

Green Chemistry Practices for Sustainability: A Review of the Research

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Abstract: Green chemistry utilizes processes that reduce waste and hazardous materials. Green is a prevention approach mainly used to reduce pollution. Green science is a great method in accomplishing sustainability. Adopting twelve principles of Green Chemistry, we can make most of the things environmental friendly, harmless, and sustainable, taking care of the future generations. In this manner, the main focus of green science is reducing hazard by disposing of unsafe materials and replacing them with nonhazardous one. Green Chemistry by taking into consideration of the scientific community emphasis on the pressing environmental needs and sustainability. Green innovations give benefits, including more secure items, diminished utilization of energy, assets and waste. This literature review summarizes instances of the effective usage of such advances and the advantages that these techniques have given to creative responses and the amalgamation of functionalized and helpful synthetic ways in a greener manner. Bio catalysis is one of the most significant tools for green chemistry. Advances in biotechnology have provided the basis for the widespread application of biocatalysts in industrial organic synthesis. Bio catalysis can catalyze transformations by eliminating multiple steps involved otherwise in complex chemical synthesis. Taking out the multiple steps diminishes hazards, improves yields, and reduces waste.

Keywords: Green Chemistry, Waste Reduction, Sustainability.

I. INTRODUCTION

Green chemistry is a concept to encourage the development of manufacturing processes and products with the lowest possible environmental impact or footprint. There is not any doubt that the improvement and implementation of green chemistry will make contributions substantially to the sustainable improvement of our society. Achieving sustainability require an elaborate balance among useful resource use, financial increase, and environmental impact. Green chemistry is a developing area of studies that addresses lots of those concerns via combining the crucial factors of environmental development, financial competitiveness, and social responsibility. Green chemistry outlines the design goals for synthesis, making progress toward any one of these goals or several goals will make a synthesis greener.¹⁻⁶

Subsequently, Anastas and Zimmerman⁷ proposed the 12 principles of green engineering, which embody the same underlying features, conserve energy and resources and avoid waste and hazardous materials. More recently, a mnemonic, PRODUCTIVELY, was proposed by Poliakoff et al.⁸, which captures the spirit of the 12 principles of green chemistry. [Table-1]

P prevent wastes
R renewable materials
O omit derivatization steps
D degradable chemical products
U use of safe synthetic methods
C catalytic reagents
T temperature, pressure ambient

I in-process monitoring
V very few auxiliary substrates
E E-factor, maximize feed in product
L low toxicity of chemical products
Y yes, it is safe

Table-1

The 2001 Chemistry Nobel Laureate Ryoji Noyori noted that catalytic procedures represent “the best strategies that provide the rational approach of manufacturing beneficial compounds in a cheap, electricity-saving. During the manufacture of fine chemicals and pharmaceuticals, waste generated is primarily a consequence of the use of stoichiometric inorganic and organic reagents that are partially incorporated into the product. Common reactions like sulfonations, nitrations, halogenations, diazotizations, and Friedel–Crafts acylations, employing stoichiometric amounts of mineral acids (H_2SO_4 , HF, H_3PO_4) and Lewis acids ($AlCl_3$, $ZnCl_2$, BF_3) are major sources of waste. The solution is evident: substitution of antiquated stoichiometric methodologies with cleaner catalytic alternatives⁹⁻¹⁴. Indeed, recyclable solid catalysts have an important role to play in waste minimization of many basic reactions in industrial organic synthesis.

Biocatalysis contributes to a wide range of business applications. Biocatalysis is environmentally benign and because it could catalyze in any other case difficult alterations it is able to get rid of multiple steps concerned in complicated chemical synthesis. Eliminating the steps reduces waste and dangers, improves yields, and cuts costs. The latest advances in biotechnology have solved a few of the practical troubles, and the improved knowledge of biochemical systems and mechanisms has made biocatalysts greater comprehensible to chemists.

II. SOURCES OF DATA

In this review, different have been searched articles from Internet Journals and books available. Selected few of the reviewed few articles. This review briefly describes the aspects related to classical methods and greener ways of production and focuses on both theoretical and practical approaches for process improvements.

III. GREEN CHEMISTRY PRACTICES

Biocatalytic methods can be carried out with isolated enzymes or through whole cellular bio transformations. Isolated enzymes have the benefit of now not being contaminated with other enzymes present within the cellular framework. On the alternative hand, using complete cells is much less costly, because it avoids separation and purification of the enzyme. In the case of dead cells, the E factors of the two techniques are basically the same; the waste cellular debris is separated earlier than or after the biotransformation. In contrast, when growing microbial cells are used, that is, in fermentation methods, vast amounts of biomass can be generated. Many fermentation approaches additionally contain the formation of copious amounts of inorganic salts which could even be the principal contributor to waste. It has been observed that there are no suggested E factors for fermentation methods. Mass balances of some fermentation methods had been documented by Petrides¹⁵ from which E factors may be calculated. For example, the E factor for the majority fermentation product, citric acid, is 1.4, which compares nicely with the E factor of <1–5, standard of bulk.

Biocatalysis has many appealing features within the context of green chemistry. Reactions are performed at optimized conditions (physiological pH and ambient temperature and pressure) with a biodegradable catalyst, an enzyme that is derived from renewable resources and in an environmental friendly solvent, water. Thus multiple steps can be avoided. This provides approaches utilizing minimum steps, low-budget, generate much less waste, and are consequently, each environmentally and economically greater attractive than traditional routes.

A) Green Synthesis of Pregabalin, Api of Lyrica (Biocatalysis For Green Chemistry and Chemical Process development, Edited By Junhua (Alex) Taoromas Kazlauskas, 2011 John Wiley & Sons.)

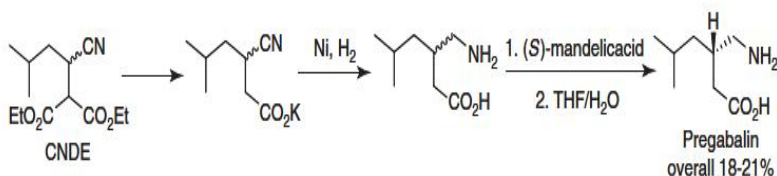
Enzymatic catalysis can achieve excessive regio- and stereo selectivity under mild situations in water, making green processes to be developed with substantial cost advantages over chemical methods. For instance, pregabalin was developed by Pfizer to be a more potent successor to gabapentin and become launched first under the brand name Lyrica® in 2004. The compound is used in the treatment of peripheral neuropathic ache as adjunctive therapy for partial seizures resulting from epilepsy and fibromyalgia. It is one of the fastest developing tablets with a global sale of over \$2.0 billion in 2008. The first-technology direction for the production of pregabalin involves diastereomeric resolution of a racemic γ -amino acid, which was prepared from a racemic cyanodiester (CNDE) after hydrolytic decarboxylation followed by hydrogenation using Raney-Ni (Scheme 1).¹⁶ In order to acquire high optical purity (>99.5%) for the very final API, (S)-mandelic acid resolution was followed by recrystallization in THF/H₂O, which has a mixed two-step yield of only 25–29%. As a result, the overall yield for this procedure is only 18–21%. Since the undesired enantiomer couldn't be recycled, poor process performance leads to high usage of raw substances, solvents, and energy.

To minimise above problems, numerous alternative routes had been developed. For example, a two metal-catalyzed process was evolved where the important transformation involves asymmetric hydrogenation of a t-butylamine salt, which was prepared from a Baylis–Hillman adduct accompanied by means of Pd-catalyzed carbonylation under high pressure reactor (Scheme 2).¹⁷ Though the overall yield is better, the method requires special high pressure reactor. Moreover, because the homogeneous catalyst is steeply-priced, its loading usually can't be better than 0.1%, which often results in issues related to technique robustness because of catalyst poisoning due to impurities within the substrates, reactor, or air.

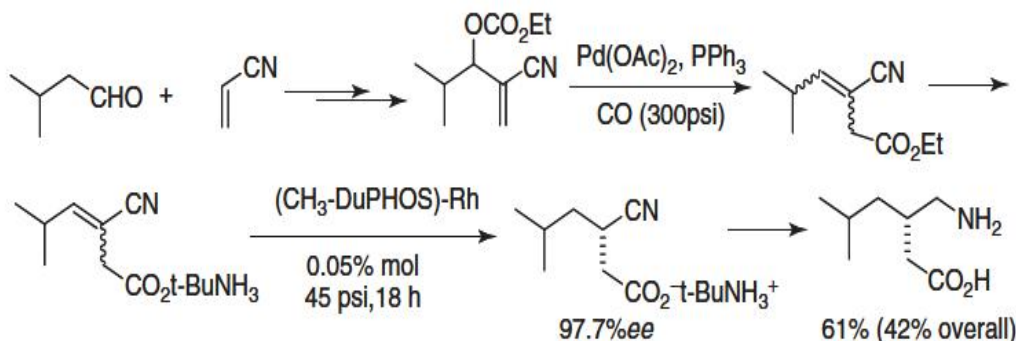
Another process was developed using enzymatic resolution, which took place in the one step and the undesired enantiomer can be recycled (Scheme 3).¹⁸⁻¹⁹ Regio- and stereospecific hydrolysis of CNDE led to a mono acid with 45% conversion and greater than 98 percentage. The enzymatic synthesis is predicted to eliminate¹⁹⁻²⁰,

- 185,000 tons of solvent, an 88% reduction
- 4800 tons of mandelic acid, a 100% reduction
- 1890 tons of Raney nickel catalyst, an 85% reduction
- 10,000 tons of starting material, a 39% reduction

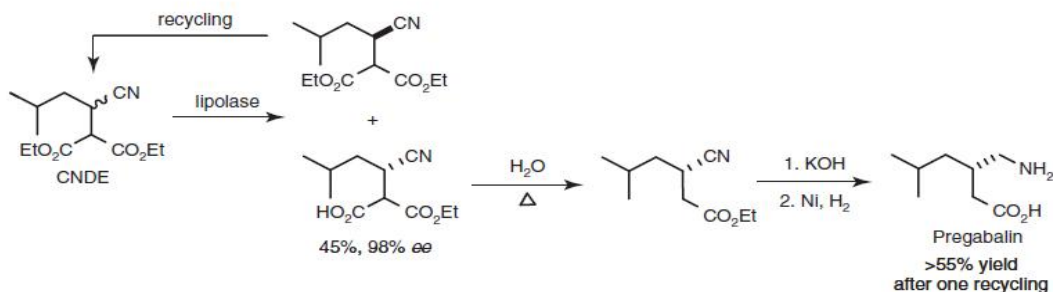
Scheme-1: Synthesis of Pregabalin by chemical resolution.



Scheme -2: Synthesis of Pregabalin under asymmetric hydrogenation.



Scheme- 3: Biocatalytic synthesis of Pregabalin



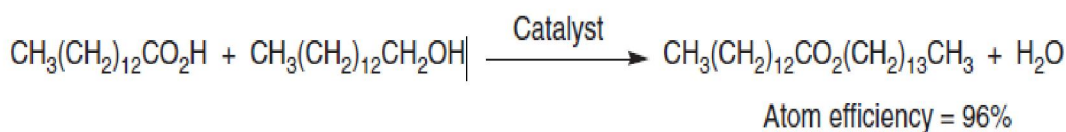
Thus, Biocatalysis is better way for the development of green chemical processes as result of ready access to enzymes capable of catalyzing a wide range of reactions, and a wide range of strategies for improving enzyme functions. Biotransformations involving the use of isolated enzymes, in contrast, tend to involve significantly higher substrate concentrations and combine a higher productivity, even though consuming less amount of water than fermentations.

B) Enzymatic Production of an Emollient Ester

In a recent report²¹, a classical chemo catalytic esterification was compared with an enzymatic equivalent for the industrial scale synthesis of the widely used emollient ester, myristyl myristate. The former involved the use of tin(II) oxalate as a catalyst at 240°C for 4 h and the latter employed an immobilized form of *Candida antarctica* lipase B, Novozyme 435, at 60°C for 12 h. (Scheme-4) The atom economy of the process is 96% and the E factor is <0.1 in both cases (even when waste water is included). Consequently, the environmental impacts of the two processes were compared in a cradle-to-gate environmental LCA. The assessment involved a comparison on the basis of five categories:

- (i) energy consumption,
- (ii) global warming
- (iii) acidification
- (iv) nutrient enrichment, and
- (v) smog formation.

CONCLUSIONS AND PROSPECTS



Chemocatalytic process: Sn oxalate at 240°C

Biocatalytic process: Novozyme 435 at 60°C

Scheme-4 : Chemo- versus biocatalytic production of myristyl myristate

Table 2: Biocatalytic Esterification: Impact on Defined Environmental

Parameters

Parameter	Units	Chemocatalytic	Biocatalytic	Savings
Energy	GJ	22.5	8.63	62%
Global warming	kg CO ₂ equivalent	1518	582	62%
Acidification	kg SO ₂ equivalent	10.58	1.31	88%
Eutrophication	kg PO ₄ equivalent	0.86	0.24	74%
Smog formation	kg C ₂ H ₄ equivalent	0.49	0.12	76%

As shown in Table 2, substantial reductions in all categories were achieved. Energy consumption was reduced by more than 60% and the formation of undesirable pollutants by up to 90%. Replacement of a tin catalyst by an enzyme and the considerably milder conditions were the major factors responsible for the significantly more eco-friendly profile of the biocatalytic process. Thus, product satisfactory changed into the one higher in the biocatalytic process, specifically because of the milder reaction conditions. Thus, higher product excellent and technique simplification are observed of the biocatalytic as opposed to the chemocatalytic method.

C) Synthesis of *hydroquinone* by several steps (benzene-cumene-phenolhydroquinone) from petroleum-derived benzene as a precursor, using the Rh on Al₂O₃ catalyst with 59% yield²²

Hydroquinone is white, odourless, crystalline solid moderately soluble in water and high soluble in alcohol with an exceedingly low vapour pressure. In the presence of water, hydroquinone can slowly oxidized to quinone. Quinine is more volatile. Hydroquinone has been used in various fields. It is used as raw material within the manufacturing of antioxidant for rubber, food grade antioxidants, and liquid-crystal polymers as a polymerization inhibitor for vinyl acetate and acrylic monomers and a topical skin-lightening agent.

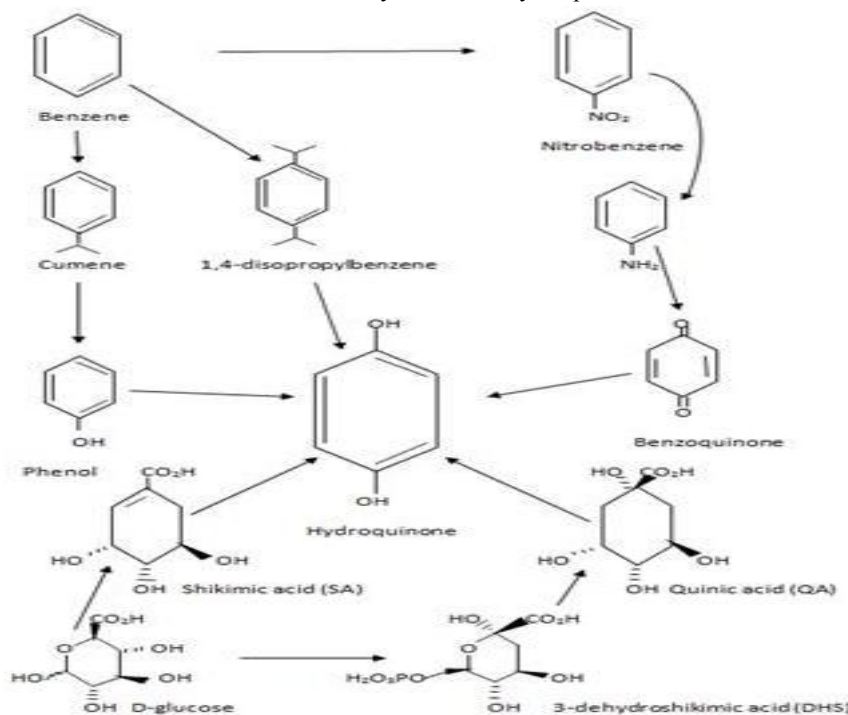
Hydroquinone synthesis utilizes benzene as the starting material(Scheme-5). The manufacture of hydroquinone is also carried out with the aid of oxidation of phenol and 1,4-diisopropylbenzene.²³ The first route begins with

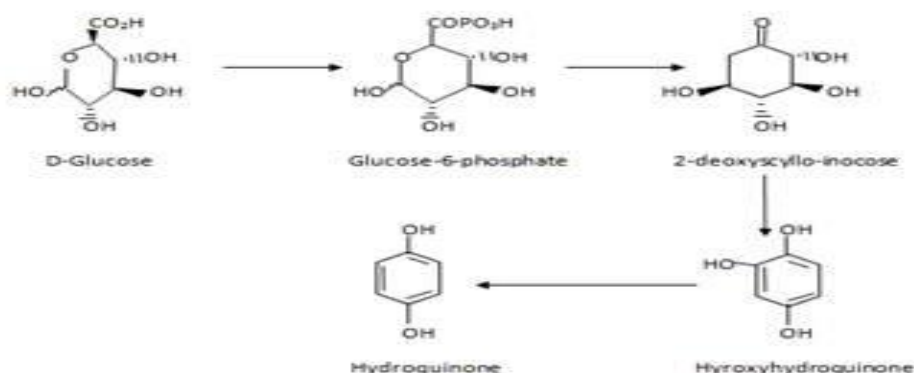
Friedel-Crafts alkylation of petroleum-derived benzene to form cumene. Subsequent Hock-type, air oxidation of the cumene results in formation of acetone and phenol. Additionally this is presently the primary approach used in the production of phenol, which amounts to 5×10^9 kg yearly.²⁴ The phenol is then oxidized by using 70% hydrogen peroxide in the presence of transition metal catalysts or in formic acid. The generated catechol and hydroquinone mixture is separated via distillation.

The second synthetic approach, is the reaction of propene and benzene to form 1,4-diisopropylbenzene, which is then converted to the hydroquinone.²⁵ Benzene reacts to nitrobenzene by using HNO_3 and H_2SO_4 and after that to the corresponding aniline. Next, benzoquinone is synthesized by means of a path employing stoichiometric amounts of MnO_2 to oxidize aniline, accompanied by iron catalyzed reduction to the corresponding hydroquinone.²⁶ While benzene is a volatile carcinogen derived from non-renewable fossil fuel feed stocks, an alternative way to hydroquinone has been elaborated (Scheme-5).²⁷

Glucose is non volatile, safe, and derived from renewable plant polysaccharides and performs an critical function by replacing benzene routes (Scheme-5). From Glucose *Escheria coli* produce shikimic acid (SA), quinic acid (QA) and 3-dehydroshikimic acid (DHS).²⁸ Shikimic acid as well as quinic acid are recognized for the hydroquinone synthesis. In 1995 the manufacture of hydroquinone and catechol has been elaborated that make use of D-glucose as the starting material and biocatalysts, a genetically modified microbe, *Escheria coli*.²⁹ Shikimic acid turned into the precursor for the quinone. Woskresensky synthesised the quinone from quinic acid.³⁰ In 1992, Drahts et al. Reported about the manufacturing of quinic acid from glucose with *Escheria coli*.³¹ They also published the oxidation of quinic acid with stoichiometric amounts of MnO_2 to benzo- and hydroquinone in low to modest yield. Next Ran and co-workers evolved a new catalytic path from quinic acid to hydroquinone. They used stoichiometric amounts of NaOCl , $(\text{NH}_4)_2\text{Ce}(\text{SO}_4)_3$, V_2O_5 or catalytic quantities of $\text{Ag}_3\text{PO}_4/\text{K}_2\text{S}_2\text{O}_8$ to afforded 74% to 91% yield. One year later Hansen and Frost published a synthesis of 2-deoxy-scylo-inosose from glucose which reacts to hydroxyhydroquinone (Scheme 6).

Scheme-5: Synthesis of Hydroquinone





Scheme-6: Synthesis of Hydroquinone (Green way- a benzene free route)

Thus, While benzene is a risky carcinogen derived from non-renewable fossil gasoline feed shares, benzene free route has been explained for the synthesis of hydroquinone. Glucose is nonvolatile, nontoxic, and derived from renewable plant polysaccharides and performs an vital function for these benzene free routes. From Glucose *Escheria coli* produce shikimic acid (SA), quinic acid (QA) and both of them are used for the hydroquinone synthesis.

IV. CONCLUSION

Green chemistry can contribute to sustainable development by application and extension of the principles of green chemistry. Many examples are available in the literature of the use of green chemistry rules. Biocatalysis is well suitable for the development of green chemical strategies for wide range of enzymes able to catalyze a extensive variety of reactions, and a extensive range of strategies for improving enzyme capabilities. The key to integrate biotransformations into the toolboxes of chemical transformations at the retrosynthetic level to reduce the intake of solvents, starting substances, and wastes. Hopefully, it has been shown that the path to green and sustainable chemicals manufacture is a catalytic one including the various subdisciplines of catalysis will have a function to play for sustainable technologies. Biocatalysis, specially, has many added benefits, which include moderate reaction conditions, employing a catalyst that is biocompatible, biodegradable, and derived from renewable sources. Processes are rather selective resulting in better product quality and decreased waste generation coupled with superior economics. Catalysis is preferred, and biocatalysis, especially, will play a key role in the transition from a global economy that is basically based on nonrenewable fossil feed stocks to a sustainable one this is based totally on renewable resources. While many exciting new greener chemical methods are being evolved still greater numbers of demanding situations lie ahead.

ACKNOWLEDGEMENT

The author is heartedly thankful of Principal, Dr. Anita Kanwar, Vivekanad Education Society's College of Arts Science and Commerce, Sindhi Society, Chembur, Mumbai, Principal and Prof. Dr. Vasant Barhate, Janardan Bhagat Shikshan Prasarak Sanstha's Changu Kana Thakur Arts, Commerce and Science College, New Panvel Raigad for constant support and encouragement. I also thank convener and organizing members of CKT college, Department of Chemistry for organizing conference on green chemistry to motivate researchers. Also, I thank Dr. Mary Stephen, IQAC coordinator, V.E.S. college for always emphasizing the role of green chemistry in innovation, application and teaching.

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