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GREEN CHEMISTRY

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1. Abstract

The object of Green Chemistry is the reduction of chemical pollutants flowing to the environment. The Chemistry and the Environmental Division of EuChem has assumed Green Chemistry as one of its areas of interests, but one question to solve is where Green Chemistry should be placed within the context of Chemistry and Environment. The concept of Green Chemistry, as primarily conceived by Paul Anastas and John Warner, is commonly presented through the twelve principles of Green Chemistry. However, these Twelve principles through fruits of a great intuition and common sense, do not a clear connection between aims, concepts, and related research areas of Green Chemistry. The Twelve unsolved questions are the object of the present article.

2. Introduction

New chemistry is required to improve the economics of chemical manufacturing and to enhance the environmental protection. The green chemistry concept presents an attractive technology to chemists, researchers, and industrialists for innovative chemistry research and applications. Primarily, green chemistry is characterized as reduction of the environmental damage accompanied by the production of materials and respective minimization and proper disposal of wastes generated during different chemical processes.

According to another definition, green chemistry is a new technique devoted to the synthesis, processing, and application of chemical materials in such manner as to minimize hazards to humankind and the environment.

Numerous new terms have been introduced associated with the concept of "green chemistry," such as eco-efficiency, sustainable chemistry, atom efficient or atom economy, process intensification and integration inherent safety, product life cycle analysis, ionic liquids, alternate feed stocks, and "Renewable Energy Source."

Hence, there is an essential need to improve the synthetic and engineering chemistry either by environmental friendly starting materials or by properly designing novel synthesis routes that reduce the use and generation of toxic substances by using modern energy sources.

Definition.

Green chemistry, also called **sustainable chemistry**, is an area of chemistry and chemical engineering focused on the design of products and processes that minimize or eliminate the use and generation of hazardous substances.

What about Green Chemistry...

- Waste minimization of source.
- Use of catalyst in place of reagents.
- Using Non toxic reagents.
- Use of renewable source.
- Improved atom efficiency.
- Use of solvent free or recyclable Environmentally benign solvent system.

3.History.

Green chemistry emerged from a variety of existing ideas and research efforts (such as atom economy and catalysis) in the period leading up to the 1990s, in the context of increasing attention to problems of chemical pollution and resource depletion. The development of green chemistry in Europe and the United States was linked to a shift in environmental problem-solving strategies: a movement from Command and Control Regulation and mandated reduction of industrial emissions at the "end of the pipe," toward the active prevention of pollution through the innovative design of production technologies themselves. The set of concepts now recognized as green chemistry coalesced in the mid- to late-1990s, along with broader adoption of the term (which prevailed over competing terms such as "clean" and "sustainable" chemistry) In the United States, the Environmental Protection Agency played a significant early role in fostering green chemistry through its pollution prevention programs, funding, and professional coordination. At the same time in the United Kingdom, researchers at the University Of York contributed to the establishment of the Green Chemistry Network within the Royal Society Of Chemistry and the launch of the journal *Green Chemistry*.

4. Basic principles of green chemistry

Green chemistry is generally based on the 12 principles proposed by Anastas and Warner Nowadays, these 12 principles of green chemistry are considered the fundamentals to contribute to sustainable development. The principles comprise instructions to implement new chemical products, new synthesis, and new processes.

I .The “better to prevent than to cure” principle

It is beneficial to a priori prevent the generation of waste instead of later on treating and cleaning up.

ii. The “atom economy” principle

Synthetic production routes have to be planned in a way maximizing the incorporation of all the compounds used in the synthesis into the desired product.

iii .The “less precarious chemical syntheses” principle

Wherever feasible, such synthetic methods have to be aspired, which resort to and generate compounds of nor only insignificant noxiousness to the environment and human health.

iv. The “designing safer chemicals” principle

Chemicals should be developed in a way affecting their desired functionality, while, at the same time, considerably reducing their toxicity.

v. The “safer solvents and safer auxiliaries” principle

Expenditure of auxiliary substances, such as solvents, separation agents, and others, should be avoided wherever possible; if not possible, harmless auxiliaries should be used.

vi. The “design for energy efficiency” principle

The environmental and economic impact of energy demands for chemical processes should be analyzed in terms of followed by optimizing the required energy input. Wherever practicable, chemical synthesis should be carried out under mild process conditions, hence, at ambient temperature and pressure.

vii. The “renewable feedstock’s” principle

Whenever feasible in technological and economic terms, synthetic processes should resort to such raw materials and feedstock’s, which are renewable rather than limited.

viii. The “derivative reduction” principle

Redundant derivatization, e.g., protection/deportation, the use of blocking groups, or temporary modification of physical/chemical processes, requires additional reagents and often contributes to additional waste generation. Therefore, wherever possible, they should be avoided or reduced to a minimum.

ix. The “catalysis” principle

Generally, catalytic reagents are intrinsically superior to stoichiometric reagents; these catalysts should be as selective as possible.

x. The “degradation” principle

Chemical products have to be designed in such a way that, at the end of their life span, they do not resist in the biosphere, but disintegrate into nontoxic degradation products.

xi. The “real-time analysis for pollution prevention” principle

Advanced analytical methods have to be developed, which permit the real-time, in-line process monitoring and control well before hazardous substances are generated.

xii. The “accident prevention by inherently safer chemistry” principle

Compounds and the compound’s formula applied in a chemical process should be chosen in a way minimizing the risk of chemical accidents, encompassing the release of chemicals, detonations, or fire formation.

Examples.

A. Green Solvents.

The major application of solvents in human activities is in paints and coatings (46% of usage). Smaller volume applications include cleaning, de-greasing, adhesives, and in chemical synthesis. Traditional solvents are often toxic or are chlorinated. Green solvents, on the other hand, are generally less harmful to health and the environment and preferably more sustainable. Ideally, solvents would be derived from renewable resources and biodegrade to innocuous, often a naturally occurring product. However, the manufacture of solvents from biomass can be more harmful to the environment than making the same solvents from fossil fuels. Thus the environmental impact of solvent manufacture must be considered when a solvent is being selected for a product or process. Another factor to consider is the fate of the solvent after use. If the solvent is being used in an enclosed situation where solvent collection and recycling is feasible, then the energy cost and environmental harm associated with recycling should be considered; in such a situation water, which is energy-intensive to purify, may not be the greenest choice. On the other hand, a solvent contained in a consumer product is likely to be released into the environment upon use, and therefore the environmental impact of the solvent itself is more important than the energy cost and impact of solvent recycling; in such a case water is very likely to be a green choice. In short, the impact of the entire lifetime of the solvent, from cradle to grave (or cradle to cradle if recycled) must be considered. Thus the most comprehensive definition of a green solvent is the following: "*a green solvent is the solvent that makes a product or process have the least environmental impact over its entire life cycle.*"

By definition, then, a solvent might be green for one application (because it results in less environmental harm than any other solvent that could be used for that application) and yet not be a green solvent for a different application. A classic example is water, which is a very green solvent for consumer products such as toilet bowl cleaner but is not a green solvent for the manufacture of polytetrafluoroethylene. For the production of that polymer, the use of water as solvent requires the addition of per fluorinated surfactants which are highly persistent. Instead, supercritical carbon dioxide seems to be the greenest solvent for that application because it performs well without any surfactant. In summary, no solvent can be declared to be a "green solvent" unless the declaration is limited to a specific application.

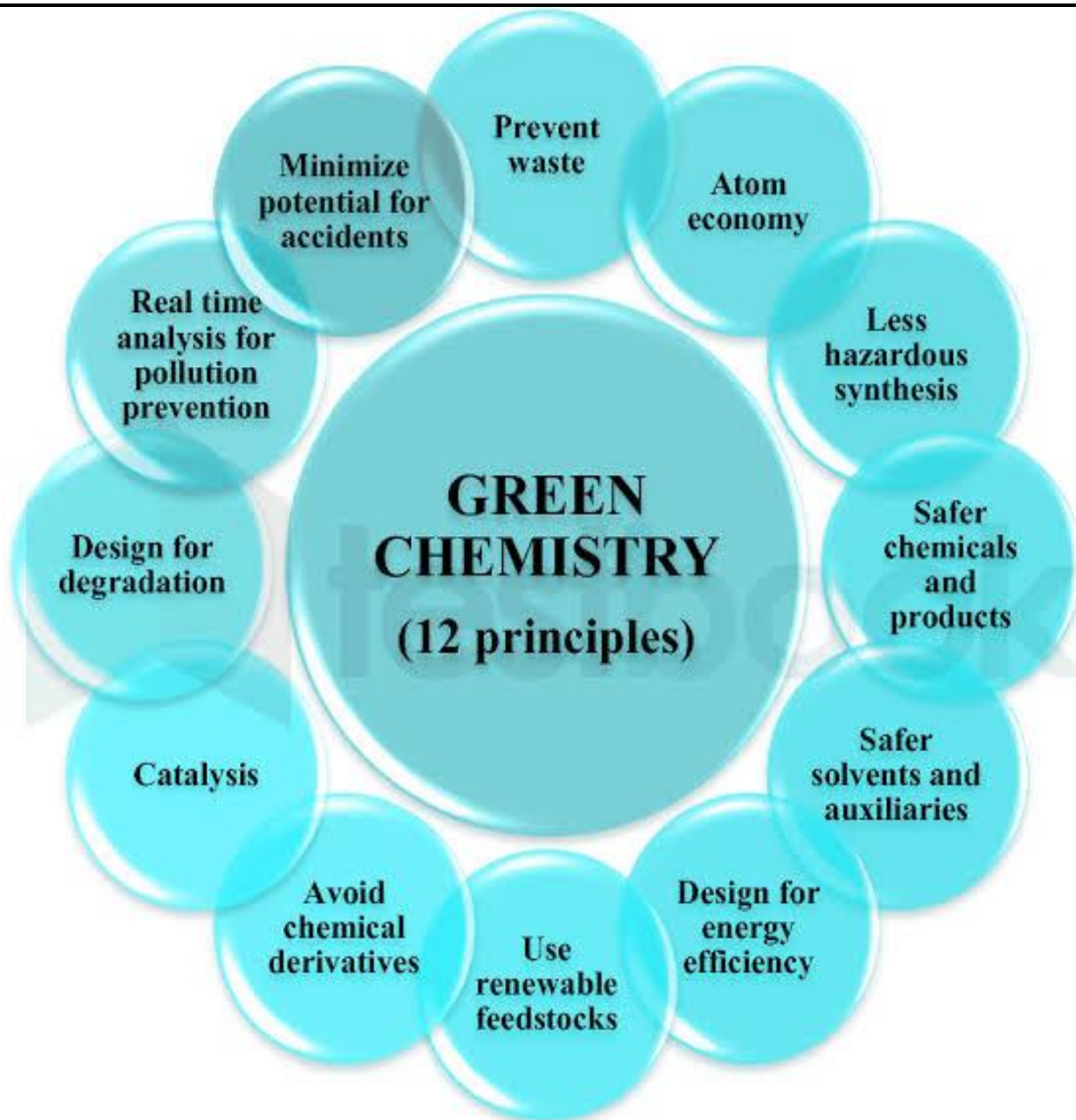
B. Synthetic techniques.

Novel or enhanced synthetic techniques can often provide improved environmental performance or enable better adherence to the principles of green chemistry. For example, the 2005 Nobel Prize for Chemistry was awarded to Yves Chauvin, Robert H. Grubbs and Richard R. Schrock, for the development of the metathesis method in organic synthesis, with explicit reference to its contribution to green chemistry and "smarter production. A 2005 review identified three key developments in green chemistry in the field of organic synthesis: use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations and the use of hydrogen in asymmetric synthesis. Some further examples of applied green chemistry are supercritical water oxidation, on water reactions, and dry media reactions.

Bioengineering is also seen as a promising technique for achieving green chemistry goals. A number of important process chemicals can be synthesized in engineered organisms, such as shikimate, a Tami flu precursor which is fermented by Roche in bacteria. Click chemistry is often cited {{citation needs date=September 2015}} as a style of chemical synthesis that is consistent with the goals of green chemistry. The concept of 'green pharmacy' has recently been articulated based on similar principles.

C. Lactide.

In 2002, Cargill Dow (now Nature Works) won the Greener Reaction Conditions Award for their improved method for polymerization of polylactic acid. Unfortunately, lactide-base polymers do not perform well and the project was discontinued by Dow soon after the award. Lactic acid is produced by fermenting corn and converted to lactide, the cyclic dimer ester of lactic acid using an efficient, tin-catalyzed cyclization. The L,L-lactide enantiomer is isolated by distillation and polymerized in the melt to make a crystallizable polymer, which has some applications including textiles and apparel, cutlery, and food packaging. Wal-Mart has announced that it is using/will use PLA for its produce packaging. The Nature Works PLA process substitutes renewable materials for petroleum feedstock's, doesn't require the use of hazardous organic solvents typical in other PLA processes, and results in a high-quality polymer that is recyclable and compostable.



5. Awards.

- Australia's Green Chemistry Challenge Awards overseen by The Royal Australian Chemical Institute (RACI).
- The Canadian Green Chemistry Medal.
- In Italy, Green Chemistry activities center on an inter-university consortium known as INCA.
- In Japan, The Green & Sustainable Chemistry Network oversees the GSC awards program.
- In the United Kingdom, the Green Chemical Technology Awards are given by Crystal Faraday.
- In the US, the Presidential Green Chemistry Challenge Awards recognize individuals and businesses.

6. It is better to prevent waste than to treat or clean up waste after its formation

This statement is one of the most popular guidelines in process optimization; it describes the ability of chemists to redesign chemical transformations in order to minimize the generation of hazardous waste as an important step toward pollution prevention. By preventing waste generation, the hazards associated with waste storage, transportation, and treatment could be minimized. This principle is easy to understand and easy to apply, and examples from both industry and academia have proven its significance, relevance, and feasibility. This pillar of green chemistry is still valid; however, we have to conceive it in a broader context, switching from a restricted interpretation of waste based on its quantity to a universal approach to deal with the topic “waste.”

(1) We have to take waste’s multidimensional nature into account.

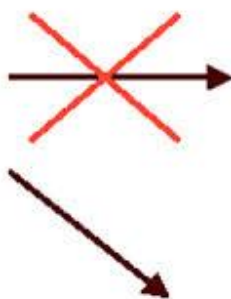
(2) We need to move from a “quantity of waste per quantity of product” principle toward a Principle addressing the “quantity of waste generated per function provided by the product.” In this context, we have to aim at making both quality and functionality of products Superior.

(3) Considering the entire life cycle of a product, we have to address the fact that not only the production process itself generates waste but, moreover, “end-of-life waste accrues after the product’s life span or its consumption. This encompasses firstly the conversion of such materials up to now considered as waste into valuable products and, secondly, their recyclability. Generally, moving toward “zero-waste production” and “waste prevention” encompasses the modernization of industrial processes through clean production techniques. These techniques aim at the reduction of gaseous emissions, effluents, solid residues, and noise generation; generally, they are developed to contribute to the protection of climate and environment.

However, the most auspicious strategy to prevent waste generation would simply be not producing the desired product. In most scenarios, this will not be practicable; however, it might be reasonable to instead produce completely novel products, which display higher quality and longer durability. Lower quantities of such novel, superior products are sufficient to fulfill a desired function. An alternative approach is to avoid that the product can be transformed into precarious waste, e.g., by making plastics accessible toward biodegradation or by a priori switching toward biodegradable plastic instead of highly recalcitrant petrochemical Plastics. According to these ideas, we need to fundamentally reconsider our understanding of waste as hazardous material that needs to be disposed by enhancing the status of waste to valued resource, which can act as starting material for generation of new products.

**“It is better to prevent waste than to
treat or clean
up waste after it is formed”**

**Chemical
Process**

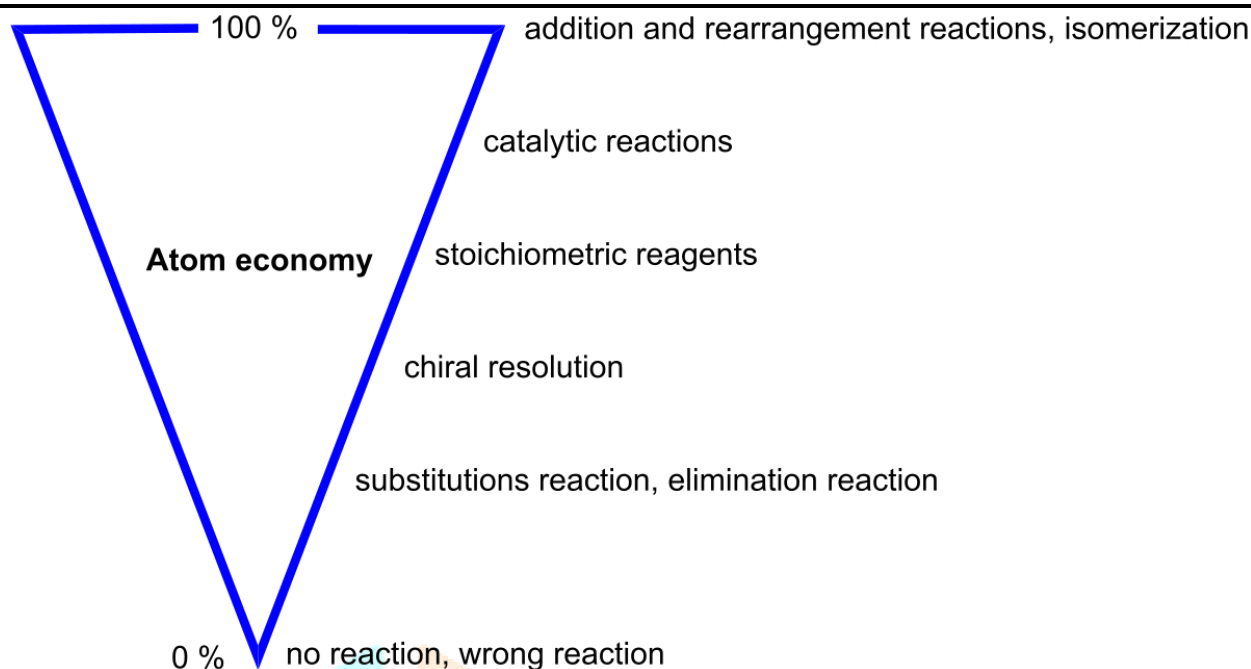


No waste

7. Maximize atom economy.

Atom economy is a concept developed in the early 1990s to evaluate the efficacy of chemical conversions on an element-by-element basis. In analogy to well-established yield calculations, the concept of “atom economy” is based on the ratio of the entire mass of atoms in the target product to the entire mass of atoms in the starting materials. One option to reduce waste generation is to plan such chemical transformations, which maximize the integration of all materials used in the process into the final product, resulting in a number of wasted atoms as low as possible. Hence, selecting such chemical conversion routes, which incorporate the major share of starting materials into desired products, displays higher efficiency and contributes

to waste reduction. This concept is nowadays widely implemented in new routes to generate various organic compounds, e.g., such substances that are used in the biomedical and pharmaceutical field. One factor that is greatly speeding the incorporation of pollution prevention into industrial manufacturing processes is the development of green chemistry.



8. Design less hazardous chemical synthesis

In synthetic organic chemistry, effecting a successful chemical transformation in a new way or with a new molecule or in a new order is what matters regarding the principles of green chemistry. Various researchers have clearly demonstrated the direct relation of toxicity and the associated hazards and risks allied with chemical reactions to the matrix of matter present in the reaction vessel. Generally, the holistic toxicity spectrum of products or processes, together with most other sustainability and green chemistry criteria, is highly impacted by the chemistry behind a process and the transformation contributing to a chemical synthesis chain. An exception is identified in such cases where a molecule is produced by purpose, which is designed to display toxicity and/or biological activity. For example, this scenario is found in the case of various molecules synthesized for pharmaceutical or agricultural applications; such compounds exhibit toxicity and/or impact living organisms. Selection of compounds and materials to be used to increase the efficacy of chemical transformations is a pivotal point in process development; chemists should dedicate increased attention to the decision on which materials to be put into reaction vessels. It is simple to disregard all the other materials and to dedicate all efforts exclusively to the chemosynthetic pathway, which provides us with the desired product. However, discounting all the other matter present in a production process ultimately results in a high price to be played, and we finally have to get rid of this scenario. Sometimes, chemists actually produce hazardous molecules, and, therefore, the subsequent principle is dedicated to the design of molecules which are intrinsically safer in their nature.

9. Design safer chemicals and products

Chemical products should be designed to achieve their desired function with at the same time minimizing their toxicity. New products can be designed that are inherently safer, while highly effective for the target application. For example, the direct incorporation of radioactive spent liquid scintillation waste into cement combined with clay materials is considered an added value in the immobilization of the hazardous organic wastes in very cheap materials and natural clay to produce a safe stabilized product easy for handling, transformation, and disposal.

10. Safer solvents and auxiliaries

This principle promotes the use of safer solvents and auxiliaries. It is about any substances that do not directly contribute to the structure of the reaction product but are still necessary for the chemical reaction or process to occur. Mostly, reactions of organic compounds take place in liquid milieus, where the solvent acts in different ways: it can enable enhanced contact between the reactants, it can stabilize or destabilize generated intermediates, or it can influence transition states. In addition, the applied solvent also governs the selection of adequate downstream and regeneration processes and recycling or discarding techniques. By taking the ecological effect of chemical processes in consideration, innovative concepts for substitution of volatile organic solvents have become a great challenge in green chemistry. A green solvent should meet numerous criteria such as low toxicity, non flammability, non mutagen city, no volatility, and widespread availability among others. Moreover, these green solvents have to be cheap and easy to handle and recycle



11. ENERGY

Energy is the capacity to do work or to transfer **heat** (the form of energy that flows from a warmer to a colder object). A farm tractor working in a field illustrates the definition of energy and several forms of energy. **Chemical energy** in the form of petroleum hydrocarbons is used to fuel the tractor's diesel engine. In the engine the hydrocarbons combine with oxygen from air,



to produce **heat energy**. As the hot gases in the engine's cylinders push the pistons down, some of this heat energy is converted to **mechanical energy**, which is transferred by the engine crankshaft, gears, and axle to propel the tractor forward. A plow or other implement attached to the tractor moves soil. The standard unit of energy is the **joule**, abbreviated **J**. A total of 4.184 J of heat energy will raise the temperature of 1 g of liquid water by 1°C. This amount of heat is equal to 1 **calorie** of energy. The science that deals with energy in its various forms and with work is **Thermodynamics**. There are some important laws of thermodynamics. The **first law of thermodynamics** states that energy is neither created nor destroyed. This law is also known as the **law of conservation of energy**.

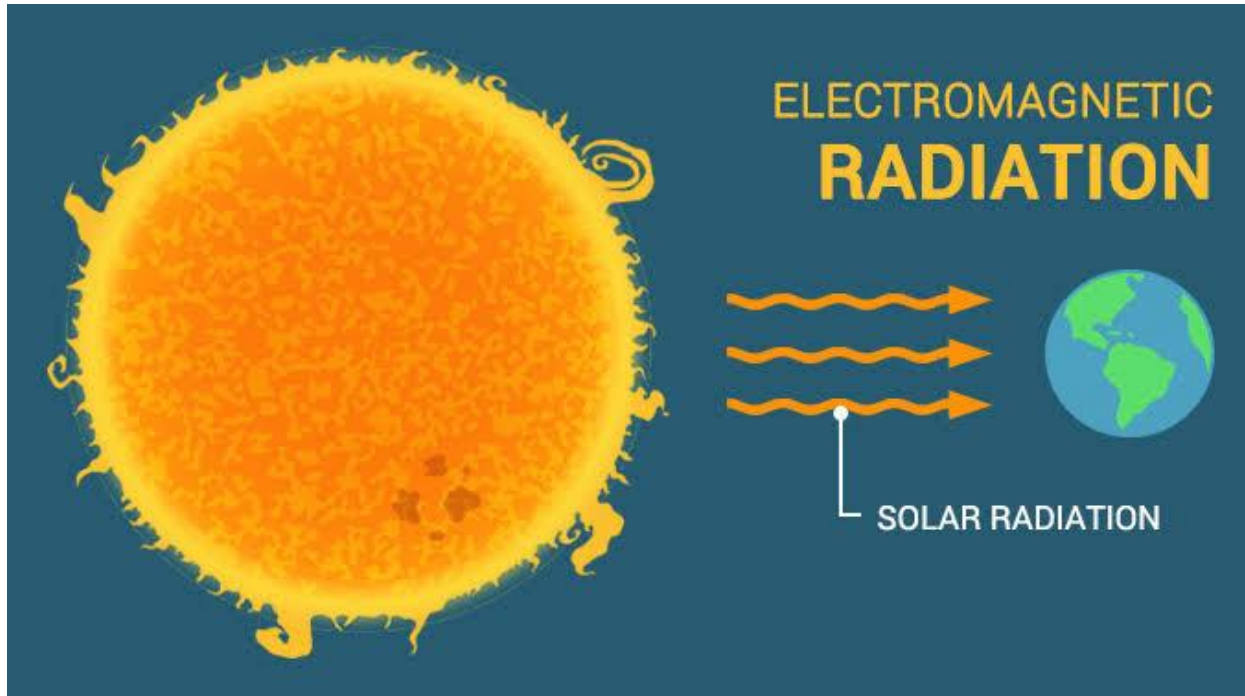


11.1. Design for energy efficiency

Usually, energy is used to enhance the human life in important ways. The traditionally used energy sources like coal, oil, and gas are limited in supply, and their combustion releases greenhouse gases. For continuous improvement of life quality, both move toward renewable energy and design for energy efficiency are needed. Designing more efficient processes by choosing the most suitable technologies and unit operations has to go in parallel with selecting proper energy sources. Using an electric motor with energy sources generated from the sun and wind is more effective in ecological terms instead of using fossil fuels. How energy is converted to useful forms and where it gets lost are the most important questions for engineers and designers to help society use energy more effectively. In addition, when developing a new production process, the effect of geographical location of production plants has to be taken into account: ecological comparison of different production scenarios for the same product, in this case bioplastics, clearly demonstrates that different energy production technologies, resources for energy production, and the effect of available energy mixes in different countries become significant for the ecological footprint of a new process.

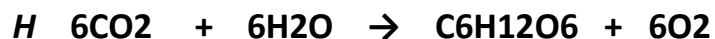
11.2. RADIANT ENERGY FROM THE SUN

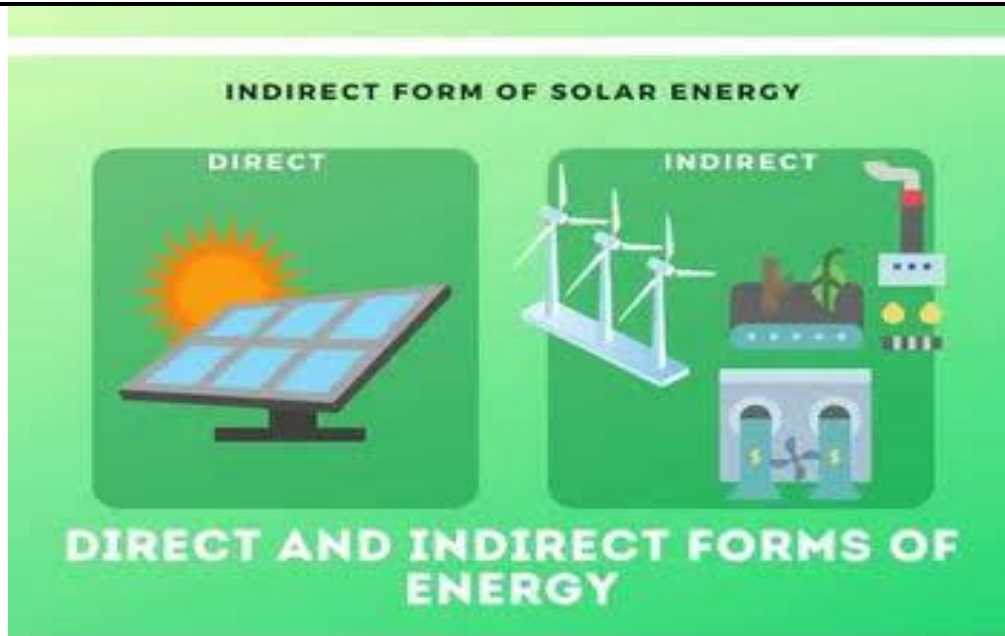
The sun is the ultimate source of most of the energy that we use. The sun gets all this energy by consuming itself in a gigantic thermonuclear fire, the same basic process that gives a “hydrogen bomb” its enormous destructive force. The fuel for the sun is ordinary hydrogen. But the energy-yielding reaction is not an ordinary chemical reaction. Instead, it is a nuclear reaction in which the nuclei of 4 hydrogen atoms fuse together to produce the nucleus of a helium atom of mass number 4, plus 2 positrons, subatomic particles with the same mass as the electron, but with a positive, instead of a negative, charge. There is a net loss of mass in the process (in nuclear reactions mass can change) and this loss translates into an enormous amount of energy. The fusion of only 1 gram of hydrogen releases as much energy as the heat from burning about 20 tons of coal.



11.3. Direct and Indirect Solar Energy

From the discussion above, it is seen that a lot of energy comes from the sun. Most of it is absorbed by the atmosphere, but a significant fraction reaches Earth’s surface directly. We certainly use that energy because it keeps us and other living organisms warm enough to sustain life. Photovoltaic cells that convert solar energy directly to electricity, enable use of solar energy as a power source. Living organisms use solar energy. Chlorophyll in plants capture the energy of photons of visible light and use it to perform photosynthesis.





ThePhoenixSun.com

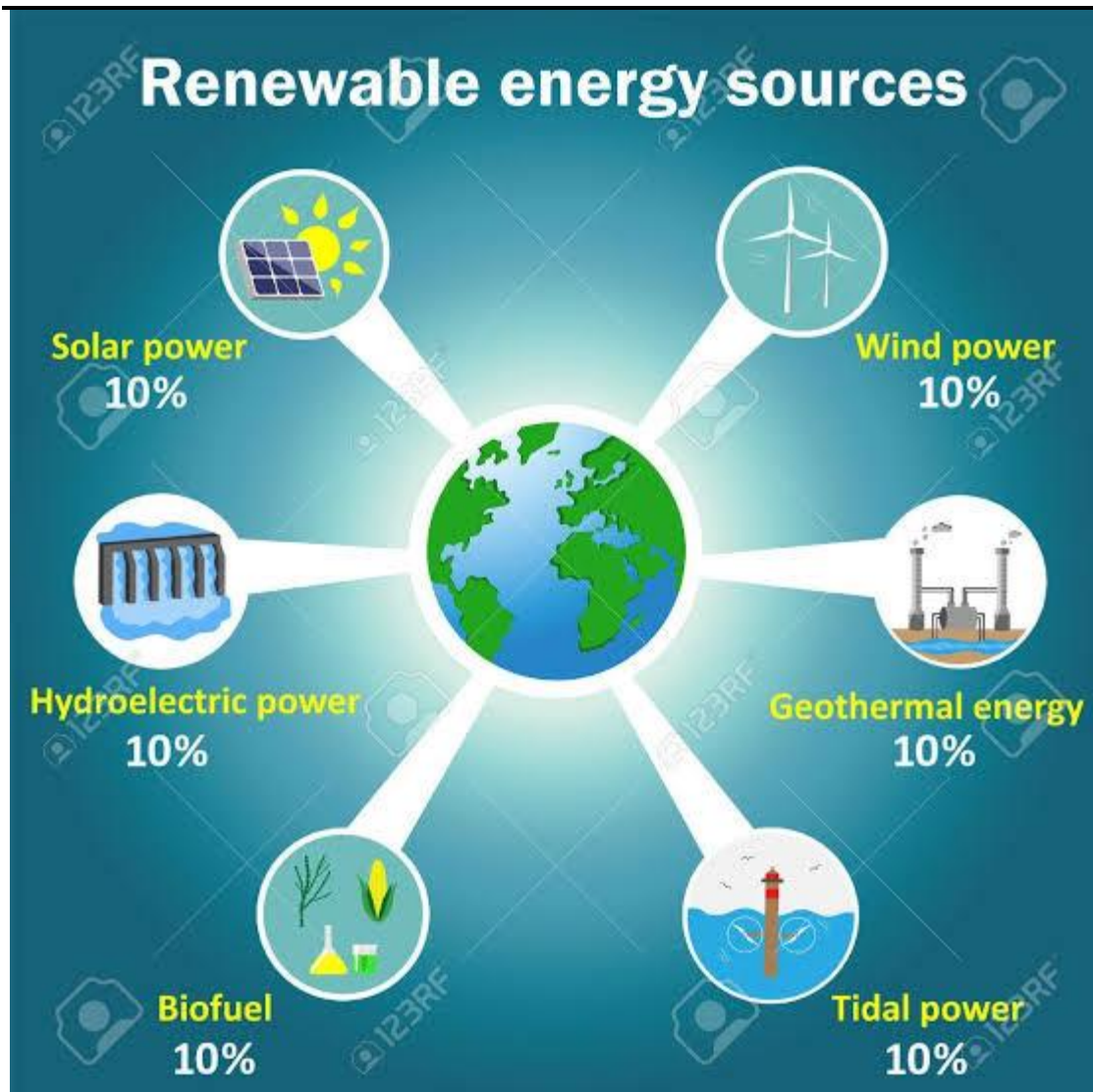
11.4. RENEWABLE ENERGY SOURCES

Ideal energy sources are those that do not pollute and never run out. Such sources are commonly called **renewable energy resources**. There are several practical renewable energy resources that are discussed briefly in this section.

Solar Energy is The Best — When The Sun Shines

Sunshine comes close to meeting the criteria of an ideal energy source, including widespread availability, an unlimited supply, and zero cost up to the point of collection. The utilization of solar energy does not cause air, heat, or water pollution. Sunshine is intense and widely available in many parts of the world. If it were possible to collect solar energy with a collection efficiency of 10%, approximately one-tenth of the area of Arizona would suffice to meet U.S.

energy needs, and at 30% collection efficiency, only about one-thirtieth of the area of that generally sunny state would suffice.



12. Use of renewable feedstock's

According to the principles of green chemistry, a raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable. Using renewable resources like microbial or plant biomass, which are embedded into nature's closed carbon cycle, represents a real option to prepare functional byproducts in a sustainable way and to contribute to energetic transition. In the context of the Green Chemistry Principle, which addresses the renewable feedstock thematic, we nowadays witness a vast number of current multidisciplinary collaborations, involving the fields of, among others, agronomy, biochemical engineering, biotechnology, chemistry, microbiology, physics, toxicology, or engineering. These collaborations result in the development of next-generation fuels, polymers, and other materials pivotal for our today's society based on renewable resources and characterized by low impact on health and environment. The current global dynamic of these developments indeed gives reason to optimism for the future. Finding a method to convert raw wastes such as spinney waste fibers into a mortar composite stabilized material could be an excellent application of this principal of green chemistry. Whenever switching from fossil feedstock's to renewable, one has to consider that using renewable resources enlarges the process concept by incorporating resource provision, transportation, storage, and other aspects of logistics into the process design. Such a switch in feedstock provision, however, results in a fundamental change in the structure of processes, used technologies, and the economical concepts of industry and society.

*Bio-based plastics are made from a wide range of renewable **BIO-BASED** feedstocks.*



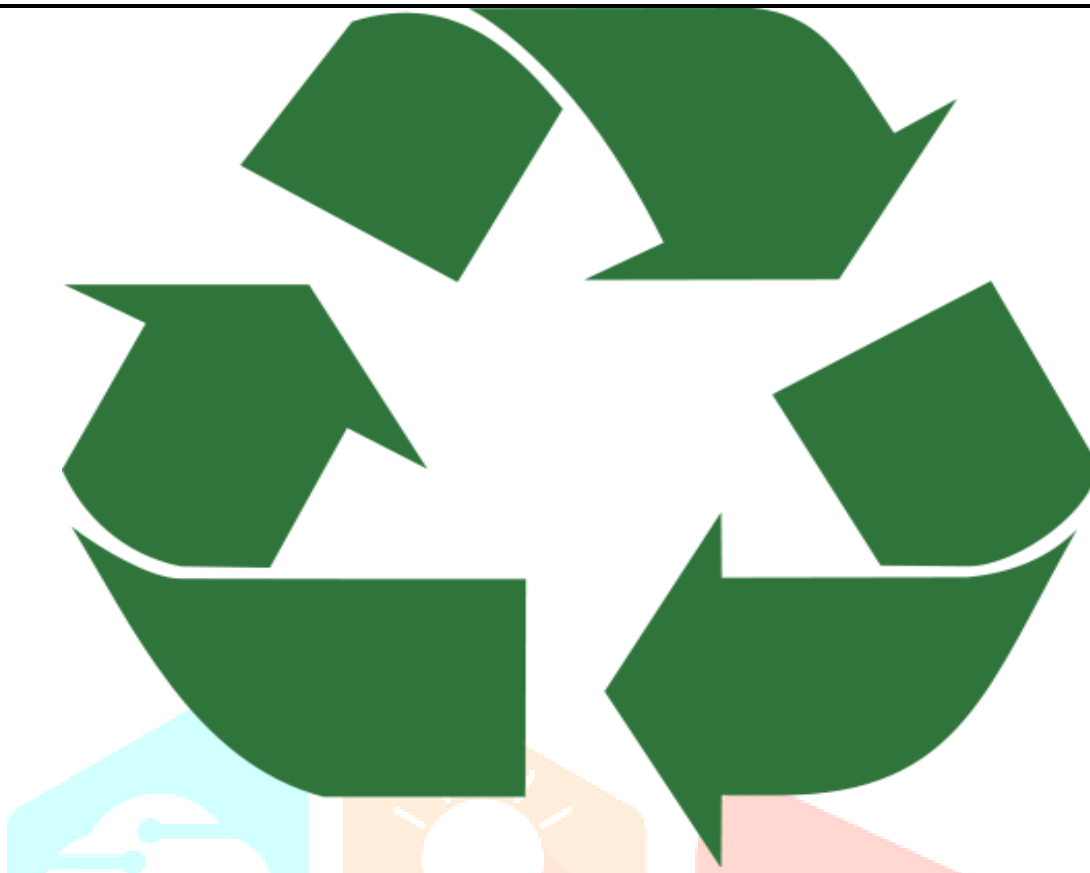
© European Bioplastics

13. Reduce derivatives

Many processes could be designed in such a way to reduce the use of additional reagents and the resulting wastes. It is commonly necessary to synthesize a derivative of a compound containing groups which are not needed in the final product, but which allow the synthesis or purification steps to proceed more easily. However, these derivatives result in lower atom economy, since they introduce atoms that are not incorporated into the final product, but finally end up as waste; this is in conflict with the atom efficiency principle according to For many reactions that have traditionally required protecting groups, chemists are urgently devoting research efforts to finding alternatives that do without them.

14. Design for degradation

One of the most important objectives of green chemistry is maximizing the production with minimizing unwanted by-products. Designing of products and processes that display reduced impact on humans and the environment, such as creating sustainable mortar composite that could be considered as an value-added product suitable for various applications as inert matrix for immobilization of some low and intermediate levels of radioactive wastes, decorative tiles, building bricks, and light concrete, is reported. In this case, highly reactive hydroxyl radicals react with the organic moieties of the spinning fiber wastes either by subtracting ions of hydrogen or by addition to the unsaturated site to yield organic radicals, which are readily oxidized by oxygen. Therefore, the end products of the degradation process were only carbon dioxide and water.



15. Real-time analysis for pollution prevention

With advancements in chemistry, the production of numerous toxic chemicals is a serious problem for the environment. One of the basic concepts of green chemistry is familiar to pollution prevention practitioners. Less hazardous materials in chemical formulations and reducing waste formation have been sounded for many years. Consequently, green chemistry aims at eliminating the usage and generation of hazardous substances by designing better manufacturing processes for chemical materials with minimum waste production by real-time

Monitoring of running processes. This consequently enables a timely intervention right before waste or toxins are generated.

16. Inherently safer chemistry for accident prevention

It is of outstanding importance to avoid highly reactive chemicals that could potentially cause accidents during the reaction. Substance and the form of a substance used in a chemical process should be chosen in such a way to minimize the potential for chemical accidents, including toxin releases, explosions, and fire formation. For example, the most abundant solution medium, water, could accidentally cause an explosion by flowing into a tank containing methyl isocyanine gas, releasing a large amount of methyl isocyanate into the surrounding area. Other well-known materials, which undergo reactions of often disastrous outcome with water, are found among alkali metals. If an alternative reaction had been developed that did not use this reagent, the risk of explosion even causing death would have been minimized.

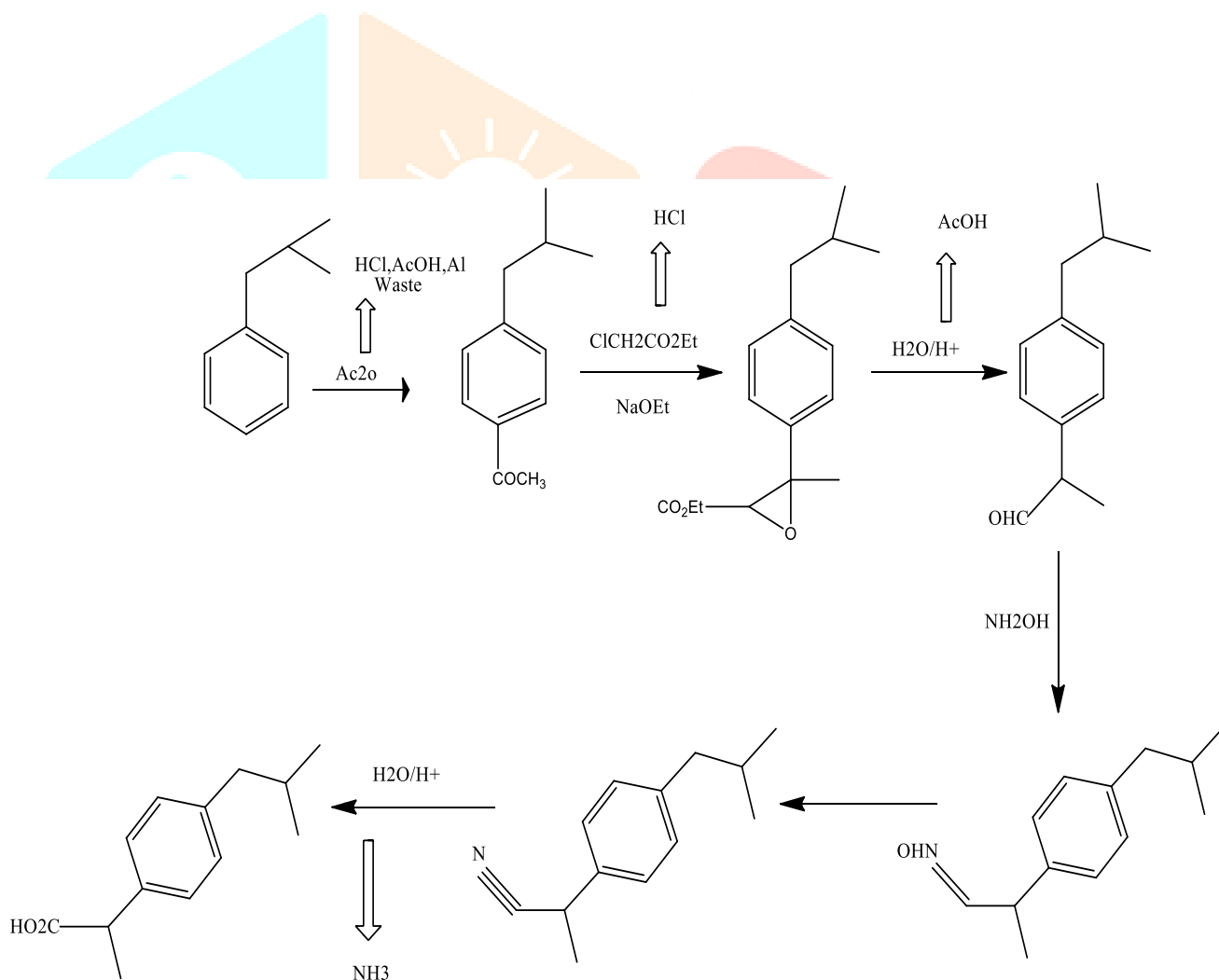
Intrinsically, safe chemistry can also be carried out in flow mode, using tubular micro reactor with reaction channels of tiny diameter. Such flow chemistry approaches drastically reduce the reaction volume, the reaction time, and catalyst requirement, intensifies the processes by boosting the space/time yield, opens new process windows in terms of extreme temperature and pressure conditions to be applied, and, moreover, even allows to carry out highly dangerous reactions in a safe way]. In addition, the application

of flow chemistry in micro reactors also displays a strategy to overcome classical drawbacks of microwave-driven processes, such as the restricted penetration depth of microwaves into absorbing media.

17. Routes Of Ibuprofen

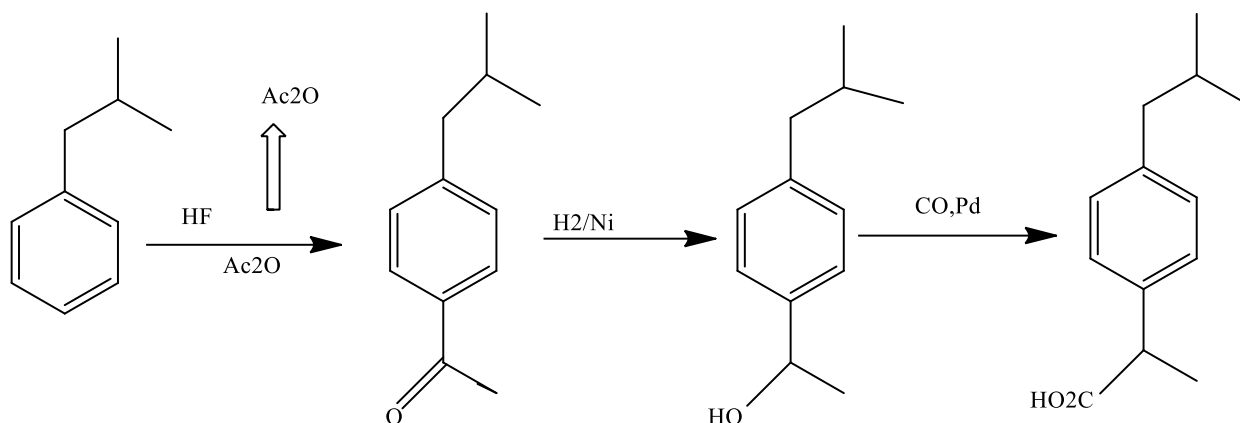
Ibuprofen is a non-selective inhibitor of an enzyme called cyclooxygenase (COX), which is required for the synthesis of prostaglandins via the arachidonic acid pathway. COX is needed to convert arachidonic acid to **prostaglandin H₂** (PGH₂) in the body. PGH₂ is then converted to prostaglandins.

17.1 Classic Route Of Ibuprofen



A name could not be generated for this structure.

17.2 Hoesch Route To Ibuprofen/Greener Synthesis Of Ibuprofen.



18. Conclusion.

Green Chemistry is now a approach that through application and extension of the principle of green chemistry can contribute to sustainable development. It is clear that the challenge for the future chemical industry is based on safer products and processes designed by utilizing new ideas in fundamental research. The success of green chemistry depends on educating offered by the green chemistry revolution, there is also exciting opportunity. Pharmaceutical companies and the contract Research And Manufacturing Services (CRAMS) providers have now started employing the principles of green chemistry in developing atom efficient router, which minimize solvents and waste, by utilizing technologies such as bio and chemo catalysis.

Understanding of Biogeochemical significant changes in the ways those cycle function. Understanding energy, energy flow and chemistry increases our understanding of organism, their environment, and how environmental systems function. Thinking in terms of whole systems can help avoid destroying the parts and connections that allow the system the function. Thus green chemistry happens to be the remedy for various environmental problems like soil pollution, food chain maintenances, water and air pollution. Green Chemistry is NOT a solution to all environmental problems BUT the most fundamental approach to prevent pollution.

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