] S. Stubbs, S. Yousaf, and I. Khan, "A review on the synthesis of bio-based surfactants using green chemistry principles," *DARU, Journal of Pharmaceutical Sciences*, vol. 30, no. 2, 2022. doi 10.1007/s40199-022-00450-y.
- [20] F. Anaya-Rodríguez, J. C. Durán-Álvarez, K. T. Drisya, and R. Zanella, "The Challenges of Integrating the Principles of Green Chemistry and Green Engineering to Heterogeneous Photocatalysis to Treat Water and Produce Green H₂," *Catalysts*, vol. 13, no. 1, 2023. doi 10.3390/catal13010154.
- [21] J. C. Mol, "Application of olefin metathesis in oleochemistry: An example of green chemistry," *Green Chemistry*, vol. 4, no. 1, Royal Society of Chemistry, pp. 5–13, 2002. doi: 10.1039/b109896a.
- [22] W. Wardencki, J. Curylo, and J. Namiensnik, "pdf-87771-21630," *Pol J Environ Stud*, vol. 14, no. 4, pp. 389–395, 2005.
- [23] W. Deng et al., "Efficient Catalysts for the Green Synthesis of Adipic Acid from Biomass," *Angewandte Chemie - International Edition*, vol. 60, no. 9, 2021, doi: 10.1002/anie.202013843.
- [24] Isabelle, "Lesage_10066.pdf", doi: 10.1515/1542-6580.2955i.
- [25] S. M. Ghoreishi and P. Moein, "Biodiesel synthesis from waste vegetable oil via transesterification reaction in supercritical methanol," *Journal of Supercritical Fluids*, vol. 76, pp. 24–31, 2013, doi: 10.1016/j.supflu.2013.01.011.
- [26] M. Poliakoff and P. Licence, "Supercritical fluids: Green solvents for green chemistry?," *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 373, no. 2057, 2015. doi: 10.1098/rsta.2015.0018.
- [27] W. Leitner and M. Poliakoff, "Supercritical fluids in green chemistry," *Green Chemistry*, vol. 10, no. 7, 2008. doi 10.1039/b809498p.
- [28] H. Machida, M. Takesue, and R. L. Smith, "Green chemical processes with supercritical fluids: Properties, materials, separations and energy," *Journal of Supercritical Fluids*, vol. 60, pp. 2–15, 2011, doi: 10.1016/j.supflu.2011.04.016.
- [29] Y. Cui, M. Xu, W. Yao, and J. Mao, "Room-temperature ionic liquids enhanced green synthesis of β -glycosyl 1-ester," *Carbohydr Res*, vol. 407, pp. 51–54, Apr. 2015, doi: 10.1016/j.carres.2015.01.010.
- [30] A. Kate, L. K. Sahu, J. Pandey, M. Mishra, and P. K. Sharma, "Green catalysis for chemical transformation: The need for the sustainable development," *Current Research in Green and Sustainable Chemistry*, vol. 5, Elsevier B.V., Jan. 01, 2022. doi: 10.1016/j.crgsc.2021.100248.
- [31] P. Bhanja and A. Bhaumik, "Porous nanomaterials as green catalyst for the conversion of biomass to bioenergy," *Fuel*, vol. 185, Elsevier Ltd, pp. 432–441, Dec. 01, 2016. doi 10.1016/j.fuel.2016.08.004.
- [32] A. Chaudhary, "Nano Catalysts: A Newfangled Gem in the Catalytic World," *Recent Advances in Petrochemical Science*, vol. 3, no. 5, Nov. 2017, doi: 10.19080/rapsci.2017.03.555625.
- [33] P. K. Tandon, S. Bahadur Singh, and P. Kumar Tandon, "Catalysis: A brief review on Nano-Catalyst," 2014. [Online]. Available: <https://www.researchgate.net/publication/284727255>
- [34] by Ram Singh, R. Sharma, N. Tewari, and D. S. Rawat, "REVIEW Nitrilase and Its Application as a Green Catalyst."
- [35] A. Nabera, I.-R. Istrate, A. Jose Martin, J. Pérez-Ramírez, and G. Guillén-Gosálbez, "Energy crisis in Europe enhances the sustainability of green chemicals," *Green Chemistry*, 2023, doi 10.1039/d3gc01053h.
- [36] Pandey Bhoopendra, Prajapati Yogesh K., and Sheth Pratik N., "Recent progress in Thermochemical Techniques to produce Hydrogen Gas from Biomass: A state of the art review," *Int J Hydrogen Energy*, vol. 44, no. 47, pp. 25384–25415, Oct. 2019.
- [37] K. W. Meereboer, M. Misra, and A. K. Mohanty, "Review of recent advances in the biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites," *Green Chemistry*, vol. 22, no. 17, Royal Society of Chemistry, pp. 5519–5558, Sep. 07, 2020. doi 10.1039/d0gc01647k.
- [38] J. Tamis, M. Mulders, H. Dijkman, R. Rozendal, Mark. C. M. van Loosdrecht, and R. Kleerebezem, "Pilot-Scale Polyhydroxyalkanoate Production from Paper Mill Wastewater: Process Characteristics and Identification of Bottlenecks for Full-Scale Implementation," *Journal of Environmental Engineering*, vol. 144, no. 10, Oct. 2018, doi: 10.1061/(asce)ee.1943-7870.0001444.

- [39] B. Colombo et al., "Enhanced polyhydroxyalkanoate (PHA) production from the organic fraction of municipal solid waste by using mixed microbial culture," *Biotechnol Biofuels*, vol. 10, no. 1, Aug. 2017, doi: 10.1186/s13068-017-0888-8.
- [40] R. A. Sheldon, "The E factor at 30: a passion for pollution prevention," *Green Chemistry*, vol. 25, no. 5. Royal Society of Chemistry, pp. 1704–1728, Jan. 17, 2023. doi 10.1039/d2gc04747k.
- [41] R. A. Sheldon and M. Norton, "Green chemistry and the plastic pollution challenge: Towards a circular economy," *Green Chemistry*, vol. 22, no. 19. Royal Society of Chemistry, pp. 6310–6322, Oct. 07, 2020. doi 10.1039/d0gc02630a.
- [42] Y. Li et al., "Sustainable Lactic Acid Production from Lignocellulosic Biomass," *ACS Sustain Chem Eng*, vol. 9, no. 3, pp. 1341–1351, Jan. 2021, doi: 10.1021/acssuschemeng.0c08055.
- [43] D. Yankov, "Fermentative Lactic Acid Production From Lignocellulosic Feedstocks: From Source to Purified Product," *Frontiers in Chemistry*, vol. 10. Frontiers Media S.A., Mar. 04, 2022. doi: 10.3389/fchem.2022.823005.
- [44] J. Kim, Y. M. Kim, V. R. Lebaka, and Y. J. Wee, "Lactic Acid for Green Chemical Industry: Recent Advances in and Future Prospects for Production Technology, Recovery, and Applications," *Fermentation*, vol. 8, no. 11. MDPI, Nov. 01, 2022. doi 10.3390/fermentation8110609.
- [45] R. Mazzoli, F. Bosco, I. Mizrahi, E. A. Bayer, and E. Pessione, "Towards lactic acid bacteria-based biorefineries," *Biotechnology Advances*, vol. 32, no. 7. Elsevier Inc., pp. 1216–1236, Nov. 15, 2014. doi 10.1016/j.biotechadv.2014.07.005.
- [46] R. Naveenkumar and G. Baskar, "Process optimization, green chemistry balance and technoeconomic analysis of biodiesel production from castor oil using heterogeneous nano catalyst," *Bioresour Technol*, vol. 320, Jan. 2021, doi: 10.1016/j.biortech.2020.124347.
- [47] N. Outili, H. Kerras, C. Nekkab, R. Merouani, and A. H. Meniai, "Biodiesel production optimization from waste cooking oil using green chemistry metrics," *Renew Energy*, vol. 145, pp. 2575–2586, Jan. 2020, doi: 10.1016/j.renene.2019.07.152.
- [48] V. G. Gude and E. Martinez-Guerra, "Green chemistry with process intensification for sustainable biodiesel production," *Environmental Chemistry Letters*, vol. 16, no. 2. Springer Verlag, pp. 327–341, Jun. 01, 2018. doi: 10.1007/s10311-017-0680-9.
- [49] V. Kumar and S. K. Yadav, "Plant-mediated synthesis of silver and gold nanoparticles and their applications," *Journal of Chemical Technology and Biotechnology*, vol. 84, no. 2. pp. 151–157, 2009. doi: 10.1002/jctb.2023.
- [50] I. M. Chung, I. Park, K. Seung-Hyun, M. Thiruvengadam, and G. Rajakumar, "Plant-Mediated Synthesis of Silver Nanoparticles: Their Characteristic Properties and Therapeutic Applications," *Nanoscale Research Letters*, vol. 11, no. 1. Springer New York LLC, pp. 1–14, Dec. 01, 2016. doi: 10.1186/s11671-016-1257-4.
- [51] J. A. Hernández-Díaz, J. J. O. Garza-García, A. Zamudio-Ojeda, J. M. León-Morales, J. C. López-Velázquez, and S. García-Morales, "Plant-mediated synthesis of nanoparticles and their antimicrobial activity against phytopathogens," *Journal of the Science of Food and Agriculture*, vol. 101, no. 4. John Wiley and Sons Ltd, pp. 1270–1287, Mar. 15, 2021. doi: 10.1002/jsfa.10767.
- [52] AEC Systems USA, "Green Chemistry: Designing safer chemicals.," Dec. 22, 2022.
- [53] R. L. Garrett, "Pollution Prevention, Green Chemistry, and the Design of Safer Chemicals," 1996. [Online]. Available: <https://pubs.acs.org/sharingguidelines>
- [54] S. C. Devito, "On the design of safer chemicals: a path forward," *Green Chemistry*, vol. 18, no. 16. Royal Society of Chemistry, pp. 4332–4347, 2016. doi: 10.1039/c6gc00526h.
- [55] S. C. Devito, "The Design of Safer Chemicals: Past, Present, and Future Perspectives," 2012.
- [56] S. C. DeVito, "The need for, and the role of the toxicological chemist in the design of safer chemicals," *Toxicological Sciences*, vol. 161, no. 2, pp. 225–240, Feb. 2018, doi: 10.1093/toxsci/kfx197.
- [57] N. D. Anastas and J. D. Warner, "The incorporation of hazard reduction as a chemical design criterion in green chemistry," *Chem Health Saf*, vol. 12, no. 2, pp. 9–13, Mar. 2005, doi: 10.1016/j.chs.2004.10.001.
- [58] "ENVIRONMENTAL PROTECTION AGENCY 40 CFR Part 702." [Online]. Available: www.epa.gov/dockets.
- [59] U. Epa and T. Release Inventory Program Division, "2014 Toxics Release Inventory National Analysis Report," 2014. [Online]. Available: www.epa.gov/trinationalanalysis/
- [60] L. Q. Shen et al., "Probabilistic diagram for designing chemicals with reduced potency to incur cytotoxicity," *Green Chemistry*, vol. 18, no. 16, pp. 4461–4467, 2016, doi: 10.1039/c6gc01058j.
- [61] A. Iles and M. J. Mulvihill, "Collaboration across disciplines for sustainability: Green chemistry as an emerging multistakeholder community," *Environmental Science and Technology*, vol. 46, no. 11. pp. 5643–5649, Jun. 05, 2012. doi: 10.1021/es300803t.

- [62] W. Mohammed and Errayes Asma, "Green Chemistry: Principles, Applications, and Disadvantages," *Chemical Methodologies*, vol. 4, no. 4, pp. 408–423, Jun. 2020, doi: 10.33945/sami/chemm.2020.4.4.
- [63] E. A. Khan and S. R. Syeda, "Chemical substitution in processes for inherently safer design: Pros and cons," in *Pure and Applied Chemistry*, De Gruyter Open Ltd, Jul. 2022, pp. 889–899. doi: 10.1515/pac-2021-1201.
- [64] S. Fukuoka et al., "A novel non-phosgene polycarbonate production process using by-product CO₂ as starting material," in *Green Chemistry*, Royal Society of Chemistry, 2003, pp. 497–507. doi: 10.1039/b304963a.
- [65] R. A. Kehoe, M. E. Light, D. J. Jones, and G. P. McGlacken, "A phosphine free, inorganic base free, one-pot tandem Mizoroki–Heck olefination/direct arylation/hydrogenation sequence, to give multicyclic alkylated heteroarenes," *Green Chemistry*, 2023, doi: 10.1039/d3gc01403g.
- [66] A. A. Elgharbawy, F. A. Riyadi, M. Z. Alam, and M. Moniruzzaman, "Ionic liquids as a potential solvent for lipase-catalysed reactions: A review," *Journal of Molecular Liquids*, vol. 251. Elsevier B.V., pp. 150–166, Feb. 01, 2018. doi: 10.1016/j.molliq.2017.12.050.
- [67] K. Ghandi, "A Review of Ionic Liquids, Their Limits and Applications," *Green and Sustainable Chemistry*, vol. 04, no. 01, pp. 44–53, 2014, doi: 10.4236/gsc.2014.41008.
- [68] F. M. Kerton, *Alternative solvents for green chemistry*. in RSC green chemistry series. RSC Publishing, 2009. Accessed: Jul. 22, 2023. [Online]. Available: <https://cir.nii.ac.jp/crid/1130000794199489152.bib?lang=en>
- [69] A. Sharma, E. Yu, G. Morose, D. T. Nguyen, and W. T. Chen, "Designing safer solvents to replace methylene chloride for liquid chromatography applications using thin-layer chromatography as a screening tool," *Separations*, vol. 8, no. 10, Oct. 2021, doi: 10.3390/separations8100172.