

CHAPTER 37**GREEN CHEMISTRY****1 INTRODUCTION**

Environment consciousness has attracted development of processes and new techniques which protect environment, in rapidly developing economies. Chemistry has provided very important processes and materials which constitute medicines, paints, bio-molecules, polymers food products dyes and chemicals. The industrial processes require huge amount of chemicals like acids, reagents, solvents, alkalis etc. which not only produce the desired products but also harmful substances in solid, liquid and gases. Thus there is pressing need for synthetic chemist to minimize pollution caused by these chemicals. Thus in 1991, the term Green Chemistry was coined with the objective of designing chemicals and processes which would be less harmful to human health.

Green chemistry¹, also called sustainable chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances. It applies to organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, and even physical chemistry. While green chemistry seems to focus on industrial applications, it does apply to any chemistry choice.

The terms '**Environmental Chemistry**' and '**Green Chemistry**' are two different aspects of environmental pollution studies. The former is the study of chemical pollutants in natural environment while the latter is an attempt to design chemical products and processes to reduce the harm they cause to the environment. Green chemistry seeks to reduce pollution at source, whereas environmental chemistry focuses on the study of pollutant chemicals and their effect on nature.

Ryoji Noyori identified three key developments in green chemistry: *use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations* and the *use of hydrogen in asymmetric synthesis*. Examples of applied green chemistry are supercritical water oxidation, on water reactions, and dry media reactions etc. Commercial application of Green chemistry has led to research to examine alternatives to existing synthetic methods.

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 Tamiflu precursor which is fermented by Roche in bacteria.

2 PRINCIPLES OF GREEN CHEMISTRY

Paul Anastas, and John C. Warner of the United States Environmental Protection Agency developed 12 principles of green chemistry, which help to explain what the definition means in practice. The

¹ The term "Green Chemistry" was coined by Paul Anastas in 1991.

principles cover such concepts as:

- the design of processes to maximize the amount of raw material that ends up in the product;
- the use of safe, environment-benign substances, including solvents, whenever possible;
- the design of energy efficient processes;
- the best form of waste disposal: not to create it in the first place.

The 12 principles are

1. It is better to prevent waste than to treat or clean up waste after it is formed.

Prevention of Waste: It is better to prevent waste than to treat or clean up waste after it is formed. The ability of chemists to redesign chemical transformations to minimize the generation of hazardous waste is an important first step in pollution prevention. The first principle suggests that prevention is better than cure i.e., stop pollution at source. The process design should be such that waste by-products are minimized. For example, **Metathesis**² Developed by Grubbs, Schrock and Chauvin, is a major advance for green chemistry. It is a reaction in which double bonds are broken and made between carbon atoms in ways that causes atom groups to change places, with the help of special catalyst molecules. It is used in the development of pharmaceuticals and advanced plastic materials, and is a great step forward for green chemistry, reducing hazardous waste through smarter production.

2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

The processes should be so redesigned to give maximum yield and maximize efficiency.

Maximize Atom Economy: Atom Economy is a concept that evaluates the efficiency of a chemical transformation, and is calculated as a ratio of the total mass of atoms in the desired product to the total mass of atoms in the reactants.

$$\% \text{ Atom Economy} = \frac{\text{No. of atoms incorporated}}{\text{No. of atoms in the reactants}} \times 100$$

Choosing transformations that incorporate most of the starting materials into the product are more efficient and minimize waste, e.g., Diels–Alder reaction is 100% Atom Economy reaction as all the atoms of the reactants are incorporated in the cycloadduct.

3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Less Hazardous Chemical Synthesis: Synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and environment. Some toxic chemicals are replaced by safer ones for a green technology, when reagent choices exist for a particular transformation. This principle focuses on choosing reagents that pose the least risk and generate only benign by-products. For example, in the manufacture of polystyrene foam sheet packing material, chlorofluorocarbons which contribute to O₃ depletion, global warming and ground level smog, have now been replaced by CO₂ as the blowing agent.

² A molecular process involving exchange of bonds between two reacting chemical species, which results in creation of product with similar or identical bonding affiliation



The chemical species may ionic or covalent.

4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.

Such products should be explored which retain their effective functions with simultaneous reduction of toxicity, if any is associated with the products. This principle emphasizes designing of safer chemical. For example, properties of super critical CO_2 makes it possible to be used as a good effective solvent.

5. The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

Development of dry reaction techniques follows this principles of Green Chemistry, making the application of solvent redundant.

6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic processes should be conducted at ambient temperature and pressure.

For example Ionic liquids, work as an excellent solvent under ambient conditions. Such methods can lead to reduction in energy requirements for creation of reaction conditions.

7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.

The raw material should be renewable for assured production. Thus techniques are being developed for such processes. For example, *preparation of adipic acid has seen replacement of benzene by glucose with reaction carried out in water*. We must note here that adipic acid is used for production of nylon and plasticizers etc.

8. Reduce derivatives - Unnecessary derivatization (blocking group, protection/ de-protection, temporary modification) should be avoided whenever possible.

Derivatization results in increase in number of steps required in the process and each additional step requires reagents and can generate more waste. Instead, more selective and better alternative synthetic sequences that eliminate the need for functional group protection should be adopted.

9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Use of Catalysts: Catalysts are used in small amounts and can carry out a single reaction many times and so are preferable to stoichiometric reagents, which are used in excess and work only once. They can enhance the *selectivity of a reaction, reduce the temperature of a transformation, reduce reagent-based waste and potentially avoid unwanted side reactions* leading to a clean technology. Catalysis is crucial to the chemical and related industries. Apart from heavy metal catalysts softer catalysts like zeolites, phase transfer catalysts, e.g., crown ethers, are finding increasing industrial applications.

10. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

Based on the lessons learned from experience of use of DDT as insecticide, this principle suggests that the breakdown of chemical product should not be harmful even in long run.

11. Analytical methodologies need to be further developed to allow real-time, in-process monitoring and control prior to the formation of hazardous substances.

Developing analytical process monitoring tools are equally important as far as the development of product is concerned. The quick detection of harmful substance can help in quick curative action.

12. Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosions, and fires.

The process and the substances used should be safe even if some accident takes place there should not be any damage to the environment. One can learn lessons from Bhopal Gas Tragedy that this principle is very important and poses great challenge for the chemical technologist.

The principles of green chemistry which focus on waste reducing, sustainable, safe chemicals and efficient processes can be examined through various dimensions such as **development of alternative feedstock, solvents, innocuous reagent application, safer chemical reaction and some alternative reaction methodology.**

3 USE OF ALTERNATIVE FEEDSTOCK

Chemical transformations should be designed to utilize raw materials and feedstock which are not only renewable, but also technically and economically practicable. Examples of renewable feedstock include agricultural products, and those of depleting feedstock include raw materials that are mined or generated from fossil fuels (petroleum, natural gas or coal). For green synthesis, the renewable feedstock should replace the traditional petroleum sources, e.g., benzene used in the commercial synthesis of adipic acid which is required in the manufacture of nylon, plasticizers and lubricants, has been replaced to some extent by the renewable and non-toxic glucose and the reaction is carried out in water. Similarly biodiesel or biofuel can be produced from vegetable oils and animal fat with transesterification. Some of the processes are explained in detail to appreciate new processes developed based on principles of Green Chemistry.

3.1 Biodiesel production

Biodiesel production is the process of producing the biofuel, biodiesel, through either transesterification or alcoholysis. It involves reacting vegetable oils or animal fats catalytically with a short-chain aliphatic alcohols (typically methanol or ethanol).

The major steps required to synthesize biodiesel are as follows:

(a) Feedstock pretreatment

If waste vegetable oil (WVO) is used, it is filtered to remove dirt, charred food, and other non-oil material. Water is removed because its presence causes the triglycerides to hydrolyze, giving salts of the fatty acids (soaps) instead of undergoing transesterification to give biodiesel.

(b) Determination and treatment of free fatty acids (FFA)

A sample of the cleaned feedstock oil is titrated with a standardized base solution in order to determine the concentration of free fatty acids (carboxylic acids) present in the waste vegetable oil sample. These acids are then either esterified into biodiesel, esterified into bound glycerides, or removed, typically through neutralization.

(c) Reactions

While adding the base, a slight excess is factored in to provide the catalyst for the transesterification. The calculated quantity of base (usually sodium hydroxide) is added slowly to the alcohol and it is stirred until it dissolves. Sufficient alcohol is added to make up three full equivalents of the triglyceride, and an excess of usually six parts alcohol to one part triglyceride is added to drive the reaction to completion.

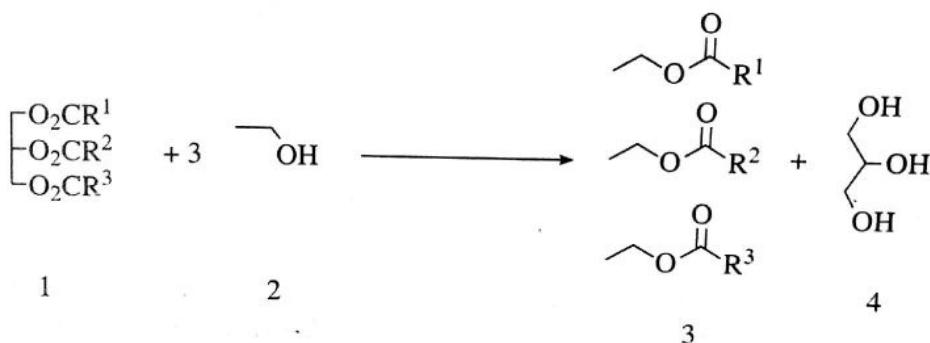
(d) Product purification

Products of the reaction include not only biodiesel, but also byproducts, soap, glycerin, excess alcohol, and trace amounts of water. All of these byproducts must be removed, though the order of removal is process-dependent.

The density of glycerin is greater than that of biodiesel, and this property is exploited to separate the bulk of the glycerin by-product. Residual methanol is typically removed through distillation and reused, though it can be washed out (with water) as a waste. Soaps can be removed or converted into acids. Any residual water must be removed from the fuel.

(e) Reactions Transesterification

Triglycerides (1) are reacted with an alcohol such as ethanol (2) to give ethyl esters of fatty acids (3) and glycerol (4):

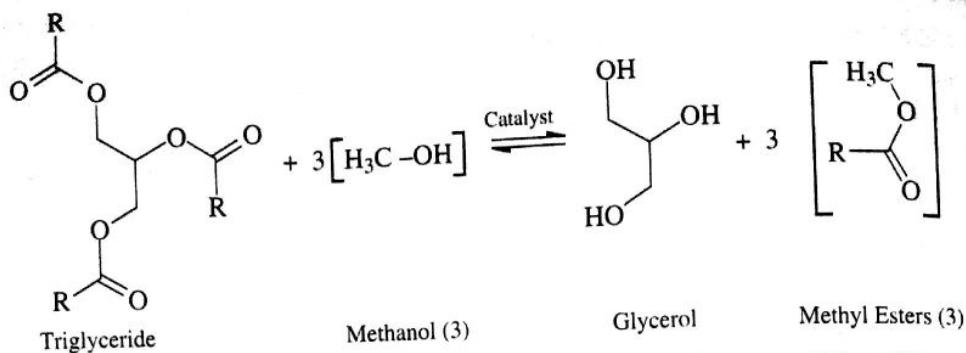


Animal and plant fats and oils are typically made of triglycerides which are esters containing three free fatty acids and the trihydric alcohol, glycerol. In the transesterification process, the alcohol is deprotonated with a base to make it a stronger nucleophile. Commonly, ethanol or methanol are used. As can be seen, the reaction has no other inputs than the triglyceride and the alcohol.

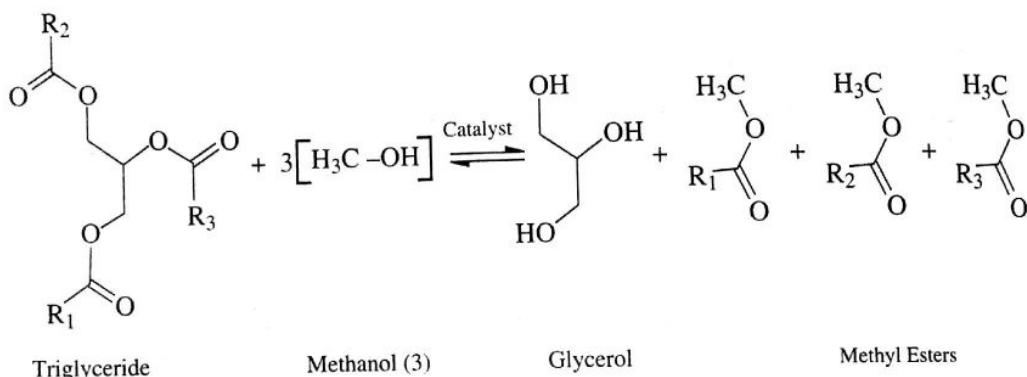
Normally, this reaction will proceed either exceedingly slowly or not at all. Heat, and acid or base are used to help the reaction proceed more quickly. It is important to note that the acids or bases are not consumed by the transesterification reaction, thus they are not reactants but catalysts.

Almost all biodiesel is produced from virgin vegetable oils using the base-catalyzed technique as it is the most economical process for treating virgin vegetable oils, requiring only low temperatures and pressures and producing over 98% conversion yield (provided the starting oil is low in moisture and free fatty acids). However, biodiesel produced from other sources or by other methods may require acid catalysis which is much slower. Since it is the predominant method for commercial-scale production, only the base-catalyzed transesterification process will be described below. An example of the transesterification reaction equation, shown in skeletal formulas:

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Since natural oils are typically used in this process, the alkyl groups of the triglyceride are not necessarily the same. Therefore, distinguishing these different alkyl groups, we have a more accurate depiction of the reaction:



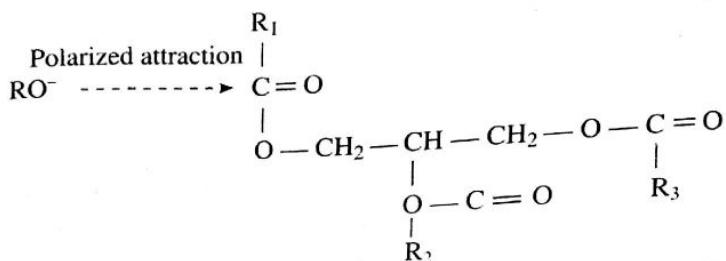
R₁, R₂, R₃ : Alkyl group.

During the esterification process, the triglyceride is reacted with alcohol in the presence of a catalyst, usually a strong alkali (NaOH, KOH, or Alkoxides). The main reason for doing a titration to produce biodiesel, is to find out how much alkali is needed to completely neutralize any free fatty acids present, thus ensuring a complete transesterification. Empirically 6.25 g / L NaOH produces a very usable fuel. One uses about 6 g NaOH when the WVO is light in colour and about 7 g NaOH when it is dark in colour. The alcohol reacts with the fatty acids to form the mono-alkyl ester (or biodiesel) and crude glycerol. The reaction between the biolipid (fat or oil) and the alcohol is a reversible reaction so the alcohol must be added in excess to drive the reaction towards the right and ensure complete conversion.

(f) Base-catalysed transesterification mechanism

The transesterification reaction is base catalyzed. Any strong base capable of deprotonating the alcohol will do (e.g., NaOH, KOH, Sodium methoxide, etc.). Commonly the base (KOH, NaOH) is dissolved in the alcohol to make a convenient method of dispersing the otherwise solid catalyst into the oil. The ROH needs to be very dry. Any water in the process promotes the saponification reaction, thereby producing salts of fatty acids (soaps) and consuming the base, and thus inhibits the transesterification reaction. Once the alcohol mixture is made, it is added to the triglyceride. The reaction that follows replaces the alkyl group on the triglyceride in a series of steps.

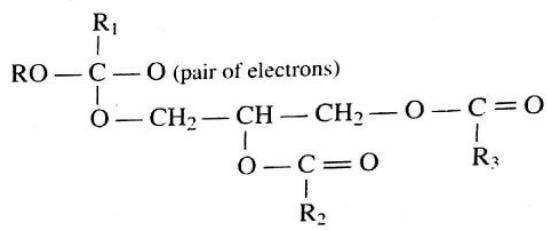
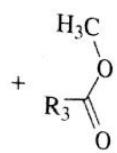
The carbon on the ester of the triglyceride has a slight positive charge, and the carbonyl oxygens have a slight negative charge. This polarization of the $C = O$ bond is what attracts the RO^- to the reaction site.



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 This yields a tetrahedral intermediate that has a negative charge on the former carbonyl oxygen:

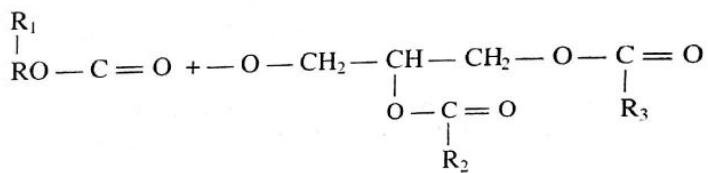


(Tetrahedral Intermediate)

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Then two more RO groups react via this mechanism at the other two $C = O$ groups. This type of reaction has several limiting factors. RO^- has to fit in the space where there is a slight positive charge on the $C = O$. MeO^- works well because it is small-in size. As the chain length of the RO^- group increases, reaction rates decrease. This effect is called steric hindrance. This effect is a primary reason the short chain alcohols, methanol and ethanol, are typically used.

There are several competing reactions, so care must be taken to ensure the desired reaction pathway occurs. Most methods do this by using an excess of RO^- .

The acid-catalyzed method is a slight variant that is also affected by steric hindrance.

Biodiesel Production methods

1. Batch process

- Preparation: care must be taken to monitor the amount of water and free fatty acids in the incoming biolipid (oil or fat). If the free fatty acid level or water level is too high it may cause problems with soap formation (saponification) and the separation of the glycerin by-product downstream.
 - Catalyst is dissolved in the alcohol using a standard agitator or mixer.
 - The alcohol/catalyst mix is then charged into a closed reaction vessel and the biolipid (vegetable or animal oil or fat) is added. The system from here on is totally closed to the atmosphere to prevent the loss of alcohol.
- The reaction mix is kept just above the boiling point of the alcohol (around 70 °C, 158 °F) to speed up the reaction though some systems recommend the reaction take place anywhere from room temperature to 55 °C (131 °F) for safety reasons. Recommended reaction time varies from 1 to 8 hours; under normal conditions the reaction rate will double with every 10 °C increase in reaction temperature. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters.
- The glycerin phase is much denser than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. In some cases, a centrifuge is used to separate the two materials faster.
 - Once the glycerin and biodiesel phases have been separated, the excess alcohol in each phase is removed with a flash evaporation process or by distillation. In other systems, the alcohol is removed and the mixture neutralized before the glycerin and esters have been separated. In either case, the alcohol is recovered using distillation equipment and is reused. Care must be taken to ensure no water accumulates in the recovered alcohol stream.
 - The glycerin by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin (water and alcohol are removed later, chiefly using evaporation, to produce 80-88% pure glycerin).
 - Once separated from the glycerin, the biodiesel is sometimes purified by washing gently with warm water to remove residual catalyst or soaps, dried, and sent to storage.

2. Supercritical process

An alternative, catalyst-free method for transesterification uses supercritical methanol at high temperatures and pressures in a continuous process. In the supercritical state, the oil and methanol are in a single phase, and reaction occurs spontaneously and rapidly. The process can tolerate water in the feedstock, free fatty acids are converted to methyl esters instead of soap, so a wide variety of feedstocks can be used. Also the catalyst removal step is eliminated. High temperatures and pressures are required, but energy costs of production are similar or less than catalytic production routes.

Ultra- and high-shear in-line and batch reactors

Ultra- and High Shear in-line or batch reactors allow production of biodiesel continuously, semi-continuously, and in batch-mode. This drastically reduces production time and increases production volume.

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The reaction takes place in the high-energetic shear zone of the Ultra- and High Shear mixer by reducing the droplet size of the immiscible liquids such as oil or fats and methanol. Therefore, the smaller the droplet size the larger the surface area the faster the catalyst can react.

Lipase-catalyzed method

Large amounts of research have focused recently on the use of enzymes as a catalyst for the transesterification. Researchers have found that very good yields could be obtained from crude and used oils using lipases. The use of lipases makes the reaction less sensitive to high FFA content which is a problem with the standard biodiesel process. One problem with the lipase reaction is that methanol cannot be used because it inactivates the lipase catalyst after one batch. However, if methyl acetate is used instead of methanol, the lipase is not inactivated and can be used for several batches, making the lipase system much more cost effective.

Note : Glycerol, a by-product of bio-fuel manufacturing is a valuable product and the same is utilized as alternative solvent. The hydrogenolysis of glycerol can result in production of ethanol, methanol, 1-propanol and propanediols etc. Thus same can be used as a feed stock.

3.2 Benzene-free synthesis of adipic acid

Strains of *Escherichia coli*, that synthesized cis,cis-muconic acid from D-glucose under fed-batch fermentor conditions were constructed and evaluated. Chemical hydrogenation of the cis,cis-muconic acid in the resulting fermentation broth was examined. Biocatalytic synthesis of adipic acid from glucose eliminates two environmental concerns characteristic of industrial adipic acid manufacture: (i) **use of carcinogenic benzene and benzene-derived chemicals as feedstocks and (ii) of nitrous oxide as a by-product of a nitric acid catalyzed oxidation.** While alternative catalytic synthesis eliminates the use of nitric acid, have been developed, most continue to rely on petroleum-derived benzene as the ultimate feedstock. An, *E. coli* was developed that synthesized 36.8 g/L of cis,cis-muconic acid in 22% (mol/mol) yield from glucose after 48 h of culturing under fed-batch fermentor conditions.

Note: Optimization of microbial cis,cis-muconic acid synthesis required expression of three enzymes not typically found in *E. coli*. Two copies of the *Klebsiella pneumoniae aroZ* gene encoding DHS dehydratase were inserted into the *E. coli* chromosome, while the *K. pneumoniae aroY* gene encoding PCA decarboxylase an enzyme and the *Acinetobacter calcoaceticus cataA* gene encoding catechol 1,2-dioxygenase were expressed from an extrachromosomal plasmid. After fed-batch culturing was complete, the cells were removed from the broth, which was treated with activated charcoal and subsequently filtered to remove soluble protein. Hydrogenation of the resulting solution with 10% Pt on *cis,cis*-muconic acid into adipic acid.

3.3 Manufacturing of Carpet Tiles with polyolefin as Feedstock

Historically, carpet tile backings have been manufactured using bitumen, polyvinyl chloride (PVC), or polyurethane (PU). While these backing systems have performed satisfactorily, there are several inherently negative attributes due to their feedstocks or their ability to be recycled. Shaw³ selected a combination of **polyolefin resins as the base polymer of choice** for manufacturing tile **due to the low toxicity of its feedstocks**, superior adhesion properties, dimensional stability, and its ability to be recycled. The EcoWorx compound also had to be designed to be compatible with nylon carpet fiber. Although

³Shaw Industries was recognized with the Designing Greener Chemicals Award for developing EcoWorx Carpet Tile in 2003.

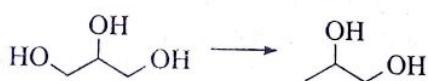
EcoWorx may be recovered from any fiber type, nylon-6 provides a significant advantage. Polyolefins are compatible with known nylon-6 depolymerization methods. PVC interferes with those processes. Nylon-6 chemistry is well-known and not addressed in first-generation production. From its inception, EcoWorx met all of the design criteria necessary to satisfy the needs of the marketplace from a performance, health, and environmental standpoint. The separation of the fiber and backing through elutriation, grinding, and air separation proved to be the best way to recover the face and backing components, but an infrastructure for returning postconsumer EcoWorx to the elutriation process was necessary.

4 USE OF INNOCUOUS REAGENTS AND NATURAL PRODUCT SYNTHESIS

Attempts are being made not only to quantify the *greenness* of a chemical process but also to factor in other variables such as *chemical yield*, the *price of reaction components*, *safety in handling chemicals*, *hardware demands*, *energy profile* and *ease of product workup and purification*. In one quantitative study, the reduction of nitrobenzene to aniline receives 64 points out of 100 marking it as an acceptable synthesis overall.

Green chemistry is increasingly seen as a powerful tool that researchers must use to evaluate the environmental impact of nanotechnology as well. As nanomaterials are developed, the environmental and human health impacts of both the products themselves and the processes to make them must be considered to ensure their long-term economic viability.

Increasing use of harmless substances for manufacturing can reduce the environmental cost. Some of examples of innocuous reagents are described below.



4.1 Glycerin to propylene glycol

Through the use of a copper-chromite catalyst, a system of converting waste, glycerin from biodiesel production to propylene glycol, wherein the requirement of temperature was lowered, enhancing the conversion efficiency. Propylene glycol produced in this way could be cheap enough to replace the more toxic ethylene glycol that is the primary ingredient in automobile antifreeze. In 2006, Professor Galen J. Suppes, from the University of Missouri in Columbia, Missouri, was awarded the Academic Award for this work.

4.2 Synthesis of tryptanthrin

Research is currently also going in the area of natural product synthesis to develop reactions which can proceed involving green chemistry principles. Recently, Atul Kumar has developed an efficient and green method for the synthesis of tryptanthrin, a biologically active natural product, employing β -cyclodextrin as a catalyst in aqueous media at room temperature from *isatoic anhydride* and *isatin* in excellent yields.

5 ALTERNATIVE SOLVENTS

A solvent is a liquid, solid, or gas that dissolves another solid, liquid, or gaseous solute, resulting in a solution that is soluble in a certain volume of solvent at a specified temperature. Common uses for organic solvents are in dry cleaning (e.g., tetrachloroethylene, dichloromethane), as a paint thinner (e.g., toluene, turpentine), as nail polish removers and glue solvents (acetone, methyl acetate, ethyl acetate), in spot removers (e.g., hexane, petrol ether), in detergents (citrus terpenes), in perfumes (ethanol), and nail polish, (part of how it stays on nails) and in chemical synthesis. The use of inorganic solvents (other than water) is typically limited to research chemistry and some technological processes. Commonly used solvents are volatile, toxic, flammable and hazardous to environment.

Ideally a green solvent should have characteristics of low toxicity, inertness, recyclable, non-contaminating.

Solvents are extensively used in most of the **synthesis**. Widely used solvents in synthesis are toxic and volatile – alcohol, benzene (known carcinogenic), CCl_4 , CHCl_3 , perchloroethylene, CH_2Cl_2 .

Purification steps also utilize and generate large amounts of solvent and other wastes (e.g., chromatography supports). These have now been replaced by safer *green solvents* like *ionic liquids*, *supercritical CO_2 fluid*, *water or supercritical water* and also *solvent-free* systems that utilize the surfaces or interiors of clays, zeolites, silica, and alumina. These are the basis of many of the cleaner chemical technologies that have reached commercial development.

5.1 Ionic liquids are liquids at Room Temperature and below

They are nonvolatile and have no vapour pressure. They can serve as optimal replacements for volatile organic traditionally used industrial solvents. The reactions in ionic liquids need no special apparatus and methodologies, and they can be recycled. However, large-scale applications are still not known. The first ionic liquid I ($[\text{EtNH}_3]^+[\text{NO}_3]^-$) was discovered in 1914. Many binary ionic liquids of type II are also used as green solvents.

5.2 Supercritical CO_2 fluid

This is another versatile green solvent group which has low viscosity and no surface tension. It has the unique ability to diffuse like gas through solids, and to dissolve a wide range of organic substances, catalysts, etc. Supercritical CO_2 fluid is now becoming an important commercial and industrial solvent for chemical separation because of its low toxicity and non-inflammability. Its stability and the relatively low temperature of the process allows most compounds to be extracted with little damage and denaturation (e.g., fragrance compounds used in perfumery). Because CO_2 is obtained as a by-product of other industrial processes, it is inexpensive and being a gas it is easily evaporated leaving no residue. (Described in detail later)

5.3 Supercritical water

Organic substances are insoluble in water. Many compounds are soluble in water when it becomes supercritical at 374°C and 218 Atm. Hence, this clean and cheap solvent is used as a green solvent for many synthetic reactions.

5.4 Reactions in aqueous phase (Water as Green Solvent)

The use of ordinary water for organic reactions was unknown till the middle of the 20th century. However, replacement of organic solvents with eco-friendly water has found success with many reactions, some of which may occur at higher rates because of its high polarity. Reactions carried out in aqueous medium include oxidations, reductions, epoxidations, polymerizations (with or without catalysts) and many named reactions.

6 DESIGN OF SAFER CHEMICALS

Design of chemicals and their forms (solid, liquid, or gas) to minimize the chemical accidents including explosions, fires and releases to the environment is must, e.g., manufacture of gold atom nanoparticles used diborane (highly toxic and bursts into flame near room temperature) and cancer-causing benzene. Now, diborane has been replaced by environmentally benign NaBH_4 which also eliminates the use of benzene. Nanoscience and nanotechnology is another important contribution to green chemistry. Nanotechnology provides huge savings in materials by development of microscopic and submicroscopic electronic and mechanical devices. Some of the important chemicals and their applications are discussed below.

6.1 Supercritical carbon dioxide

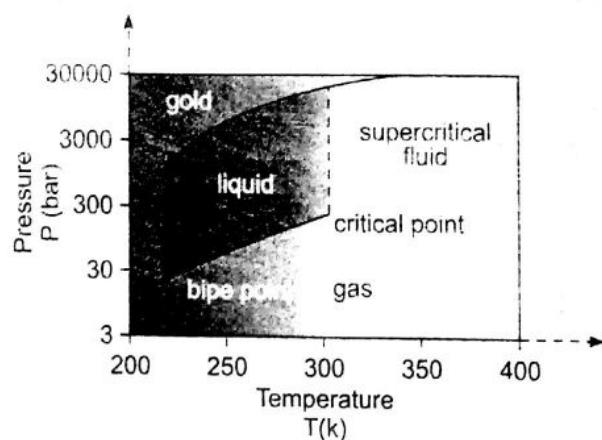


Fig. 1. Carbon dioxide pressure-temperature phase diagram.

Supercritical carbon dioxide is a fluid state of carbon dioxide where it is held at or above its critical temperature and critical pressure. Carbon dioxide usually behaves as a gas in air at STP or as a solid called dry ice when frozen. If the temperature and pressure are both increased from STP to be at or above the critical point for carbon dioxide, it can adopt properties midway between a gas and a liquid. More specifically, it behaves as a *supercritical fluid* above its critical temperature (31.1 °C) and critical pressure (72.9 atm/7.39 MPa), expanding to fill its container like a gas but with a density like that of a liquid.

Supercritical CO_2 is becoming an important commercial and industrial solvent due to its role in chemical extraction in addition to its low toxicity and environmental impact. The relatively low

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temperature of the process and the stability of CO₂ also allows most compounds to be extracted with little damage or denaturing. In addition, the solubility of many extracted compounds in CO₂ varies with pressure, permitting selective extractions.

Note: In 1996, Dow Chemical won the 1996 Greener Reaction Conditions award for their 100% carbon dioxide blowing agent for polystyrene foam production. Polystyrene foam is a common material used in packing and food transportation. Traditionally, CFC and other ozone-depleting chemicals were used in the production process of the foam sheets, presenting a serious environmental hazard. Flammable, explosive, and, in some cases toxic hydrocarbons have also been used as CFC replacements, but they present their own problems. Dow Chemical discovered that supercritical carbon dioxide works equally as well as a blowing agent, without the need for hazardous substances, allowing the polystyrene to be more easily recycled. The CO₂ used in the process is reused from other industries, so the net carbon released from the process is zero.

Applications of Supercritical CO₂ as

(a) Solvent

1. Carbon dioxide is gaining popularity amongst coffee manufacturers looking to move away from some of the classic decaffeinating solvents of the past, many of which lead to public outcry because of real or perceived dangers related to their use in food preparation. Supercritical CO₂ is forced through the green coffee beans and then they are sprayed with water at high pressure to remove the caffeine. The caffeine can then be isolated for resale (e.g., to the pharmaceutical industry or to beverage manufacturers) by passing the water through activated charcoal filters or by distillation, crystallization or reverse osmosis.
2. Supercritical carbon dioxide can also be used as a more environmentally friendly solvent for dry cleaning as compared to more traditional solvents such as hydrocarbons and perchloroethylene.
3. Supercritical carbon dioxide is used as the extraction solvent for creation of essential oils and other herbal distillates. Its main advantages over solvents such as hexane and acetone in this process are that it is non-toxic and non-flammable. Furthermore, separation of the reaction components from the starting material is much simpler than with traditional organic solvents, merely by allowing it to evaporate into the air recycling it by condensation into a cold recovery vessel. Its advantage over steam distillation is that it is used at a lower temperature, which can separate the plant waxes from the oils.
4. In laboratories, supercritical carbon dioxide is used as an extraction solvent, e.g., in determination of Total Recoverable Hydrocarbons from soils, sediments, fly-ash, and other media, and determination of PAHs in soil and solid wastes. Supercritical fluid extraction has also been used in determination of hydrocarbon components in water.
5. Processes which use supercritical carbon dioxide to produce micro and nano scale particles, often for pharmaceutical uses, are currently being developed. The gas antisolvent process, rapid expansion of supercritical solutions, and supercritical antisolvent precipitation (as well as several related methods) are some methods that have been shown to process a variety of substances into particles.

(b) Manufactured products

1. Environmentally beneficial, low-cost substitutes for rigid thermoplastic and fired ceramic, are made using supercritical carbon dioxide as a chemical reagent. The supercritical carbon dioxide in these processes is reacted with the alkaline components of fully hardened hydraulic cement or gypsum plaster to form various carbonates. The primary byproduct is water.

2. Supercritical carbon dioxide is also used in the foaming of polymers. Many corporations utilize supercritical carbon dioxide to saturate the polymer with solvent (carbon dioxide). Depressurization and heating the carbon dioxide rapidly expands, causing voids within the polymer matrix, i.e., creating a foam. Research is also ongoing at many universities in the production of microcellular foams using supercritical carbon dioxide.

(c) Working fluid

- There is considerable work being done to develop a supercritical carbon dioxide closed-Brayton-cycle gas turbine to operate at temperatures near 550 °C. This is a significant usage, which could have large implications for bulk thermal and nuclear generation of electricity, because the supercritical properties of carbon dioxide at above 500 °C and 20 MPa enable very high thermal efficiencies, approaching 45 percent. This could increase the electrical power produced per unit of fuel required by 40 percent or more. Given the volume of polluting fuels used in producing electricity, the environmental impact of cycle efficiency increases would be significant.
- Supercritical carbon dioxide is also an important emerging natural refrigerant, being used in new, low carbon solutions for domestic heat pumps. These systems are undergoing continuous development with supercritical carbon dioxide heat pumps already being successfully marketed in Asia. The EcoCute systems from Japan, developed by Mayekawa, develop high temperature domestic water with small inputs of electric power by moving heat into the system from their surroundings. Their success makes a future use in other world regions possible.
- Supercritical carbon dioxide has been used for more than 30 years to enhance oil recovery in mature oil fields. At the same time, there is the possibility of using the various "clean coal" technologies which are emerging to combine such enhanced recovery methods with carbon sequestration efforts. Using gasifiers instead of conventional furnaces, coal and water is reduced to hydrogen gas, carbon dioxide, and ash. This hydrogen gas can be used to produce electrical power in combined-cycle gas turbines, while the CO₂ is captured, compressed to the supercritical state, and injected into geological storage, possibly into existing oil fields to improve yields. The unique properties of supercritical CO₂ ensure that it will remain out of the atmosphere.

(d) Sterilization of biomedical materials

Recent studies have proved SC-CO₂ is an effective alternative for terminal sterilization of biological materials and medical devices. Moreover, this process is gentle, as the morphology, ultra structure, and protein profiles of inactivated microbes are maintained.

6.2 Hydrogen peroxide

Hydrogen peroxide (H₂O₂) is the simplest peroxide (a compound with an oxygen-oxygen single bond) and an oxidizer. Hydrogen peroxide is a clear liquid, slightly more viscous than water. In dilute solution it appears colourless. Hydrogen peroxide with its oxidizing properties is often used as a bleach or cleaning agent. The oxidizing capacity of hydrogen peroxide is so strong that it is considered a highly reactive oxygen species.

Hydrogen peroxide is used as a propellant in rocketry. It is naturally produced in organisms as a by-product of oxidative metabolism. Nearly all living things (specifically, all obligate and facultative aerobes) possess enzymes known as catalase peroxidases, which harmlessly and catalytically decompose low concentrations of hydrogen peroxide to water and oxygen. Thus various applications make it environment friendly.

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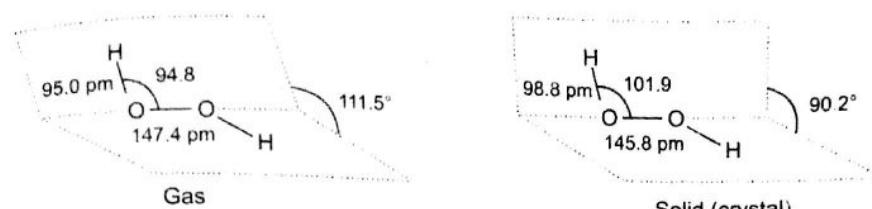


Fig. 2. Structure of H_2O_2 .

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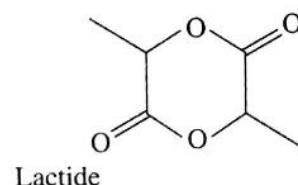
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Municipal wastewater applications

For over 50 years the standard way to deal with odors entering wastewater treatment plants was to pre-chlorinate the effluent sewers. Recently, however, hydrogen peroxide (H_2O_2) has been considered as a good deodorizer. The results show that hydrogen peroxide can replace chlorine with little to no increase in costs, and with notable benefits to downstream operations.

7 DESIGN OF ALTERNATIVE REACTION METHODOLOGY

The industrial processes involve large number of reactions which use huge quantities of reagents, solvents, acids alkali, etc. which may be highly polluting the environments. So one way to comply with principles of Green chemistry to design alternative reaction methods which do not require hazardous solvents, chemicals or by-products. Some examples are being discussed here.



7.1 Polylactic acid polymerization process(PLA)

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 use in many applications including textiles and apparel, cutlery, and food packaging. The PLA process substitutes renewable materials for petroleum feedstocks, 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. In 2002, Cargill Dow (now NatureWorks) won the Greener Reaction Conditions Award for their **improved Polylactic acid polymerization process(PLA)**.

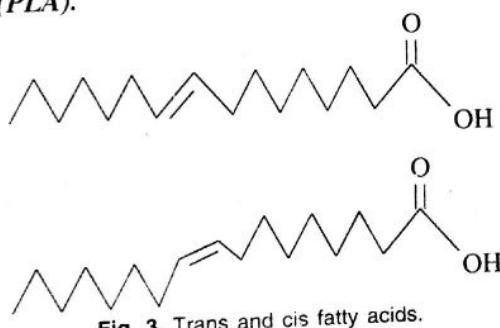


Fig. 3. Trans and cis fatty acids.

7.2 Enzyme interesterification process⁴

It is a clean, enzymatic process for the interesterification of oils and fats by interchanging saturated and unsaturated fatty acids. The result is commercially viable products without *trans*-fats. In addition to the human health benefits of eliminating *trans*-fats, the process has reduced the use of toxic chemicals and water, prevents vast amounts of by-products, and reduces the amount of fats and oils wasted.

7.3 Supramolecular chemistry

It is a technique to develop reactions which can proceed in the solid state without the use of solvents. The cycloaddition of *trans*-1,2-bis(4-pyridyl)ethylene is directed by resorcinol in the solid state is one such example. This solid-state reaction proceeds in the presence of UV light in 100% yield.

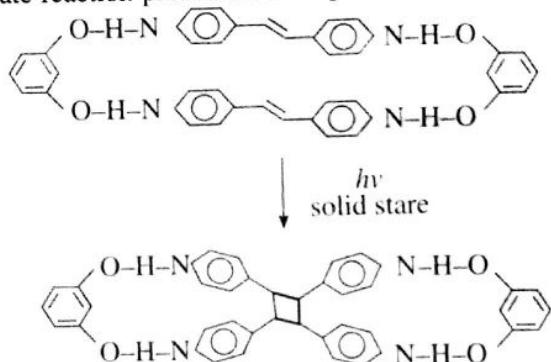
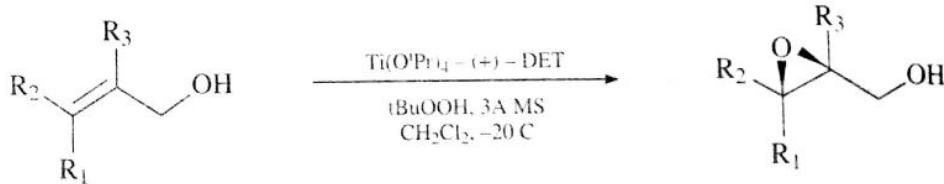


Fig. 4. Cycloaddition of *trans* - 1, 2 bits (4-pyridyl) ethylene.

7.4 Asymmetric synthesis



Asymmetric synthesis: Sharpless epoxidation

Asymmetric synthesis, also called **chiral⁵ synthesis**, **enantioselective synthesis** or **stereoselective synthesis**, is organic synthesis that introduces one or more new and desired elements of chirality. This is important in the field of pharmaceuticals because the different enantiomers or diastereomers of a molecule often have different biological activity. Kinetic resolution of racemic⁶ compounds is a familiar

⁴In 2005, Archer Daniels Midland (ADM) and Novozymes N.A. won the Greener Synthetic Pathways Award for their **enzyme interesterification process**. In response to the U.S. Food and Drug Administration (FDA) mandated labeling of trans-fats on nutritional information by January 1, 2006, Novozymes and ADM worked together to develop this process.

⁵The term **chiral** in general is used to describe an object that is non-superimposable on its mirror image. **Achiral** (not chiral) objects are objects that are identical to their mirror image. A **chiral molecule** is a type of molecule that lacks an internal plane of symmetry and thus has a non-superimposable mirror image. The feature that is most often the cause of chirality in molecules is the presence of an asymmetric carbon atom.

⁶Mixture of optical isomers

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method for the preparation of optically active compounds. However, an inevitable and critical drawback from the point of view of green chemistry is the **consequent wastage of half of the starting compound**. A catalytic asymmetric synthesis of 5-arylcyclohex-2-enones was developed starting from *racemic* 5-(trimethylsilyl)cyclohex-2-enone, which overcomes the drawback of kinetic resolution.

Approaches

There are three main approaches to asymmetric synthesis: (1) chiral pool synthesis (2) chiral auxiliaries (3) **asymmetric catalysis**. In practice, a mixture of all three is often used in order to maximize the advantages of each method.

Chirality must be introduced to the substance first. Then, it must be maintained. Care needs to be taken when planning the synthesis: The chirality might be removed by a chemical change that makes the substance isotropic. This process is called **epimerization**. For example, a S_N1 substitution reaction converts a molecule that is chiral by merit of non-planarity into a planar molecule, which has no handedness. In a S_N2 substitution reaction, on the other hand, the chirality inverts, *i.e.*, when you start with a right-handed mixture, you'll end up with left-handed one.

1. Chiral pool synthesis. Chiral pool synthesis is the easiest approach: A chiral starting material is manipulated through successive reactions using achiral reagents that retain its chirality to obtain the desired target molecule. This is especially attractive for target molecules having the similar chirality to a relatively inexpensive naturally occurring building-block such as a sugar or amino acid. However, the number of possible reactions the molecule can undergo is restricted, and tortuous synthetic routes may be required. Also, this approach requires a stoichiometric amount of the enantiopure starting material, which may be rather expensive if not occurring in nature, whereas chiral catalysis requires only a catalytic amount of chiral material.

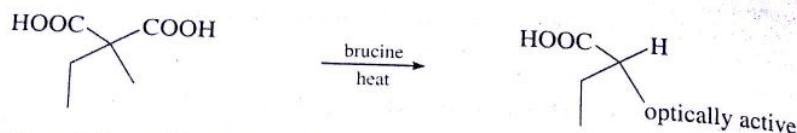
Asymmetric induction. What many strategies in chiral synthesis have in common is **asymmetric induction**. The aim is to make enantiomers into diastereomers, since diastereomers have different reactivity, but enantiomers do not. To make *enantiomers* into *diastereomers*, the reagents or the catalyst need to be incorporated with an enantiopure chiral center. The reaction will now proceed differently for different enantiomers, because the transition state of the reaction can exist in two diastereomers with respect to the enantiopure center, and these diastereomers react differently.

Asymmetric induction can also occur intramolecularly when given a chiral starting material. This chirality transfer can be exploited, especially when the goal is to make several consecutive chiral centers to give a specific enantiomer of a specific diastereomer. An aldol reaction, for example, is inherently diastereoselective: if the aldehyde is enantiopure, the resulting aldol adduct is diastereomerically and enantiomerically pure.

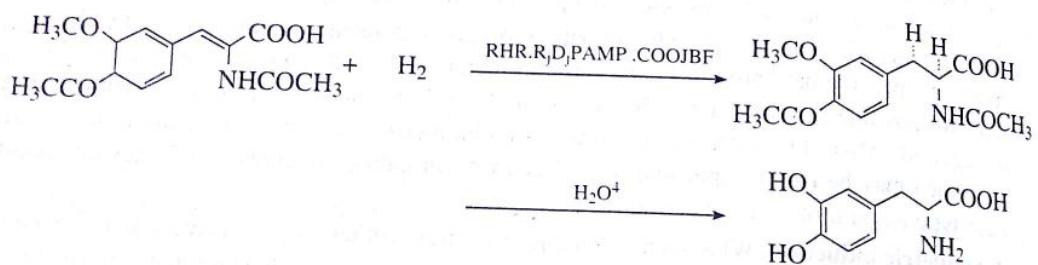
2. Chiral auxiliary. One asymmetric induction strategy is the use of a chiral auxiliary, which forms an adduct to the starting materials and physically blocks the other trajectory for attack, leaving only the desired trajectory open. Assuming the chiral auxiliary is enantiopure, the different trajectories are not equivalent, but diastereomeric. The auxiliary shares problems similar to protecting groups: like protecting groups, auxiliaries require a reaction step to add and another to remove, increasing cost and decreasing yield.

3. Asymmetric catalysis. The oldest asymmetric synthesis is the enantioselective decarboxylation of the malonic acid 2-ethyl-2-methylmalonic acid mediated by brucine (forming the salt) as reported

by Willy Marckwald in 1904: Small amounts of chiral, enantiomerically pure (or enriched) catalysts promote reactions and lead to the formation of large amounts of enantiomerically pure or enriched products.



Mostly, three different kinds of chiral catalysts are employed: (1) metal ligand complexes derived from chiral ligands (2) chiral organocatalysts (3) biocatalysts. The first methods were pioneered by William S. Knowles and Ryôji Noyori (Nobel Prize in Chemistry 2001). Knowles in 1968 replaced the achiral triphenylphosphine ligands in Wilkinson's catalyst by the chiral phosphine ligands P(Ph)(Me)(Propyl), thus creating the first asymmetric catalyst. This experimental catalyst was employed in an asymmetric hydrogenation with a modest 15% enantiomeric excess result. The methodology was ultimately used by him (while working for the Monsanto Company) in an asymmetric hydrogenation step in the industrial production of L-DOPA:



Examples of asymmetric catalysis include:

1. BINAP, a chiral phosphine, used in combination with compounds of ruthenium or rhodium. These complexes catalyse the hydrogenation of functionalised alkenes well on only one face of the molecule. This process also developed by Ryôji Noyori is commercialized as the industrial synthesis of menthol using a chiral BINAP-rhodium complex.
2. The other part of that Nobel prize concerned the Sharpless bishydroxylation.
3. Naproxen is synthesized with a chiral phosphine ligand in a hydrocyanation reaction.
4. Asymmetric catalytic reduction and oxidation.

Alternatives

Apart from asymmetric synthesis, racemic mixtures of compounds may be separated by various techniques in chiral resolution. Where the cost in time and money of making such racemic mixtures is low, or if both enantiomers may find use, this approach may remain cost-effective.

7.5 Supercritical water oxidation or SCWO

Supercritical water oxidation or SCWO is a process that occurs in water at temperatures and pressures above a mixture's thermodynamic critical point. Under these conditions water becomes a fluid with

⁶ The pioneer German University cause spontaneous

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unique properties that can be used to advantage in the destruction of hazardous wastes such as PCBs. The fluid has a density between that of water vapor and liquid at standard conditions, and exhibits high gas-like diffusion rates along with high liquid-like collision rates. In addition, the behavior of water as a solvent is altered (in comparison to that of subcritical liquid water) - *it behaves much less like a polar solvent*. As a result, the *solubility behavior is "reversed"* so that chlorinated hydrocarbons become soluble in the water, allowing single-phase reaction of aqueous waste with a dissolved oxidizer. The reversed solubility also causes salts to precipitate out of solution, meaning they can be treated using conventional methods for solid-waste residuals. Efficient oxidation reactions occur at low temperature (400-650 °C) with reduced NOx production.

SCWO can be classified as green chemistry or as a Clean Technology. The elevated pressures and temperatures required for SCWO are routinely encountered in industrial applications such as petroleum refining and chemical synthesis. A unique addition to the world of supercritical water (SCW) oxidation is generating high-pressure flames⁶ inside the SCW medium. These flames would cause instabilities to the system and its components.

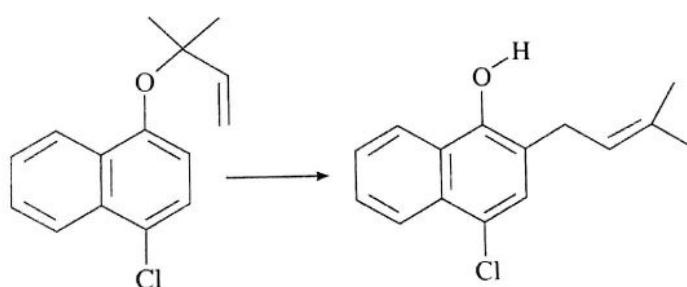
Applications of Supercritical water oxidation

SCWO in supercritical reactors is used to destroy hazardous wastes. Widespread commercial application of SCWO technology requires a reactor design capable of resisting fouling and corrosion under supercritical conditions.

SCWO technology for treatment of spent chemical catalysts to recover the precious metal.

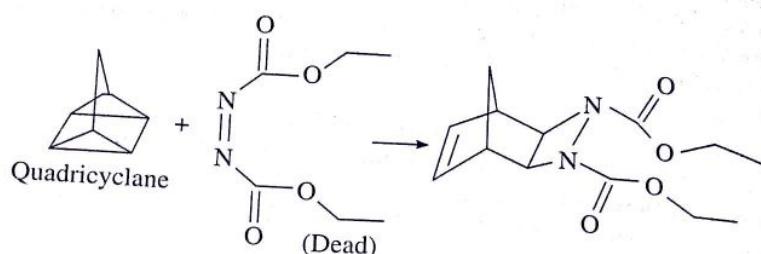
7.6 On water reaction

On water reactions are a group of organic reactions that *take place as an emulsion in water and accelerated* exhibit unusual as reaction rate compared to the same reaction in an organic solvent or compared to the corresponding dry media reaction. This effect has been known for many years but in 2005 researchers in the group of K. Barry Sharpless presented a systematic study into this phenomenon. In one typical example of this reaction at room temperature the chemical yield was found to be 100% **on water** after 120 hours compared to 16% with the same reaction in toluene or 73% in the neat reaction.



⁶ The pioneer works on high-pressure Supercritical Water Flames were carried out by professor EU Franck at the German University of Karlsruhe in the late 80s. The works were mainly aimed at anticipating conditions which would cause spontaneous generation of non-desirable flames in the flameless SCW oxidation process.

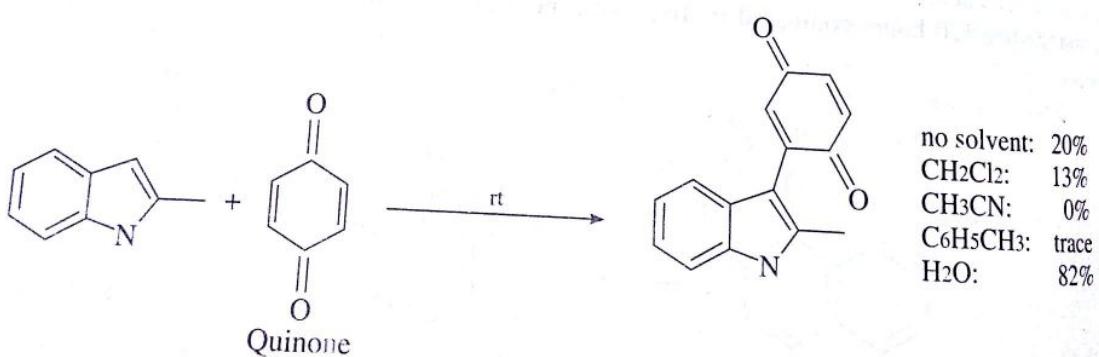
Enhanced reactivity is also found in cycloadditions⁷. The reaction of quadricyclane with diethyl azodicarboxylate DEAD is a $2\sigma + 2\sigma + 2\pi$ cycloaddition that on water takes place within 10 minutes at room temperature with 82% yield. The same reaction in toluene takes 24 hours at 80°C with 70% yield. An emulsion reaction in fluorinated cyclohexane takes 36 hours and the neat reaction takes even longer (48 hours).



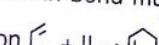
Other reactions with *apolar reactants* such as **Ene reactions** and **Diels-Alder**⁸ reactions also exhibit rate accelerations. It involves hydrogen bonding and the presence of a small amount of dissolved solute. This reaction type is of interest to green chemistry because it greatly reduces the usage of organic solvents, reaction product isolation is relatively easy, and it increases the yields and chemical purity with little extra expenditure, if not less.

Examples

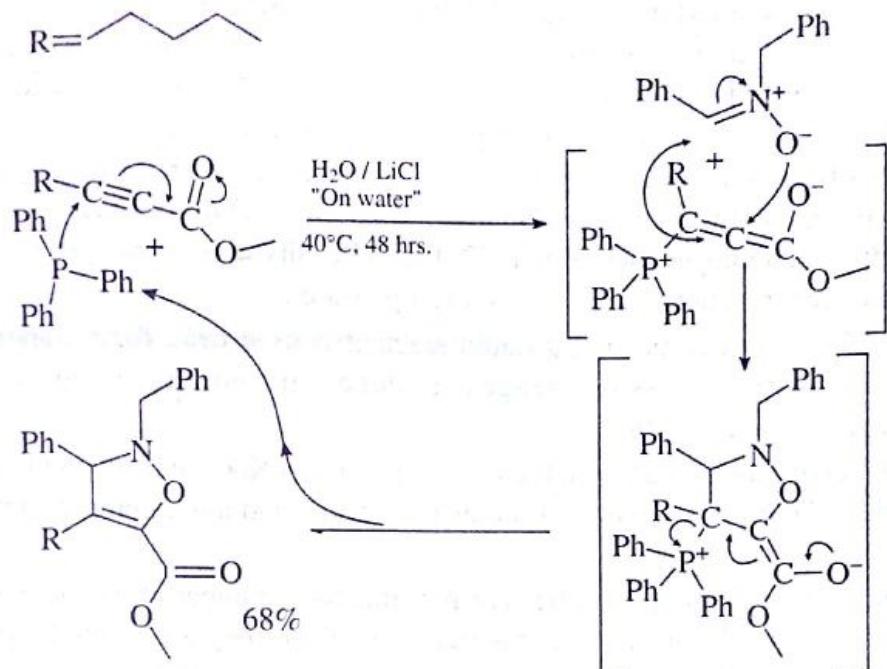
In one study a coupling reaction between an indole and a quinone takes place at room temperature without catalyst in water in 82% chemical yield even though reactants and products are insoluble in this medium. The reaction is much less efficient in homogeneous systems such as dichloromethane, toluene and acetonitrile or even the solvent free reaction or even the water reaction but now at 50°C.



⁷A cycloaddition is a pericyclic chemical reaction in which two or more unsaturated molecules combine with formation of cyclic adduct in which there is a net reduction in bond multiplicity.

⁸Diels-Alder reaction is diene + dinophile → cycloaddition 

The *On water* effect is also studied in cycloadditions of the type.



In this reaction the alkyne *methyl 2-octynoate* reacts with triphenylphosphine to an intermediate zwitterionic allenolate, a dipolarophile for the 1,3-dipole 2-phenylnitrone. The primary regioselective [3+2]dipolar cycloaddition product then rearranges to a -dihydroisoxazole with regeneration of the phosphine. This reaction only takes place in water with lithium chloride added even though the reactants do not dissolve in this medium. In organic solvents such as toluene or dichloromethane no reaction takes place.

7.7 Reaction in presence of water

An alternative classification with broader scope is suggested by Yujiro Hayashi as he describes certain organocatalytic Aldol reactions as taking place **in the presence of water**. The observed effect in these reactions is *not rate acceleration* (that would be *On Water*) but happens to be increase in *enantioselectivity*.

Biocatalysis & organocatalysis. Biocatalysis makes use of *enzymes* to effect chemical reagents stereoselectively. Some small organic molecules can also be used to help accelerate the desired reaction; this method is known as *organocatalysis*. If the organic molecule is chiral, it may react preferentially with the substrate of a certain chirality.

In the context of organocatalysis both concepts of on-water reactions and in-the-presence-of-water reactions have been criticized as not so environmentally friendly as separation of reaction product from the water phase usually requires organic solvent anyway and in reported aqueous systems the water phase can in reality be less than 10% of the total reaction mixture with another component forming the actual solvent. The observed rate-acceleration in presence of water is in fact due to water suppressing reaction deactivation.



7.8 Dry media reaction/reactions in solid phase

A **dry media reaction** or **solid-state reaction** or **solventless reaction** is a chemical reaction system in the absence of a solvent. Large number of reactions occurs in solid state without the solvent. These reactions are simple to operate, economical and solvent-related pollution is avoided. The drive for the development of dry media reactions in chemistry is (1) economics (save money on solvents), (2) ease of purification (no solvent removal post-synthesis), (3) high reaction rate (due to high concentration of reactants), (4) environmentally friendly (solvent is not required) and drawbacks to overcome are (1) reactants should mix to a homogeneous system, (2) high viscosity in reactant system, (3) unsuitable for solvent assisted chemical reactions. Some of the examples are :

In one type of solventless reaction a liquid reactant is used neat, for instance the reaction of, 1-bromonaphthalene with Lawesson's reagent is done with no added liquid solvent, but the 1-bromonaphthalene acts as a solvent.

A reaction which is closer to a true solventless reaction is a Knoevenagel condensation of ketones with (malononitrile) where a 1:1 mixture of the two reactants (and ammonium acetate) is irradiated in a microwave oven.

Colin Raston's research group have been responsible for a number of new solvent free reactions. In some of these reactions all the starting materials are solids, they are ground together with some sodium hydroxide to form a liquid, which turns into a paste which then hardens to a solid.

In another development the two components of an aldol reaction are combined together with the asymmetric catalyst S-proline in a ball mill in a mechanosynthesis. The reaction product has 97% enantiomeric excess.

8 DESIGN SYNTHESIS FOR ENERGY EFFICIENCY

Energy requirements of the chemical processes should be recognized for their environmental and economic impacts and should be kept to a minimum. Microwave ultrasonic radiations are used for green synthesis to reduce energy consumption.

8.1 Microwave radiation

Microwave radiations are the electromagnetic (300MHz-300GHz) radiations which work on the principles of **dipolar dielectric polarisation and conduction to offer clean, efficient, fast and economical synthesis**. These radiations are non-ionizing unlike others X-rays and gamma rays, do not alter the molecular structure while heating the compounds. The rapidly changing electric field affects the molecules which try to align themselves with changing field. In the process electromagnetic energy gets transformed into thermal energy. The ability of a material to convert electromagnetic to thermal energy depends on its dielectric constant *i.e.*, larger the constant larger is microwave coupling and more heating. The substance like water methanol, acetone etc. gets heated quickly, whereas CCl_4 , hexane etc. don't get heated. Microwave heating has advantages of being high speed, efficiency, uniformity, reduced wastage and low operating cost.

Reactions with microwave sources have been carried out in a solid support like clay, silica gel, etc. eliminating the use of solvents or with minimum amount of solvents. The reactions take place at a faster rate than thermal heating.

For example, Beckmann rearrangement⁹ of oximes in the solid state with microwave irradiation gave quantitative yields of the products without the use of acid catalysts. Current research is being directed into using commercial microwave ovens to provide the heat needed in the transesterification process in production of biofuels. The microwaves provide intense localized heating that may be higher than the recorded temperature of the reaction vessel. A continuous flow process producing 6 liters/minute at a 99% conversion rate has been developed and shown to consume only one-fourth of the energy required in the batch process. Although it is still in the lab-scale, development stage, the microwave method holds great potential to be an efficient and cost-competitive method for commercial-scale biodiesel production.

8.2 Ultrasonic radiation (Sonochemistry)

Ultrasound is a mechanical wave beyond the audible frequency range of 20Hz-16 KHz, i.e., frequency band of 16 KHz and above. These waves are high energy waves enhancing homogeneous effects and induction of new reaction. Unique selectivity and reactivity enhancement are real benefits of Ultrasonic waves.

Reactions using ultrasound energy are carried out at room temperature with excellent yields. For example, Ullmann's coupling (coupling reaction between aryl halides with copper) which takes place at higher temperature giving low yields by conventional method, gives increased yields at low temperature and in short duration with ultrasound energy. In the ultrasonic reactor method for production of biodiesel/biofuel, the ultrasonic waves cause the reaction mixture to produce and collapse bubbles constantly. This cavitation provides simultaneously the mixing and heating required to carry out the transesterification process. Thus using an ultrasonic reactor for biodiesel production drastically reduces the reaction time, reaction temperatures, and energy input. Hence the process of transesterification can run inline rather than using the time consuming batch processing. Industrial scale ultrasonic devices allow for the industrial scale processing of several thousand barrels per day.

Short Answer Questions

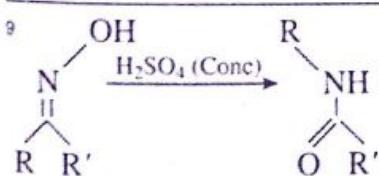
1. What is Green Chemistry?

Ans. Green chemistry, is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use and generation of hazardous substances.

2. What is the concept of atom economy?

Ans. Atom Economy is a concept that evaluates the efficiency of a chemical transformation, and is calculated as a ratio of the total mass of atoms in the desired product to the total mass of atoms in the reactants.

$$\% \text{ Atom Economy} = \frac{\text{No. of atoms incorporated}}{\text{No. of atoms in the reactants}} \times 100$$



An acid induced rearrangement of oxime to an amide.

