Semester-VI

16CHU603A GREEN CHEMISTRY 4H 4C

Instruction Hours/week: L:4 T:0 P:0 Marks: Internal:40 External: 60 Total:100

Programme objectives

1. To introduce the concept of Green chemistry, principles and designing a chemical synthesis.
2. To Understand the Energy requirements for reactions and using catalytic reagents.
3. To demonstrate Examples of Green Synthesis/ Reactions
4. To demonstrate some real world cases
5. To understand the future trends in green chemistry.

Programme outcome

The student

1. Knows the concept of Green chemistry, principles and designing a chemical synthesis.
2. Understands the Energy requirements for reactions and using catalytic reagents.
3. Understands about the Green Synthesis/ Reactions
4. Able to analyse some real world cases
5. Understand the future trends in green chemistry.

UNIT I

Introduction to Green Chemistry

What is Green Chemistry? Need for Green Chemistry.Goals of Green Chemistry.Limitations/ Obstacles in the pursuit of the goals of Green Chemistry

Principles of Green Chemistry and Designing a Chemical synthesis

Twelve principles of Green Chemistry with their explanations and examples and special emphasis on the following: Designing a Green Synthesis using these principles; Prevention of Waste/ byproducts; maximum incorporation of the materials used in the process into the final products ,Atom Economy, calculation of atom economy of the rearrangement, addition, substitution and elimination reactions. Prevention/ minimization of hazardous/ toxic products reducing toxicity.risk = (function) hazard × exposure; waste or pollution prevention hierarchy. Green solvents– supercritical fluids, water as a solvent for organic reactions, ionic liquids, fluorous biphasic solvent, PEG, solventless processes, immobilized solvents and how to compare greenness of solvents.

UNIT II

Energy requirements for reactions – alternative sources of energy: use of microwaves and ultrasonic energy. Selection of starting materials; avoidance of unnecessary derivatization – careful use of blocking/protecting groups. Use of catalytic reagents (wherever possible) in preference to stoichiometric reagents; catalysis and green chemistry, comparison of heterogeneous and homogeneous catalysis, biocatalysis, asymmetric catalysis and photo catalysis. Prevention of chemical accidents designing greener processes, inherent safer design, principle of ISD “What you don’t have cannot harm you”, greener alternative to Bhopal Gas Tragedy (safer route to carcarbaryl) and Flixiborough accident (saferroute to cyclohexanol) subdivision of ISD, minimization, simplification, substitution, moderation and limitation. Strengthening/ development of analytical techniques to prevent and minimize thegeneration of hazardous substances in chemical processes.

UNIT III
Examples of Green Synthesis/ Reactions and some real world cases

1. Green Synthesis of the following compounds: adipic acid, catechol, disodiumimino diacetate (alternative to Strecker synthesis)
2. Microwave assisted reactions in water: Hofmann Elimination, methyl benzoate to benzoic acid, oxidation of toluene and alcohols; microwave assisted reactions in organic solvents Diels-Alder reaction and Decarboxylation reaction
3. Ultrasound assisted reactions: sonochemical Simmons-Smith Reaction (Ultrasonic alternative to Iodine)
4 Surfactants for carbon dioxide – replacing smog producing and ozone depleting solvents with CO_2 for precision cleaning and dry cleaning of garments.
5 Designing of Environmentally safe marine antifoulant.

UNIT IV
1. Rightfit pigment: synthetic azopigments to replace toxic organic and inorganic pigments.
2 An efficient, green synthesis of a compostable and widely applicable plastic (polylactic acid) made from corn.
3 Healthier fats and oil by Green Chemistry: Enzymatic interesterification for production of no Trans-Fats and Oils
4 Development of Fully Recyclable Carpet: Cradle to Cradle Carpeting

UNIT V
Future Trends in Green Chemistry
Oxidation reagents and catalysts; Biomimetic, multifunctional reagents; Combinatorial green chemistry; Proliferation of solventless reactions; co crystal controlled solid state synthesis(C_2S_3); Green chemistry in sustainable development.

Suggested Readings
Text Books:

1. Ahluwalia, V.K. & Kidwai, M.R. (2005).*New Trends in Green Chemistry*, Anamalaya Publishers.
2. Anastas, P.T. & Warner, J.K.(1998).*Green Chemistry - Theory and Practical*. Oxford University Press.
3. Matlack, A.S. (2001).*Introduction to Green Chemistry*. Marcel Dekker.
4. Cann, M.C. & Connely, M.E.(2000).*Real-World cases in Green Chemistry*. Washington: American Chemical Society.

Reference Books:

1. Ryan, M.A. & Tinnes and, M. (2002). *Introduction to Green Chemistry*. Washington: American Chemical Society.

2. Lancaster, M. (2010).*Green Chemistry: An Introductory Text.* 2nd Edition. RSC Publishing.

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LECTURE PLAN
DEPARTMENT OF CHEMISTRY

STAFF NAME: Dr. S.RAVI
SUBJECT NAME: Green Chemistry SUB.CODE:16CHU603A
SEMESTER: V CLASS: III B.Sc (CHEMISTRY)

S.No.	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos
		UNIT-I	
1	1	What is Green Chemistry? Need for Green Chemistry.Goals of Green Chemistry.Limitations/ Obstacles in the pursuit of the goals of Green Chemistry	T1: 1-5
2	1	Twelve principles of Green Chemistry with their explanations and examples	T1: 5-15
3	1	Designing a Green Synthesis using these principles; Prevention of Waste/ byproducts;	T1: 2-5
4	1	maximum incorporation of the materials used in the process into the final products	T1:5-8
5	1	Atom Economy, calculation of atom economy of the rearrangement, addition, substitution and elimination reactions.	T1:5-8
6	1	Prevention/ minimization of hazardous/ toxic products reducing toxicity.risk = (function) hazard × exposure; waste or pollution prevention hierarchy.	T1:8-9
7	1	Green solvents– supercritical fluids, water as a solvent for organic reactions, ionic liquids, fluorous biphasic solvent, PEG, solventless processes, immobilized solvents and how to compare greenness of solvents.	T1:232-240
8	1	Recapitulation	
	Total No of Hours Planned For Unit 1=08		
		UNIT-II	
1	1	Energy requirements for reactions – alternative sources of energy: use of microwaves and ultrasonic energy.	T1:59-66

2	1	Selection of starting materials; avoidance of unnecessary derivatization – careful use of blocking/protecting groups. Use of catalytic reagents (wherever possible) in preference to stoichiometric reagents;	T1:1-3
3	1	catalysis and green chemistry, comparison of heterogeneous and homogeneous catalysis, biocatalysis, asymmetric catalysis and photo catalysis.	T1:27-36
4	1	Prevention of chemical accidents designing greener processes, inherent safer design, principle of ISD "What you don't have cannot harm you", greener alternative to Bhopal Gas Tragedy (safer route to carcarbaryl) and Flixiborough accident (saferroute to cyclohexanol)	T3:6-10
5	1	subdivision of ISD, minimization, simplification, substitution, moderation and limitation.	
6	1	Strengthening/ development of analytical techniques to prevent and minimize the generation of hazardous substances in chemical processes.	
7	1	Recapitulation	
	Total No of Hours Planned For Unit II=07		
		UNIT-III	
1	1	Green Synthesis of the following compounds: adipic acid, catechol, disodiumimino diacetate (alternative to Strecker synthesis)	T1:242-242
2	1	Microwave assisted reactions in water: Hofmann Elimination, methyl benzoate to benzoic acid,	T1:61-63
3	1	oxidation of toluene and alcohols; microwave assisted reactions in organic solvents Diels-Alder reaction and Decarboxylation reaction	T1:62-65
4	1	Ultrasound assisted reactions: sonochemical Simmons-Smith Reaction (Ultrasonic alternative to Iodine)	T1:73-78
5	1	Surfactants for carbon dioxide – replacing smog producing and ozone depleting solvents with CO_2 for precision cleaning and dry cleaning of garments.	T1:253-255; T3:210-229
6	1	Designing of Environmentally safe marine antifoulant.	T1:255-256

7	1	Recapitulation	
	Total No of Hours Planned For Unit III=07		
		UNIT-IV	
1	1	Examples of Green Synthesis/ Reactions and some real world cases	T2:1-83
2	1	Rightfit pigment: synthetic azopigments to replace toxic organic and inorganic pigments.	T2:53-63
3	1	An efficient, green synthesis of a compostable and widely applicable plastic (polylactic acid) made from corn.	T2:1-9
4	1	Healthier fats and oil by Green Chemistry:	T2:9-17
5	1	Enzymatic interesterification for production of no Trans-Fats and Oils	T2:9-17
6	1	Development of Fully Recyclable Carpet: Cradle to Cradle Carpeting	T2:77-83
7	1	Recapitulation	
	Total No of Hours Planned For Unit IV=07		
		UNIT-V	
1	1	Oxidation reagents and catalysts	T1:29-33
2	1	Biomimetic, multifunctional reagents	T3:51-53
3	1	Combinatorial green chemistry	T3:118-120
4	1	Proliferation of solventless reactions	T3: 201-229
5	1	co crystal controlled solid state synthesis(C_2S_3)	T1:189-211
6	1	Green chemistry in sustainable development.	T3: 361-365
7	1	Recapitulation	
8	1	Discussion of previous year end semester question papers	
9	1	Discussion of previous year end semester question papers	
10	1	Discussion of previous year end semester question papers	
	Total No of Hours Planned for unit V=10		
Total Planned Hours	**39**		

Text Books:

1. Ahluwalia, V.K. & Kidwai, M.R. (2005).*New Trends in Green Chemistry*, Anamalaya Publishers.
2. Cann, M.C. & Connely, M.E.(2000).*Real-World cases in Green Chemistry*. Washington: American Chemical Society.
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UNIT I

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Green chemistry

1. The term *green chemistry* was coined by Paul Anastas in 1991.
2. It is also called as sustainable chemistry
3. It 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.
4. Green chemistry seeks to reduce and prevent pollution at its source.
5. Green chemistry applies to organic chemistry, inorganic chemistry, biochemistry, analytical Chemistry, and even physical chemistry.
6. It seems to focus on industrial applications. The focus is on minimizing the hazard and maximizing the efficiency of any chemical choice.

Difference between Green chemistry and Enviornmental chemistry

EnvironmentalChemistry is the chemistry of the natural environment, and of pollutant chemicals in nature, It does apply to any chemistry. It is distinct from environmental chemistry which focuses on chemical phenomena in the environment.

Recent key developments in green chemistry:

1. Use of supercritical carbon dioxide as green solvent,
2. Use of aqueous hydrogen peroxide for clean oxidations
3. Use of hydrogen in asymmetric synthesis.
4. On water reactions, and
5. Dry media reactions.

Definition of Green Chemistry

Green Chemistry is defined as the design of chemical products and processes that reduce and/or eliminate the use and/or the generation of hazardous substances.

This approach requires an open and interdisciplinary view of material and product design, applying the principle that it is better to consider waste prevention options during the design and development phase, rather than disposing or treating waste after a process or material has been developed.

Through a principle-based approach, green chemistry results in increased efficiency, reduced hazards and the elimination of waste.

The symptoms of good product design

Designing safer, economical, and efficacious processes and products.

All of these aspects can result in economic benefit for institutions that implement these practices. Green Chemistry offers a concrete path to achieve sustainable and safe laboratory practices.

What is Sustainability

Sustainability is most commonly defined as:

"Development that meets the needs of the present without compromising the ability of future generations to meet their own needs."

It's about innovative and environmentally sustainable products that compete in a global economy. It's about achieving the highest standards of safety, health and environmental stewardship. It's about being responsible to our customers, our employees, the community and our planet.

Nobel Prize for Green Chemistry

The 2005 Nobel Prize for Chemistry was awarded for "the development of the metathesis method in organic synthesis,"

The Nobel Prize Committee states that, "this represents a great step forward for 'green chemistry', reducing potentially hazardous waste through smarter production. Metathesis is an example of how important basic science has been applied for the benefit of man, society and the environment."

Tools used in the Green Chemistry

1. Avoiding hazardous materials

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 toxic hydrocarbons have also been used as CFC replacements, but they present their own problems.

Dow Chemical discovered that **supercritical carbon dioxide** works well as a blowing agent, without the need for hazardous substances, allowing the polystyrene to be more easily recycled.

The CO_2 used in the process is reused from other industries, so the net carbon released from the process is zero.

For this in 1996, Dow Chemical won the 1996 Greener Reaction Conditions award.

2. Reneawable raw materials

a. **Polylactic acid Polymerization process**.

Lactic acid is produced by fermenting corn and converted to lactide, using tin-catalyzed cyclization.

The polymer, is used in textiles, cutlery, and food packaging.

The process substitutes renewable materials for petroleum feedstocks, doesn't require the use of hazardous organic solvents, and results in a high-quality polymer that is recyclable and compostable.

In 2002, Nature Works won the Greener Reaction Conditions Award for their improved

polylactic acid polymerization process.

b. **Production and downstream applications of bio-based succinic acid.**

Succinic acid is a platform chemical that is an important starting material in the formulations of everyday products.

Traditionally, succinic acid is produced from petroleum-based feedstocks.
BioAmber has developed a technology that produces succinic acid from the fermentation of renewable feedstocks at a lower cost and lower energy expenditure than the petroleum equivalent while sequestering CO_2 rather than emitting it.
In 2011, the Outstanding Green Chemistry Accomplishments by a Small Business Award went to BioAmber Inc.

3. Reduction of waste products

Enztyme interesterification process.

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(For the human health benefits)

The process has reduced the use of toxic chemicals and water, prevents vast amounts of byproducts, and reduces the amount of fats and oils wasted.

In 2005, Novozymes was awarded the Greener Synthetic Pathways Award

5. Catalyst

Converting waste glycerin from biodiesel production to propylene glycol.

Through the use of a copper-chromite catalyst he was able to lower the required temperature of conversion while raising the efficiency of the distillation reaction.

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, was awarded the Academic Award

6. Microwave Oven

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 irradated in a microwave oven.

7. Selection of solvents

Ionic liquids

The choice of solvent is the main component of a reaction system by volume (approx. 90%).

Chlorinated solvents should be avoided, as many of these solvents are toxic and volatile, and are implicated in the destruction of the ozone layer.

Alternative solvents include ionic liquids, for example, which are non-volatile and can provide non-aqueous reaction media of varying polarity.

Ionic liquids have significant potential, since if systems can be developed in which the products can be removed by extraction or distillation and the catalyst remains in the ionic liquid.

The solvent and the catalyst can be reused.

Water as a solvent

The solvent of choice for green chemistry is water, which is a non-toxic liquid but with limited chemical compatibility.

The Diels-Alder Reaction are often even accelerated when run in an aqueous medium, while on the other hand, many reactants and reagents, including most organometallic compounds, are totally incompatible with water.

Supercritical CO_2 medium

Chemical reactions run under neat conditions (no solvent) and in a supercritical CO_2 medium can also be considered as green choices.

Green Chemistry

A traditional concept in process chemistry has been the optimization of the Reaction time and yield.

From our modern perspective, this limited viewpoint must be enlarged,

For example

1. toxic wastes can destroy natural resources.

2. Many feedstocks for the production of chemicals are based on petroleum, which is not a renewable resource.

In order to address the following points :

1.What alternatives can be developed and used.

2. we must ensure that future generations can also use these new alternatives.

3. "Sustainability" is a concept that is used to distinguish methods and processes that can ensure the long-term productivity of the environment, so that even subsequent generations of humans can live on this planet. Sustainability has environmental, economic, and social dimensions.
Paul Anastas of the U.S. Environmental Protection Agency formulated some simple rules of thumb for how sustainability can be achieved in the production of chemicals - the "Green chemical principles":

The 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.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
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.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

7. A raw material or feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Reduce derivatives - Unnecessary derivatization (blocking group, protection/ deprotection, temporary modification) should be avoided whenever possible.
9. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
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.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
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.

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

It is most appropriate to carry out a synthesis by following a pathway so that formation of waste is minimum or absent. One type of waste product common and often avoidable is the starting material or reagent that remains unreacted. The well known saying “Prevention is better than cure should be followed”.

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

If one mole of the starting material produces one mole of the product, the yield is 100 %. However, such a synthesis may generate significant amount of waste or by product which is not visible in the above calculation. Such a synthesis, even though gives 100% yield, is not considered to be green synthesis. In order to find, if a particular reaction is green, the concept of atom economy was developed by Berry Trost of Stanford University. This considers the amount of stating materials incorporated into the desired final product. Thus by incorporation of greater amounts of the atoms contained in the starting materials (reactants) in to the formed products, fewer waste by products are obtained. In this way, using the concept of atom economy along with ideas of selectivity and yield, “greener” more efficient synthesis can be developed. The atom economy for a reaction can be calculated using the following equation:

$$\text{Percent atom economy} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weights of all reactants}} \times 100\%$$

To illustrate the benefits of atom economy, consider the synthesis of ibuprofen.In the former process, developed in the 1960s, only 40% of the reactant atoms were incorporated into the desired ibuprofen product; the remaining 60% of the reactant atoms found their way into unwanted by-products or waste that required disposal .The new method requires fewer reaction steps and recovers 77% of the reactant atoms in the desired product. This ‘green’ process eliminates millions of pounds of waste chemical by-products every year, and it reduces by millions of pounds the amount of reactants needed to prepare this widely used analgesic.

3. Whenever practicable synthetic methodologies should be designed to use and generate a substance that poses little or no toxicity to human health and the environment.

Wherever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment. Redesigning existing transformations to incorporate less hazardous materials is at the heart of Green Chemistry.

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

The designing of safer chemical is now possible since there have been great advances in the understanding of chemical toxicity. It is now fairly understood that a correlation exist between chemical structure e.g. presence of functional groups and the existence of toxic effects. The idea is to avoid the functionality related to the toxic effect. Chemical properties of a molecule, such as water solubility, polarity etc. so that they can manipulate molecules to the desired effects.

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

An auxiliary substance is one that helps in manufacture of a substance, but does not become an integral part of the chemical. Such substances are used in the manufacture, processing at every step. Major problem with many solvents is their volatility that may damage human health and the environment. Even processes like recrystalisation require energy and substances to change the solubility. The problem of solvents has been overcome by using such solvents which do not pollute the environment. Such solvents are known as green solvents. Examples include liquidcarbon dioxide (supercritical CO2), ionic liquid water. Even reactions have been conducted in solid state. For example the condensation reaction of orthoesters with ophenylenediamines in presence of KSF clay under solvent free conditions using microwave.

Many solvents used in traditional organic synthesis are highly toxic. The Green Chemistry approach to the selection of solvents has resulted in several strategies. One method that has been developed is to use supercritical carbon dioxide as a solvent .Supercritical carbon dioxide is formed under conditions of high pressure in which the gas and the liquid phases of carbon dioxide combine to a single –phase compressible fluid that becomes an environmentally benign solvent (temperature 31oC, 7280 kPa, or 72 atmospheres). Supercritical CO2 has remarkable properties .It behaves as a material whose properties are intermediate between those of a solid and those of a liquid .The properties cab be controlled by manipulating temperature and pressure .Supercritical CO2 is environmentally benign because of its low toxicity and easy recyclability.
Carbon dioxide is not added to the atmosphere; rather, it is removed from the atmosphere for use in chemical processes. It is used as a medium to carry out a large number of reactions that would otherwise have many negative environmentalconsequences. It is even possible to perform stereoselective synthesis in supercritical CO2.

Some reactions can be carried out in ordinary water, the most green solvent possible. Recently, there has been much success in using near-critical water at higher temperatures where water behaves more like an organic solvent .Eckert and Liotta were able to run Friedel-Crafts reactions in near –critical water without the need for the acid catalyst AlCl3, which is normally used in large amounts in these reactions. In the past 5 years, many new ionic liquids have been developed with a broad range of properties. By selecting the appropriate ionic liquid, it is now possible to carry out many types of organic reactions in these solvents. In some reactions, a well –designed ionic solvent can lead to better yields under milder conditions than is possible with traditional solvents.

Another approach to making organic chemistry greener involves the way in which a reaction is carried out ,rather than in the selection of starting material, reagents, or solvents. Microwave technology can be used in some reactions to provide the heat energy required to make the transformation go to completion .With microwave technology ,reactions can take place with less toxic reagents and in ashorter time, with fewer side reactions, all goals of Green Chemistry. Microwave technology has also been used to create supercritical water that behaves more like an organic solvent and could replace more toxic solvents in carrying out organic reactions.

Another Green Chemistry approach is the use of a catalyst which facilitates transformations without the catalyst being consumed in the reaction and without being incorporated in the final product. Therefore, use of catalyst should be preferred whenever possible.

6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized.

Energy generation, as we know has a major environmental effect. The requirement of energy can be kept to a base minimum in certain cases by the use of a catalyst. For example in conversion of benzyl chloride into benzyl cyanide if we use phase transfer catalyst, the conversion goes to completion in a very short time.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} + \text{aq } KCN \longrightarrow \underset{\text{Benzyl cyanide}}{C_6H_5CH_2CN} + KCl$$

Conventionally, we have been carrying reaction by heating on wire gauze, in oil bath or heating mantels. It is now possible that the energy to a reaction can be supplied by using microwaves, by sonication or photo chemically. Simple examples are,

$$\text{(a)}\quad C_6H_5CONHC_6H_5 \xrightarrow[\text{MW,12 MINS}]{} C_6H_5COOH$$

$$\text{(b)}\quad RCOOH + ROH \xrightarrow[H_2SO_4,\text{Ultrasound}]{\text{Esterification}} RCOOR$$

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

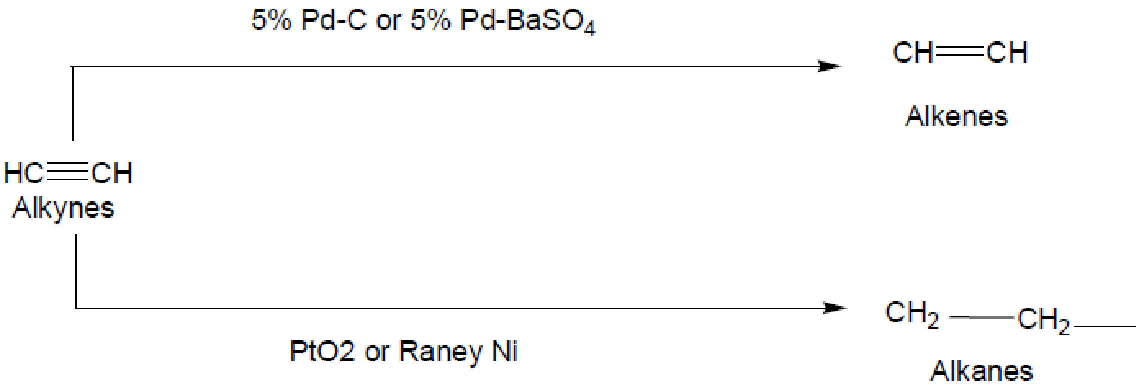
Non reversible or depleting sources can exhausted by their continual use. So these are not regarded as sustainable from environmental point of view. The starting materials which are obtained agricultural or biological processes are referred to as renewable starting materials. Substances like carbon dioxide (generated from natural sources or synthetic routes like fermentation etc) and methane gas (obtained from natural sources such as marsh gas, natural gas etc) are available in reasonable amounts and so are considered as renewable starting material. Methane, a constituent of biogasand natural gas can easily be converted into acetylene by partial combustion. Acetylene is a potential source of number of chemicals such as ethyl alcohol, acetaldehyde, vinyl acetate etc.

8. Unnecessary derivatization (blocking group, protection, deportation, temporary modification of physical/chemical processes) should be avoided whenever possible.

A commonly used technique in organic synthesis is the use of protecting or blocking group. These groups are used to protect a sensitive moiety from the conditions of the reaction, which may make the reaction to go in an unwanted way if it is left unprotected. This procedure adds to the problem of waste disposal.

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

The catalyst as we know facilitates transformation without being consumed or without being incorporated into the final product. Catalysts are selective in their action in that the degree of reaction that takes place is controlled, e.g. mono addition v/s multiple addition. A typical example is that reduction of triple bond to a double bond or single bond.



In addition to the benefits of yield and atom economy, the catalysts are helpful in reducing consumption of energy. Catalysts carry out thousands of transformation before being exhausted.

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.

It is extremely important that the products designed to be synthesized should be biodegradable. They should not be persistent chemicals or persistent bio accumulators. It is now possible to place functional groups in a molecule that will facilitate its biodegradation. Functional groups which are susceptible to hydrolysis, photolysis or other cleavage have been used to ensure that products will be biodegradable. It is also important that degradation products do not possess any toxicity and detrimental effects to the environment. Plastic, Pesticides (organic halogen based) are examples which pose to environment.

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

Methods and technologies should be developed so that the prevention or minimization of generation of hazardous waste is achieved. It is necessary to have accurate and reliable reasons, monitors and other analytical methodologies to assess the hazardous that may be present in the process stream. These can prevent any accidents which may occur in chemical plants.

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

The occurrence of accidents in chemical industry must be avoided. It is well known that the incidents in Bhopal (India) and Seveso (Italy) and many others have resulted in the loss of thousands of life. It is possible sometimes to increase accidents potential inadvertently with a view to minimize the generation of waste in order to prevent pollution. It has been found that in an attempt to recycle solvents from a process (for economic reasons) increases the potential for a chemical accident or fire.

Green chemistry & Pollution

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal. Green chemistry is also known as sustainable chemistry.

Green chemistry:

- Prevents pollution at the molecular level
- Is a philosophy that applies to all areas of chemistry, not a single discipline of chemistry
- Applies innovative scientific solutions to real-world environmental problems
- Results in source reduction because it prevents the generation of pollution
- Reduces the negative impacts of chemical products and processes on human health and the environment
- Lessens and sometimes eliminates hazard from existing products and processes
- Designs chemical products and processes to reduce their intrinsic hazards

How green chemistry differs from cleaning up pollution

Green chemistry reduces pollution at its source by minimizing or eliminating the hazards of chemical feedstocks, reagents, solvents, and products.

This is unlike cleaning up pollution (also called remediation), which involves treating waste streams (end-of-the-pipe treatment) or cleanup of environmental spills and other releases. Remediation may include separating hazardous chemicals from other materials, then treating them so they are no longer hazardous or concentrating them for safe disposal. Most remediation activities do not involve green chemistry. Remediation removes hazardous materials from the environment; on the other hand, green chemistry keeps the hazardous materials out of the environment in the first place.

If a technology reduces or eliminates the hazardous chemicals used to clean up environmental contaminants, this technology would qualify as a green chemistry technology. One example is replacing a hazardous sorbent [chemical] used to capture mercury from the air for safe disposal with an effective, but nonhazardous sorbent. Using the nonhazardous sorbent means that the hazardous sorbent is never manufactured and so the remediation technology meets the definition of green chemistry.

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Green chemistry's 12 principles

These principles demonstrate the breadth of the concept of green chemistry:

1. Prevent waste: Design chemical syntheses to prevent waste. Leave no waste to treat or clean up.

2. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. Waste few or no atoms.

3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to either humans or the environment.

4. Design safer chemicals and products: Design chemical products that are fully effective yet have little or no toxicity.

5. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If you must use these chemicals, use safer ones.

6. Increase energy efficiency: Run chemical reactions at room temperature and pressure whenever possible.

7. Use renewable feedstocks: Use starting materials (also known as feedstocks) that are renewable rather than depletable. The source of renewable feedstocks is often agricultural products or the wastes of other processes; the source of depletable feedstocks is often fossil fuels (petroleum, natural gas, or coal) or mining operations.

8. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

9. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are effective in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and carry out a reaction only once.

10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

11. Analyze in real time to prevent pollution: Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. Minimize the potential for accidents: Design chemicals and their physical forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Twelve principles of green chemistry bookmarks

Download a one-sided or two-sided bookmark showing the twelve principles of green chemistry.

Green chemistry's roots in the Pollution Prevention Act of 1990

To stop creating pollution in the first place became America's official policy in 1990 with the Federal Pollution Prevention Act .

The law defines **source reduction** as any practice that:

- Reduces the amount of any hazardous substance, pollutant, or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment, or disposal.
- Reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants.

The term "source reduction" includes:

- Modifications to equipment or technology
- Modifications to process or procedures
- Modifications, reformulation or redesign of products
- Substitution of raw materials
- Improvements in housekeeping, maintenance, training, or inventory control

Section 2 of the Pollution Prevention Act establishes a pollution prevention hierarchy, saying:

- The Congress hereby declares it to be the national policy of the United States that pollution should be prevented or reduced at the source whenever feasible;
- Pollution that cannot be prevented should be recycled in an environmentally safe manner, whenever feasible;
- Pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; an
- Disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner.

Green chemistry aims to design and produce cost-competitive chemical products and processes that attain the highest level of the pollution-prevention hierarchy by reducing pollution at its source.

- Less toxic to organisms

- Less damaging to ecosystems
- Not persistent or bioaccumulative in organisms or the environment
- Inherently safer to handle and use because they are not flammable or explosive

For those who are creating and using green chemistry, the hierarchy looks like this:

- Source Reduction and Prevention of Chemical Hazards
- Designing chemical products to be less hazardous to human health and the environment*
- Making chemical products from feedstocks, reagents, and solvents that are less hazardous to human health and the environment*
- Designing syntheses and other processes with reduced or even no chemical waste
- Designing syntheses and other processes that use less energy or less water
- Using feedstocks derived from annually renewable resources or from abundant waste
- Designing chemical products for reuse or recycling
- Reusing or recycling chemicals
- Treating chemicals to render them less hazardous before disposal
- Disposing of untreated chemicals safely and only if other options are not feasible

*Chemicals that are less hazardous to human health and the environment are:

Risk is the probability that **exposure** to a **hazard** will lead to a negative consequence, or more simply, a **hazard** poses no **risk** if there is no **exposure** to that **hazard**. **Risk**can be defined as the likelihood or probability of a given **hazard** of a given level causing a particular level of **loss** of damage
Hazard is the potential of a substance to cause damage
– Toxicity is the hazard of a substance which can cause poisoning
• Risk is a measure of the probability that harm will occur under defined conditions of exposure to a chemical
– If there can be no exposure to a chemical, no matter how dangerous (hazardous) it may be, there is no risk of harm

The relation of risk to hazard may be expressed as;
– $R = f (H \times E) = f (H \times D \times t)$ – Where R is risk, f is function of, H is hazard, E is exposure, D is dose and t is time

Thus, chemicals which pose only a small hazard but to which there is frequent or excessive exposure may pose as much risk as chemicals which have a high degree of hazard but to which only limited exposure occurs.

Reducing risk is based on reducing exposure

- For example, some chemicals, such as pesticides, needed for food production may be fairly toxic, but their use may cause little or no risk to those who use them if exposure is kept low by using no more than is needed.
- However, many people have suffered illness as a result of careless use of pesticides
- All pesticides must be stored and handled with care and precautions taken to prevent exposure of people, pets, or animals that we do not wish to harm.

Designing a Green synthesis using these principles: prevention of waste/ byproducts

- An ideal reaction is
- Is Simple.
- Is Safe.
- Has a High Yield and Selectivity.
- Is Energy Efficient.
- Uses Renewable and RecyclableReagents and Raw Materials.

There are a wide range of things that need to be considered when designing a chemical reaction, including alternative raw materials, solvents, reaction pathways and reaction conditions (which will be discussed further in this chapter). The design of a chemical reaction can become quite tedious, specially when attempting to minimize or eliminate it's environmental impact. The given criteria (on the slide) for an ideal chemical reaction should all be considered, but it can become extremely difficult to match all points, therefore the goal is to optimize the balance of the criteria. In this chapter, we will discuss how to best tackle this task.

This is a brief qualitative description of different equations that can be used to determine alternative reaction pathways. In order to assess the equations more, a semi-quantitative approach can be taken, using atom and math efficiency. These techniques and other tools will be discussed further along in the module. Also, an example of each possible alternative reaction pathway is given below.

Addition(A + B----- AB)

No waste needs to be treated because the reaction is direct.

Addition reactions incorporate the starting materials into the final product and, therefore, do not produce waste that needs to be treated, disposed of, or otherwise dealt with.

The addition of HX to an alkene is an organic reaction in chemistry where HX, or a halogen sigma bonded to a hydrogen atom, adds to the carbon-carbon double bond of an alkene following Markovnikov's rule (Markovnikov's rule is observed).

The general chemical formula of the reaction is as follows:

C=C + HX ----------- H-C-C-X

Substitution (AB + C ----- AC + B)

Necessarily generates stoichiometric quantities of substances as byproducts and waste that are not part of the target molecule.

Substitution reactions, necessarily generate stoichiometric quantities of substances as byproducts and waste

In chemistry, Nucleophilic Substitution is a type of chemical reaction in which one nucleophile (electron donor) replaces another as a covalent substituent of some atom. In the examples given here, the nucleophilic atom is carbon.

An example of nucleophilic substitution is the hydrolysis of an alkyl bromide, R-Br, under alkaline conditions, where the "attacking" nucleophile is hydroxide ion, OH-:

R-Br + OH ---------- R-OH + Br-

The bromide ion, Br-, is said to be the leaving group.

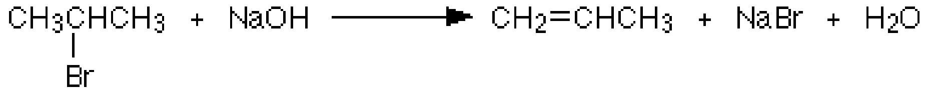
Elimination(AB----- A + B)

Does not require other substances, but does generate stoichiometric quantities of waste that are not part of the final target molecule.

Elimination reactions do not require input of materials during the course of the reaction other than initial input of a starting materials, but they do generate stoichiometric quantities of substances that are not part of the final target molecule.

Halogenoalkanes also undergo Elimination Reactions in the presence of sodium or potassium hydroxide.

The 2-bromopropane has reacted to give an alkene - propene.

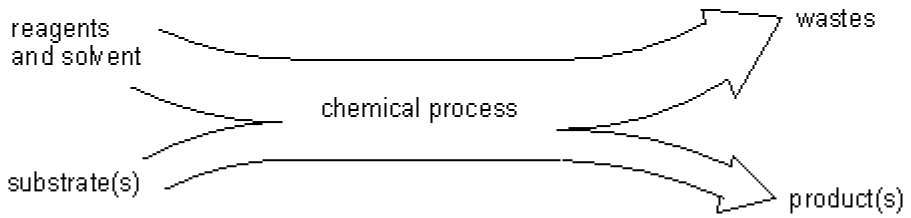


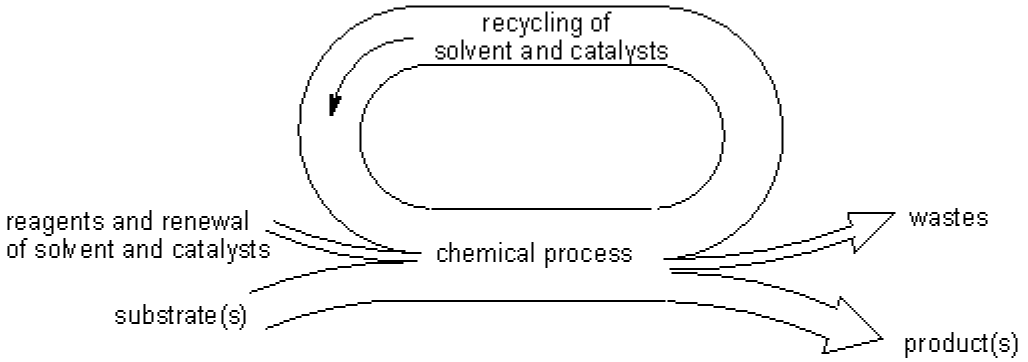
$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 + NaOH \longrightarrow CH_2{=}CHCH_3 + NaBr + H_2O$$

Notice that a hydrogen atom has been removed from one of the end carbon atoms together with the bromine from the centre one. In all simple elimination reactions the things being removed are on adjacent carbon atoms, and a double bond is set up between those carbons.

Evaluating chemical reactions according to their yield

A typical chemical process generates products and wastes from raw materials such as substrates, solvents and reagents. If most of the reagents and the solvent can be recycled, the mass flow looks quite different:





Thus, the prevention of waste can be achieved if most of the reagents and the solvent are recyclable. For example, catalysts and reagents such as acids and bases that are bound to a solid phase can be filtered off, and can be regenerated (if needed) and reused in a subsequent run. In the production of chemical products on very large scale, heterogeneous catalysts and reagents can be kept stationary while substrates are continuously added and pass through to yield a product that is continuously removed (for example by distillation).

The mass efficiency of such processes can be judged by the E factor (Environmental factor):

$$\textbf{E factor} = \frac{\textbf{Mass of wastes}}{\textbf{Mass of product}}$$

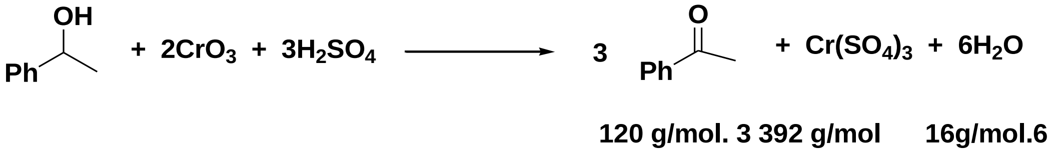
Whereas the ideal E factor of 0 is almost achieved in petroleum refining, the production of bulk and fine chemicals gives E factors of between 1 and 50. Typical E factors for the production of pharmaceuticals lie between 25 and 100. Note that water is not considered in this calculation, because this would lead to very high E factors. However, inorganic and organic wastes that are diluted in the aqueous stream must be included. Sometimes it is easier to calculate the E factor from a different viewpoint, since accounting for the losses and exact waste streams is difficult:

$$\textbf{E factor} = \frac{\textbf{Mass of raw materials - Mass of product}}{\textbf{Mass of product}}$$

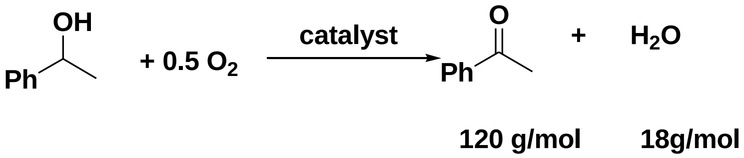
In any event, the E factor and related factors do not account for any type of toxicity of the wastes. Such a correction factor (an “unfriendliness” quotient, Q) would be 1 if the waste has no impact on the environment, less than 1 if the waste can be recycled or used for another product, and greater than 1 if the wastes are toxic and hazardous. Such discussions are at a very preliminary stage, and E factors can be used directly for comparison purposes as this metric has already been widely adopted in the industry.

Another attempt to calculate the efficiency of chemical reactions that is also widely used is that of atom economy or efficiency. Here the value can be calculated from the chemical equation:

$$\textbf{atom efficiency} = \frac{\textbf{molecular weight of desired product}}{\textbf{molecular weight of all substances formed}}$$



$$\text{atom efficiency} = \frac{3.120}{3.120 + 392 + 6.18} = 42\%$$



$$\text{atom efficiency} = \frac{120}{120 + 18} = 87\%$$

Atom efficiency is a highly theoretical value that does not incorporate any solvent, nor the actual chemical yield.

An experimental atom efficiency can be calculated by multiplying the chemical yield with the theoretical atom efficiency.

Anyway, the discussion remains more qualitative than quantitative, and does not yet quantify the type of toxicity of the products and reagents used.

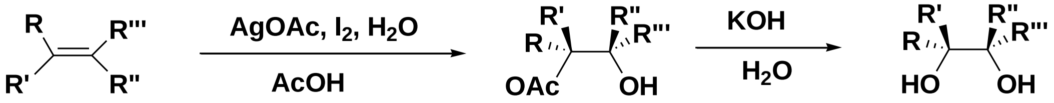
Still, atom economy as a term can readily be used for a direct qualitative description of reactions.

Considering specific reactions, the development of green methods is focused on two main aspects:

1. choice of solvent, and

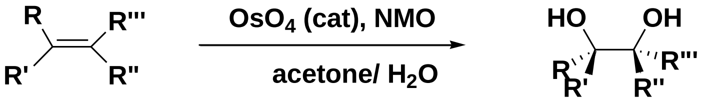
2. the development of catalyzed reactions.

Example: The development of catalyzed reactions for dihydroxylations have made possible the replacement of the Woodward Reaction in the manufacture of steroids, in which huge amounts of expensive silver salts were used and produced, and thus had become an economic factor:



Woodward Reaction

The Woodward reaction can be replaced through the use of stoichiometric quantities of OsO_4, but osmium tetroxide is both very toxic and very expensive, making its use on a commercial scale prohibitive. Only in its catalytic variant, which employs *N*-methylmorpholine-*N*-oxide as the stoichiometric oxidant and catalytic quantities of OsO_4, can this be considered a green reaction that can be used on industrial scale.



Upjohn Dihydroxylation

Some systems have already been reported in which H_2O_2 is used to reoxidize the *N*-methylmorpholine, allowing this material also to be used in catalytic amounts. Considering the atom efficiency using H_2O_2 as the terminal oxidant, H_2O as the stoichiometric byproduct is much better than *N*-methylmorpholine. Notably, catalytic systems are available in which the osmium catalyst is encapsulated in a polyurea matrix or bound to a resin, so that the catalyst can be more easily recovered and reused. An additional advantage of such polymer-bound catalysts is the avoidance of toxic transition metal impurities, for example in pharmaceutical products.

Industrial chemists evaluate synthetic routes and their associated economic and evironmental costs by calculating the relative efficiency of the chemicalreactions involved. Percentage yield provides a means of comparison of thetheoretical and actual quantity of product, and historically has been the main means of evaluating reaction efficiency. More recently, however, calculation of ‘atom economy’ has become a more important means of comparing the efficiency of chemical reactions.

The concept of ‘atom economy’ was developed by Professor Barry Trost at Stanford University and derives from the principles of ‘green chemistry’.Green chemistry is the design of chemical products/processes that reduce or eliminate the use or generation of hazardous substances.

Historically, the chemical industry responded to environmental legislation by treatment, rather than prevention of waste. However, with waste treatment costs becoming increasingly economically unviable, chemical manufacturers are being forced to consider the economic benefits of applying the principles of green chemistry. Atom economy is a measure of the proportion of reactant atoms which are incorporated into the desired product of a chemical reaction. Calculation of atom economy therefore also gives an indication of the proportion of reactant atoms forming waste products. Chemists commonly calculate percentage yield (Equation 1) to ascertain the efficiency of a particular reaction.

Equation I

$$\% \text{ Yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

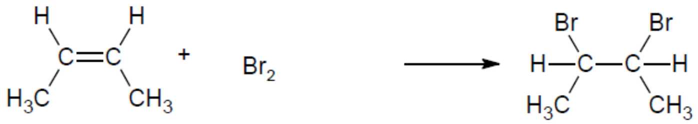
Using this strategy, a reaction proceeding with 100% yield of desired productis deemed to be perfectly efficient. However, calculation of percentage yieldprovides no information about the extent to which unwanted products areformed in the reaction pathway. In the chemical industry there are manyexamples of highly ‘efficient’ reactions that generate waste far greater inmass and volume than the desired product. With the inadequacies of calculating percentage yield clearly established,Trost developed an equation for atom economy

$$\boxed{\% \text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100}$$

13,000 tonnes per annum of the painkiller Ibuprofen have been produced since its introduction in the 1980s. Initially, Boots used a six-step production process with an overall atom economy of just 40.1%. In the 1990s the Hoechst Celanese Corporation (in collaboration with Boots) developed a new, improved three-stage process to producing Ibuprofen with an atom economy of 77.4%. This improvement in atom economy resulted in a reduction in the quantity of unwanted by-products, and therefore in significant environmental and economic cost savings. The atom economy of a reaction depends on the reagents used and the type of chemical reaction involved.

Most chemical reactions can be classified as rearrangement (eg migration of an alkyl group), addition (Example 1),substitution (eg chlorination of methane) or elimination (eg dehydration).Rearrangement and addition reactions are atom economical by their very nature, since they simply involve reactant atoms being repositioned within the same molecule or incorporated within a second molecule. Substitution reactions, however, involve replacement of one group with another and therefore have intrinsically poor atom economy. Elimination reactions (Example 2) are also inherently atom uneconomical since eliminated atoms are always lost as waste. In developing an atom economical reaction pathway, therefore, the industrial chemist may well prefer rearrangement and addition reactions over less environmental friendly substitution and elimination reactions.

Example 1: Addition reaction – halogenation of an alkene



(Z)-but-2-ene	Bromine	2,3-dibromobutane
C_4H_8	Br_2	$C_4H_8Br_2$
1mol	1mol	1mol
(12 x 4) + (8 x 1)	2 x 79.9	(12 x 4) + (8 x 1) + (79.9 x 2)
= 56g	= 159.8g	= 215.8g

Total mass of reactants = 56 g + 159.8 g = 215.8 g
(Note: Product mass is also 215.8 g)

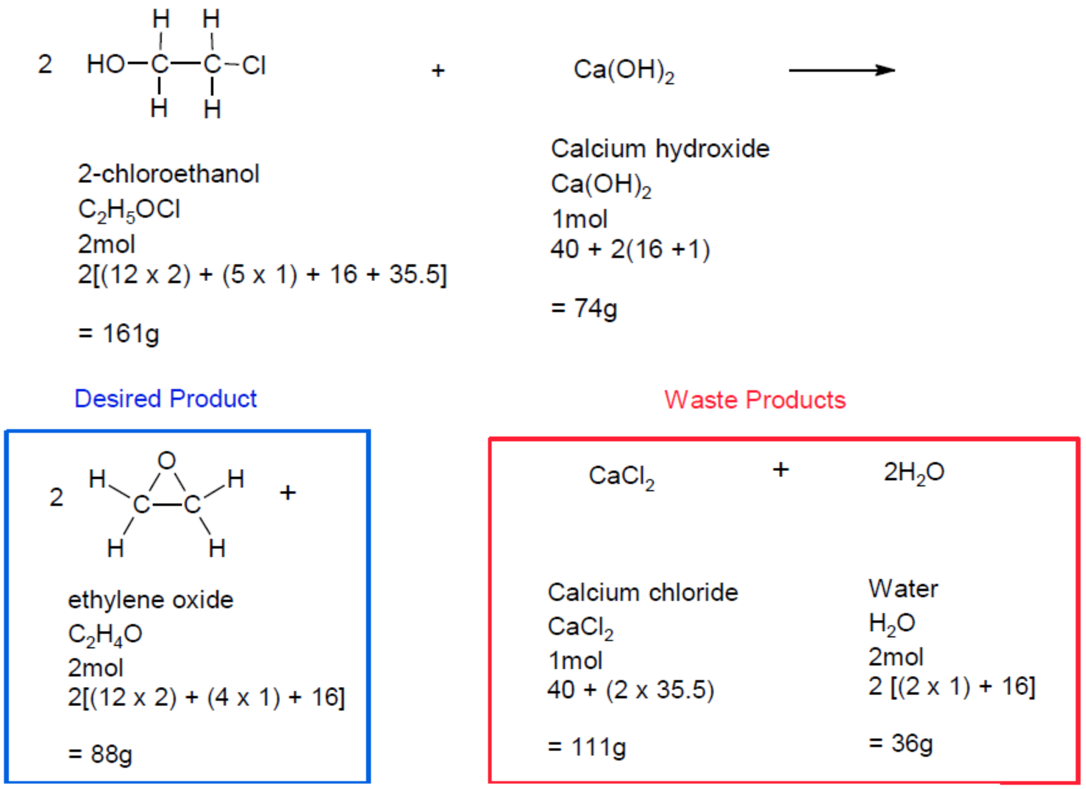
Mass of desired product (2,3-dibromobutane) = 215.8 g

$$\boxed{\%\text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100}$$

$$\%\text{ atom economy} = \frac{215.8}{215.8} \times 100 = \mathbf{100\%}$$

This process is 100% atom efficient, with all the reactant atoms included within the desired product.

Example 2: Elimination reaction



2-chloroethanol
C_2H_5OCl
2mol
2[(12 x 2) + (5 x 1) + 16 + 35.5]

= 161g

Calcium hydroxide
$Ca(OH)_2$
1mol
40 + 2(16 +1)

= 74g

Desired Product

ethylene oxide
C_2H_4O
2mol
2[(12 x 2) + (4 x 1) + 16]

= 88g

Waste Products

Calcium chloride
$CaCl_2$
1mol
40 + (2 x 35.5)

= 111g

Water
H_2O
2mol
2 [(2 x 1) + 16]

= 36g

Total mass of reactants = 161 g + 74 g = 235 g
(Note: Total product mass = 235 g)

Mass of desired product ethylene oxide = 88 g

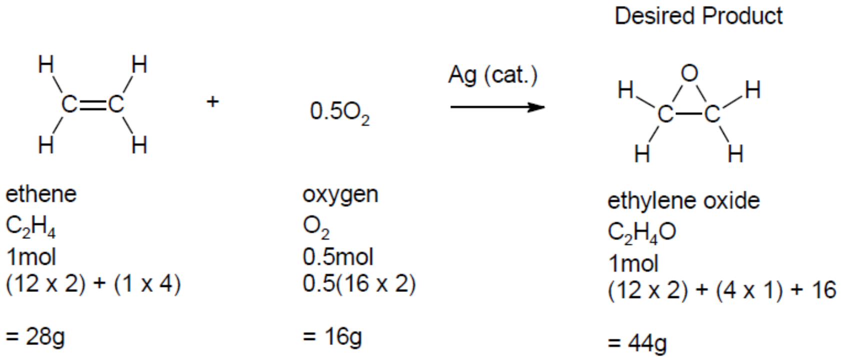
$$\text{\% atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100$$

$$\text{\% atom economy} = \frac{88}{235} \times 100 = \mathbf{37.4\%}$$

This elimination reaction is therefore only 37.4% atom efficient, with the remaining 62.6% in the form of unwanted waste products (calcium chloride and water).

Catalysts have a crucial role in improving the atom economy of chemical reactions. They allow the development of more effective synthetic reaction routes, which produce fewer waste products, and can be recovered and reused time and again. Catalysts also allow reactions to be run at lower temperature, reducing energy costs. The dramatic effect of a catalyst on improving atom economy is illustrated in Example 3. The introduction of a silver catalyst into the ethylene oxide production process in Example 2 improves the atom economy of the reaction from 37.4% to 100%. Although the silver catalyst is initially costly, it can be reused many times in the process.

Example 3: Use of catalyst in ethylene oxide production



Total mass of reactants = 28 g + 16 g = 44 g
(Note: Total product mass = 4 4g)

Mass of desired product ethylene oxide = 44 g

$$\boxed{\%\text{ atom economy} = \frac{\text{Mass of desired product(s)}}{\text{Total mass of reactants}} \times 100}$$

$$\%\text{ atom economy} = \frac{44}{44} \times 100 = \mathbf{100\%}$$

Atom economical approaches have become increasingly popular in the last decade due to the rising cost of raw materials (particularly petrochemicals)and increasing awareness of environmental concerns. Energy consumption, raw material costs, the nature of waste products/pollutants and the value of the final of product are also factors that will influence the selection of a particular synthetic route.

Why Are Reactions Performed Using Solvents?

• To dissolve reactants. • To slow or increase the rate of reactions. • To act as a heat sink or heat transfer agent. • To prevent hot spots and run-away reactions

Issues with Organic Solvents

• Organic solvents are of concern to the chemical industry because of the sheer volume used in synthesis, processing, and separation. • Organic solvents are expensive • Organic solvents are highly regulated. • Many organic solvents are volatile, flammable, toxic, and carcinogenic.

Solvent alternatives

A. Use of solventless reactions B. Use of “non-organic” solvents C. Processing technology

Advantages to Solventless Organic Reactions

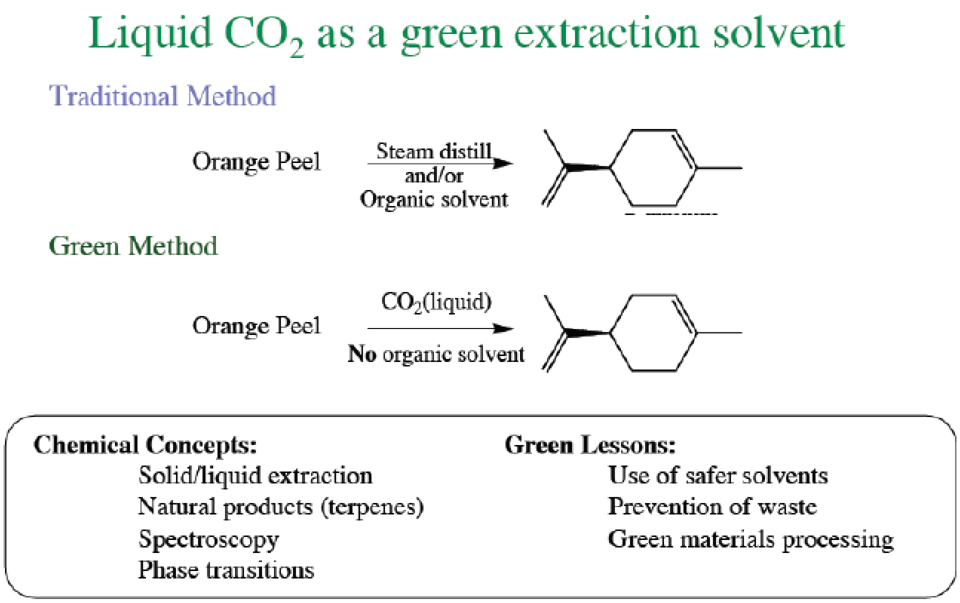
• There is no reaction medium to collect, purify, and recycle. • Reaction times can be dramatically shortened. • Lowered energy usage. • Considerable reduction in batch size volume. • Less expensive

Ways to be Solvent-Free

• Neat – reagents react together in the liquid phase in the absence of a solvent. • Solid-state synthesis – two macroscopic solids interact directly and form a third, solid product without the intervention of a liquid or vapor phase.

Use of non-organic solvents

• Liquid and supercritical CO 2 • Ionic liquids • Fluorous Phase Chemistry • Water



Liquid CO_2 as a green extraction solvent

Traditional Method

Orange Peel $\xrightarrow[\text{Organic solvent}]{\text{Steam distill and/or}}$

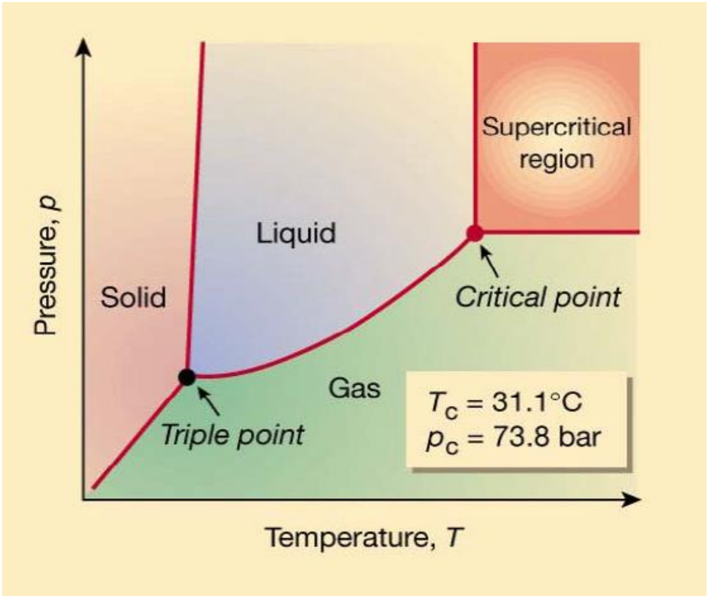
Green Method

Orange Peel $\xrightarrow[\text{No organic solvent}]{CO_2\text{(liquid)}}$

Chemical Concepts:
Solid/liquid extraction
Natural products (terpenes)
Spectroscopy
Phase transitions

Green Lessons:
Use of safer solvents
Prevention of waste
Green materials processing

Supercritical CO2
• What does it mean to be supercritical



Properties of scCO2

- Combination of properties from both theliquid and gas state.
- At liquid-like densities, scCO2 exhibits lowviscosity and high diffusion rates.
- High compressibility of the supercritical phase allows for solvent properties to be varied by small changes in temperature and pressure.

Properties of scCO2

- Can be handled in standard high-pressure equipment on lab or industrial scale.
- Non-toxic, non-flammable, and inexpensive.
- Non-protic and generally unreactive.
- Product isolation to total dryness is achieved by simple decompression.
- CO2 can be recovered and reused.

Commercial Applicationsof scCO2

- Natural product extraction (decaffeination)
- Polymer synthesis
- Dry cleaning

Examples of scCO2 as Solvent inSynthetic Organic Chemistry

- Hydrogenation
- Hydroformylation
- Photochemical and radical reactions
- Dies-Alder cycloadditions
- Oxidations
- Palladium mediated couplings
- Biotransformations

Limitations of scCO2

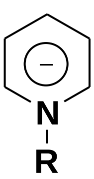
- Poor solubility of many substrates in scCO2.
- Modifiers (organic solvents) can be added to regulate solubility, but this move the process away from being green.
- CO2-philic surfactants are being developed.

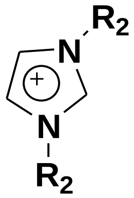
– Are expensive and have to be separated fromproducts.

Ionic Liquids

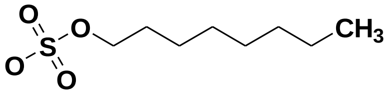
- Organic salts with melting points below100°C, often below room temperature.

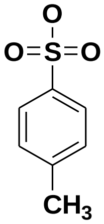
$[NR_xH_{4-x}]^+$ $[PR_xH_{4-x}]^+$

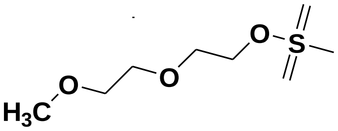




Alkylammonium, alklyphosphonium, N-alkykpyridinium, and N,N'-dialkylimidazolium cations







Octyl sulphate, 2-(2-methoxyethoxy)ethyl sulphate, and tosylate anions

BF_4^- PF_6^- SbF_6^- $CH_3CO_2^-$ HSO_4^- NO_3^- NO_2^- $AlCl_4^-$

Properties of IonicLiquids

- Good solvents for a wide range of both organic and inorganic materials.
- Have potential to be highly polar yet noncoordinating.

- By varying cations and anions, ionic liquids can be tailored for specific applications.
- Possibility for reaction rate enhancement, higher selectivity and higher yields.

Properties of IonicLiquids

- High thermal stability
- Often immiscible with organic solventsand/or water
- No measurable vapor pressure
- Non-flammable
- Can be recycled
- Are they safer than solvents?

Ionic liquids have been used as solvents in a variety of reactions

- Heck Reaction
- Friedel-Crafts reactions
- Diels-Alder reactions
- Hydrogenation reactions

Other Applications of Ionic Liquids

- As biphasic systems in combination withorganic solvent or water in extraction and separation technologies.
- For catalyst immobilization and recycling.
- As electrolytes in electrochemistry

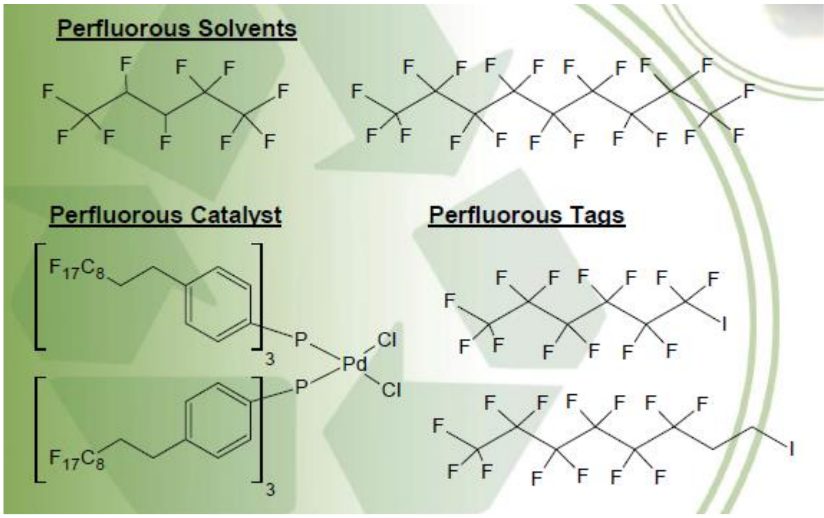
Limitations of Ionicl iquids

- Very expensive compared to organic solvents (100 to 1000 x).
- Have to be made, often using solvent.
- Products have to be extracted from ionic liquid using solvent.
- May have to wash with water prior to reuse.

Fluorous PhaseChemistry

- What does it mean to be “fluorous”?

- What does it mean to be “perfluorinated”?



Physical Properties of PerfluorinatedOrganic Compounds

- High affinity for other fluorinated compounds.
- High solubility in scCO2.
- Immiscible in water and most common organicsolvents at room temperature.
- Forms homogenous solutions at elevatedtemperatures with many of these solvents.
- Chemically inert.

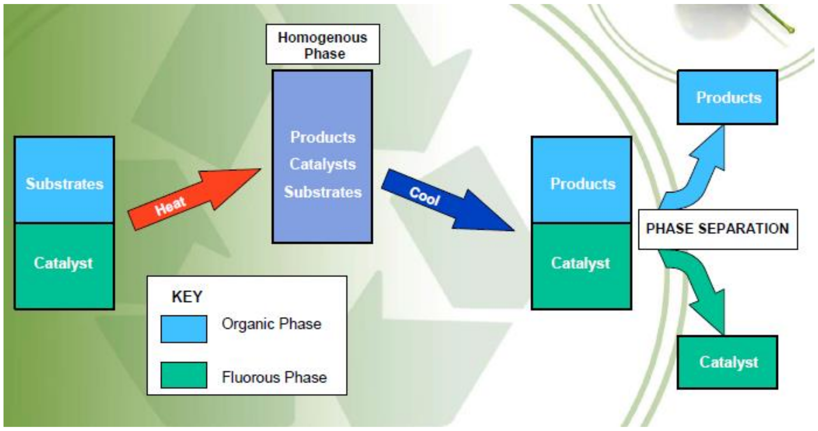
– Is this good or bad?

Uses for Fluorous Chemistry

- For the recovery and recycling of fluorouscatalysts and fluorous reagents.

- Fluorous biphasic organic synthesis.

Principle of fluorous biphasic catalysis



Advantages

- Facile recovery of expensive catalysts.
- Complementary to other biphase chemistries.
- More facile separation.
- Design of novel catalysts and reagents.
- Alternative to the solid phase in combinatorial chemistry.
- Non-toxic?

Limitations

- Fluorous solvents and reagents are very expensive.
- 60% fluorine is usually considered the lower cut off point for efficient fluorous extraction.
- Still requires use of a second solvent for biphase.

Water as a solvent

The solvent of choice for green chemistry is water, which is a non-toxic liquid but with limited chemical compatibility.

The Diels-Alder Reaction are often even accelerated when run in an aqueous medium, while on the other hand, many reactants and reagents, including most organometallic compounds, are totally incompatible with water.

Water as a solvent is not only inexpensive & environmentally benign but also shows completely different reactivity to Organic solvents. Organic reactions in water are varied and have many applications such as, in the synthesis of biologically active compounds from carbohydrates & the chemical modification of biomolecules.

Aqueous reactions could be the answer to the future of organic chemistry. The types of organic reactions in water are broad including pericyclic reactions, reaction of carbanion& carbocation equivalents, reactions of radicals &carbenes, transition-metal catalyses and oxidations-reductions.

The upside of Water as a green solvent are a) Non toxic (liquid + vapour), b) Non flammable, c) Abundantly available (better availability than organic solvent in less developed countries), d) Inexpensive.

The downside are a) Corrosion, b) Heat sink, c) High boiling point {Water-based reactions are energy intensive}, d) Solubility of organic matter is generally poor, e) Reaction range is narrower than organic solvents, f) A vital resource to be conserved & protected {100 litres of water is needed to dye 1 Kg of fibre} and g) Expands when freezes.

Most of the world’s chemistry occur in aqueous media

Diels-Alder reactions
Claisen-rearrangement
Aldol reactions
Allylation reactions
Oxidations
Hydrogenations

• Cost - water is the world’s cheapest solvent. • Safety – doesn’t get any safer than water. • Some reactions work better in water.

Limitations of Water as a Solvent

• Some reactions will never work in water.

• Poor solubility of most organic compounds.

• Solubility may be increased by use of organic co-solvents, pH control, surfactants, and hydrophilic auxiliaries.

The product may need to be extracted into an organic solvent to purify it. • This generates aqueous effluent containing solvent, which must be properly disposed.

Processing Principles

Greenness through technology

- Goal is to minimize the number of effluent streams generated and the quantity of each stream.

- Organic solvents are not necessarily bad.

Loss of Greenness

Anytime water is used in an organic reaction, an additional waste stream is created. • Solvent • Aqueous quench / workup • Aqueous wash

Green Process

A purely organic solvent-based process (with solvent-based workup), with solvent recovery, would generate little waste. • The use of technology and good environmental practices to reduce VOCs.

Benefits of Organic Solvents

- Cheap relative to ionic liquids and fluorous solvents.

- Volatile – it takes less energy to remove solvents by evaporation.

- Solvents can be recycled by distillation, creating little waste.

- Regulated – Most countries already have industrial requirements limiting the release of VOCs.
- Chemistry is known.

Chemical reactions used to manufacture important compounds such as medicinals are essentially always carried out in solution, and this is also true of the research work that is used to invent the new compounds and to develop appropriate ways to manufacture them. In the past, continuing into the present, the solvents used are normally volatile organic compounds (VOCs), and these pose an environmental problem. Their vapors can contribute to the greenhouse effect that causes global warming, and in some cases the solvent vapors can catalyze the destruction of the ozone layer that protects the Earth and its living inhabitants from short-wavelength ultraviolet solar radiation. The vapors may also be toxic to humans, plants, or animals, or they may cause diseases. The liquids themselves can be a problem. If they are released into the earth, rivers or the ocean, they can cause direct environmental damage, while also slowly releasing their vapors. In principle, the solvents can be completely captured and purified for reuse during manufacturing, but it is difficult to prevent some loss to the environment. Hence there is interest in using environmentally benign liquids as the solvents in chemical reactions. One possibility is supercritical carbon dioxide, which is a liquid under pressure and which has attractive solvent properties. However, unless it is completely contained and reused, it will release gaseous carbon dioxide, a greenhouse gas. Thus interest has increasingly turned to water as the solvent for chemical reactions. Water is the solvent in which biochemical reactions are performed in Nature, and it is environmentally benign. However, it is a good solvent only for organic chemicals that have polar groups, such as alcohols and carboxylic acids. This may not be an insuperable problem. Over 20 years ago we reported that the special selectivities seen in water solution (see below) were also seen in some water suspensions, where one soluble component reacted with one that was poorly soluble. We pointed out that such suspensions in water could well be generally more practical ways to use water in manufacturing. Recently, Sharpless and co-workers described a remarkable acceleration of a reaction in such a suspension, which they called reactions ON water. The large reported rate effect was seen in only one particular case, but even without a large acceleration the selectivities that we describe below could perhaps make suspensions in water a practical way for the environmentally benign properties of water to be generally useful even with insoluble reaction components. One industry that has switched from VOCs to water is the paint industry. We are all familiar with the water-based paints that no longer emit strong solvent odors, and these have been widely adopted for painting automobiles, for instance. It is essentially impossible to capture all the solvent vapors that are released when a vehicle is spray painted, but when the solvent is water there is no problem. Water is not simply an environmentally benign solvent; it has special properties that are essentially unique, related to what is called the hydrophobic effect. This is the tendency for hydrocarbons or molecules with hydrocarbon components to avoid contact with water, and to associate instead with other hydrocarbon species in water. This is what makes aqueous soap solutions dissolve grease, and it is the driving force in biology for the associations that produce cell membranes, and that cause nucleic acids to form the famous double helix. It drives the folding of proteins into their shapes in enzymes and antibodies, and it also promotes the binding of biological substrates into enzymes and antibodies. As described below, the hydrophobic effect has now been used to mimic biological chemistry and to provide remarkable selectivities in the field called biomimetic chemistry. It has even been used to permit the discovery of the geometries of the transition states for some interesting reactions, information that is otherwise inaccessible.

Supercritical CO_2 medium

Chemical reactions run under neat conditions (no solvent) and in a supercritical CO_2 medium can also be considered as green choices.

Major problem with many solvents is their volatility that may damage human health and the environment. Even processes like recrystalisation require energy and substances to change the solubility. The problem of solvents has been overcome by using such solvents which do not pollute the environment. Such solvents are known as green solvents. Examples include liquid carbon dioxide (supercritical CO2), ionic liquid water. Even reactions have been conducted in solid state. For example the condensation reaction of orthoesters with phenylenediamines in presence of KSF clay under solvent free conditions using microwave. Many solvents used in traditional organic synthesis are highly toxic. The Green Chemistry approach to the selection of solvents has resulted in several strategies. One method that has been developed is to use supercritical carbon dioxide as a solvent .Supercritical carbon dioxide is formed under conditions of high pressure in which the gas and the liquid phases of carbon dioxide combine to a single – phase compressible fluid that becomes an environmentally benign solvent (temperature 31oC, 7280 kPa, or 72 atmospheres). Supercritical CO2 has remarkable properties .It behaves as a materialwhose properties are intermediate between those of a solid and those of a liquid .Theproperties cab be controlled by manipulating temperature and pressure .SupercriticalCO2 is environmentally benign because of its low toxicity and easy recyclability.

Carbon dioxide is not added to the atmosphere; rather, it is removed from the atmosphere for use in chemical processes. It is used as a medium to carry out a large number of reactions that would otherwise have many negative environmental consequences. It is even possible to perform stereoselective synthesis in supercritical CO2.

Some reactions can be carried out in ordinary water, the most green solvent possible. Recently, there has been much success in using near-critical water at higher temperatures where water behaves more like an organic solvent .Eckert and Liotta were able to run Friedel-Crafts reactions in near –critical water without the need for the acid catalyst AlCl3, which is normally used in large amounts in these reactions. In the past 5 years, many new ionic liquids have been developed with a broad range of properties. By selecting the appropriate ionic liquid, it is now possible to carry out many types of organic reactions in these solvents. In some reactions, a well –designed ionic solvent can lead to better yields under milder conditions than is possible with traditional solvents.

Fluorous solvents:

Fluorous chemistry involves the use of per fluorinated compounds or perfluorinated substituents to facilitate recovery of a catalyst or reaction product. Per fluorinated groups impart unique physical properties including high solubility in perfluorinated solvents. This property can be useful in organic synthesis and separation methods such as solid phase extraction. In practice, a perfluorinated alkyl group is incorporated into an organic reagent as an affinity tag. These reagents can then be separated from organic solvents by extraction with fluorinated solvents such as perfluorohexane.

Fluorouschemistry molecules consists of both nonfluorous and fluorous parts. The fluorouspart is a substituent contributing solubility in the fluorocarbon medium. Such perfluorosubstituents are called ponytails. Typical fluorous ponytails have the formula $CF_3(CF_2)_n(CH_2)_m$- where n is about 10 and m is about 3

Through the use of fluorous tags (ponytails) for fluorous phases or fluorous-derivatized solid phases allows for complete recovery of the tagged reagent making the use of fluorous chemistry techniques a popular topic in green chemistry.

Two main classes of fluorous solvents

1. Perfluorocarbons (PFCs)
2. Hydrofluoroethers (HFEs).

Both PFCs and HFEs are fluorous phases into which fluorous molecules may partition. They have found extensive use in fluorous liquid-liquid extraction separations.

Perfluorocarbons (PFCs)

Traditionally, fluorous solvents have been perfluorocarbons (PFCs) such as perfluorohexane, perfluoromethylcyclohexane, or perfluorodecalin. Used extensively in the electronics industry, PFCs are generally very non-polar and posess boiling points similar to their non-fluorous analogs.

These solvents are generally not miscible with either organic or aqueous solvents at ambient temperature or pressure.

Hydrofluoroethers

Hydrofluoroethers (HFEs) are an emerging class of fluorous solvents that are finding increased use in fluorous separations. They are represented by molecules such as nonafluorobutyl methyl ether, sold under the trade name HFE-7100. These solvents retain many of the fluorous characteristics of perfluorocarbons, but possess higher overall solvating power due to increased polarity relative to PFCs.

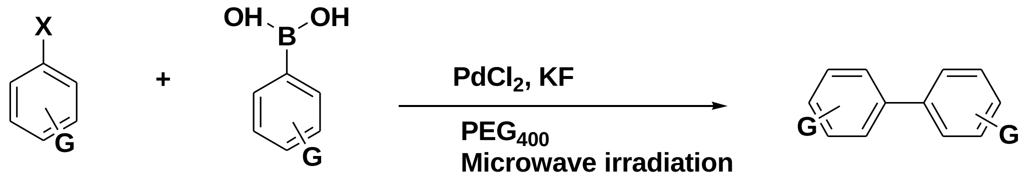
It's possible to select a perfluorinated hydrocarbon that is immiscible in another organic solvent, forming a distinct phase boundary. Such systems may become miscible at elevated temperature which is exploited in the design of some catalytic processes. Adding gaseous CO2 to the biphasic system also makes the phases miscible in many cases due to the high solubility of CO2 in both fluorous and organic solvents.

Fluorous solvents have the odd property of being both hydrophobic and lipophobic and thus are not miscible with either aqueous or many organic solvents. Fluorine, as the most electronegative element, does odd things to a molecule (and is often used in pharmaceutical compounds just because of some of these odd properties). In the perfluorinated hydrocarbons, the carbon-fluorine bonds are quite polar with the electron density higher toward the fluorine. The solvents themselves, however, are not polar due to free rotation about the C-C bonds, so they are not miscible with polar solvents and are hydrophobic.

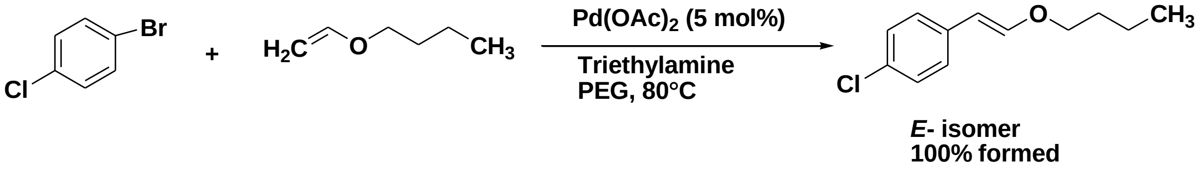
Because the F is so electronegative, the electrons are quite tightly held and the molecules have a low polarizability and unusually weak London dispersion forces, so they aren't miscible with non-polar solvents either. These weak London forces are explaied by the fact that the perfluorinated hydrocarbons have nearly the same boiling point as their corresponding normal hydrocarbon, inspite having more mass.

Polyethylene glycols (PEG) are known as compounds with wide spread industrial and medical applications. PEGs are readily soluble in polar and non-polar solvents and insoluble in aliphatic hydro carbons and supercritical CO2. A very interesting aspect of these compounds is behind their applications as solvent in organic reactions. They are inexpensive and significantly less hazardous than other organic solvents. Additionally, PEGs are stable under ambient condition because they have negligible vapor pressure and do not release VOCs. They have good stability in both acidic and basic media and are suitable reaction media for oxidation/reduction reactions. PEGs have compatibility as reaction media for various organic transformations such as N-arylation O-arylation S-arylation , allylation reactions, multicomponent reactions, oxidation , cycloaddition , polymerizations , N-alkynylation , asymmetric hydrogenation and asymmetric sharplessdihydroxylation. The important achievements related to the application of PEGs in various "well-known reactions" for carbon–carbon bond formation. In most cases, PEGs are used as alternative reaction media. Other important roles of PEGs in reactions such as phase transfer catalyst (PTC) and their stabilization properties are highlighted and 82 discussed in the proper situations.

Suzuki reaction (also known as Suzuki–Miyaura reaction) is a palladium catalyzed carbon–carbon bond formation between organoboron compounds with aromatic halides. An interesting example for Suzuki reaction in PEG . It was shown that the reaction was preceded in high yield in PEG400 (note: subscripts in all cases are average molecular weight of the applied PEG) as an inexpensive and non-toxic reaction medium.



Heck or Mizoroki–Heck reaction is a palladium-catalyzed coupling for preparation of substituted alkenes from aryl halides (or triflates) and alkenes. The first example of the Heck reaction in PEGwas reported in 2002 by Chandrasekhar et al. . They used PEG2000 as a solvent and carried out stereo- and regioselectivities Heck reaction without using additional ligands or PTC. Good to excellent E/Z diastero-isomer selec-tivitieswere obtained regardless on the electronic nature of the starting olefin. For example, a quantitative yield of E-isomer was isolated when4-chlorobromobenzene was reacted with butyl vinyl ether.



1. SOLVENTLESS REACTIONS ⎫ A dry media reaction or solid-state reaction or solventless reaction is a chemical reaction system in the absence of a solvent. ⎫ The drive for the development of dry media reactions in chemistry is:
   • Economics (save money on solvent)
   • Not required to remove a solvent after reaction completion ultimetly purification step not required
   • Reaction rate is high due more availability of reactants.
   • Environmentaly friendly because solvent is not required.

2. Solid state reaction follows the fifth principle of green chemistry which avoid using toxic solvents in the chemical reaction.

3. ADVANTAGES
   • More efficient with more selectivity compared to reactions carried out in solvents.
   • Reactions are simple to handle, reduce pollution, comparatively. Cheaper to operate and are especially important in industry.

   ● Halogenation
   • Michael Addition • Aldol Condensation
   • Grignard Reaction Reformatsky Reaction
   • Pinacol-Pinacolone Rearrangement
   • Benzil-benzilic acid rearrangement
   • Beckmann Rearrangement
   • Armoatic Substitution Reactions Oxidative coupling of phenols

4. HALOGENATION
   Bromination of powdered (E)-o-stillbene carboxylic acid
   • Bromination with bromine in solution gives 1,2,4-bromo-3-phenyl- 3,4-dihydroisocoumarin as the major product.
   • HBr.Br2 complex in solid state at room temperature gave 12 selectively erythro-l ,2-dibromo-l ,2-dihydro stilbene carboxylic acid.

5. MICHAEL ADDITION
   • The Michael addition of chalcone to 2-phenyl cyclohexanone give 2,6-disubstituted cyclohexanone derivative in high distereoselectivity.

6. ALDOL CONDENSATION
   • The aldol condensation of the lithium enolateofmethyl 3,3-dimethyl butanoate with aromatic aldehydes gives mixture of the syn and anti products in 70% yield

Advantages

A solvent-free or solid state reaction may be carried out using the reactants alone or incorporating them in clays, zeolites, silica, alumina or other matrices. Thermal process or irradiation with UV, microwave or ultrasound can be employed to bring about the reaction.

· Solvent-free reactions obviously reduce pollution and bring down handling costs due to simplification of experimental procedure, work up technique and saving in labour. These would be especially important during industrial production

· Often, the products of solid state reactions turn out to be different from those obtained in solution phase reactions. This is because of specific spatial orientation or packing of the reacting molecules in the crystalline state. The orientational requirements of the substrate molecules in the crystalline state have provided excellent opportunities to achieve high degree of stereoselectivity in the products. This has made it possible to synthesize chiral molecules from prochiral ones either by complexation with chiral hosts or formation of intermediates with chiral partners.

·If two or more substrates are involved in the reaction, they are thoroughly ground together in a glass mortar or cocrystallized and allowed to stay at room temperature or transferred to a suitable apparatus and heated carefully in an oil bath or exposed to appropriate radiation until the reaction is complete. More sophisticated reaction procedures are also adopted, if necessary. The progress of the reaction can be monitored by TLC. In some cases, a small quantity of water or a catalyst may be added. If it is a single-compound reaction, it is subjected to heat or radiation directly. Care is to be taken to collect the volatile products, if they are produced.

POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What is Green Chemistry?
2. Why do we need Green Chemistry?
3. Write a comparative statement on green chemistry and synthetic chemistry.
4. What are the economic benefits of Green Chemistry?
5. What is the goal of the Green Chemistry Initiative?
6. Give one example to 100% atom economy?
7. What is meant by Green Chemistry?
8. What are the educational challenges lying behind the Green Chemistry?
9. What is the difference between Environmental Science and Green Chemistry?
10. Is Green Chemistry more expensive that traditional Chemistry?
11. What is meant by Less Hazardous Chemical Synthesis
12. Explain the greener reagents with two examples.
13. How do you evaluate the chemical reactions according to their yield and atom efficiency?
14. Why are reactions performed using solvents?
15. What is meant by Non-organic solvents? Give examples.
16. What are fluorous solvents. Give two examples.
17. What are the advantages in carrying out the reactions using a micro wave oven
18. Explain the principle of prevention of waste in Green chemistry
19. What is meant by atom economy
20. Explain atom economy with a suitable example
21. Compare the atom economy of an addition and elimination reactions
22. What is meant by super critical carbon di oxide
23. What are the advantages of taking water as a solvent in organic synthesis
24. What is meant by a green solvent
25. What is meant by an ionic liquid. Give an example
26. What is meant by a fluorous solvent.
27. Give an example for substitution reaction

PART C (8 Mark Questions)

1. What is green Chemistry? What are the twelve principles of green chemistry
2. “Green Chemistry is important in alternate reaction pathways”-Explain

3. How does the Green Chemistry Initiative differ from traditional efforts to reduce pollution?
4. Explain the following reactions with special reference to green chemistry. (a) Aldol condensation (b) Diels-Alder reaction
5. Explain the advantages and limitations of solventless reactions. Give some examples for solid state reactions.
6. Write notes on organic reactions in aqueous media.
7. What are the tools used in the green chemistry
8. Comment on “designing safer chemicals” in green chemistry
9. Explain an atom efficient Process taking an Elimination reaction as an example
10. Explain atom economy with suitable examples
11. Explain atom economy of addition, elimination, substitution and rearrangement reactions
12. Compare and contrast conventional and green solvents
13. What are the advantages in using supercritical carbon di oxide as a solvent.
14. What are the advantages of taking water as a green solvent
15. Illustrate with examples to show that water is a green solvent
16. What is meant a Ionic liquid. What are the properties of ionic liquid. Classify them with suitable examples
17. Explain how to carryout a reaction in fluorous solvent

KARPAGAM ACADEMY OF HIGHER EDUCATION

CLASS: III B.Sc CHEMISTRY COURSE NAME: GREEN CHEMISTRY

COURSE CODE: 16CHU603A UNIT: I (Introduction to Green Chemistry) BATCH:2018-2020

Green Chemistry

UNIT I

S.No	Question	a	b	c	d	Answer
1.	Which of the following are among the 12 principles of green chemistry?	Design commercially viable products	Use only new solvents	Use catalysts,not stoichiometric reagents	Re-use waste	Use catalysts, not stoichiometric reagents
2.	Green chemistry aims to?	Design chemical products and process that maximise profits	Design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances	Design chemical products and processes that work most efficiently	Utilize non-renewable energy	Design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances
3.	Green chemists reduce risks by?	Reducing the hazard inherent in a chemical product or process	Minimizing the use of all chemicals	Inventing technologies that will clean up toxic sites	Developing recycled products	Reducing the hazard inherent in a chemical product or process
4.	Which of the following is challenging for chemists?	Awarness of the benefits of green chemistry	Developing chemicals that are recyclable	Training for cleaning up chemical spills	Knowing when to reduce and eliminate hazardous waste	Knowing when to reduce and eliminate hazardous waste
5.	What is the U.S. Presidental	An award related to	An award for	The only chemistry	Challenge	The only chemistry

	green chemistry challenge award?	recycling	industry only	award given by the president	companies to become fuel efficient	award given by the president
6.	The first listed of the 12 principles of green chemistry is?	Prevent waste	Catalysis	Atom economy	Benign solvents	Prevent waste
7.	This word is synonymous with green chemistry and also means harmless, or gentle and not life threatening?	Sustainable	Benign	User friendly	Greenness	Benign
8.	An example for green chemistry is ?	Recycled carpet	A product made on earth day	A sublimation reaction	Bio plastics	Bio plastics
9.	Biodiesel is an example of which of the 12 principles of green chemistry?	1-Waste prevention	7-Use of renewable feedstocks	9-Use of catalysis	5-Safer solvents	7-Use of renewable feedstocks
10	Which is fulfilling the needs of the present generation without compromising the ability of future generations to meet their needs?	Sustainability	Green chemistry	Life cycle assessment	Recycling	Sustainability
11	The first listed of the 12 Principles of Green Chemistry is?	Prevent waste	Catalysis	Atom economy	Benign solvents	Prevent waste
12	Green chemists reduce risk by?	Reducing the hazard inherent in a chemical product or process	Minimizing the use of all chemicals	Inventing technologies that will clean up toxic sites	Developing recycled products	Reducing the hazard inherent in a chemical product or process
13	Which of the following is a challenge for green chemists?	Awareness of the benefits of green chemistry	Developing chemicals that are recyclable	Training for cleaning up chemical spills	Knowing when to reduce and eliminate hazardous waste	Knowing when to reduce and eliminate hazardous waste
14	Heart of green chemistry is	to maximize the	to minimize the	to increase the	to increase toxic	to minimize the

		waste products formation	waste products formation	toxic materials	materials and waste products formation	waste products formation
15	Maximum amount of ozone (O3) is present in	troposphere	stratosphere	mesosphere	thermosphere	stratosphere
16	Upset caused in natural balance of concentration of greenhouse gases is called	pollution	global warming	atmospheric poisoning	earth heating	global warming
17	Ozone gas (O3) has	unpleasant odor	pleasant odor	no odor	orange color	unpleasant odor
18	Gas responsible for global warming is	oxygen	carbon dioxide	carbon monoxide	nitrogen	carbon dioxide
19	Which of the following is not one of the twelve principles of green chemistry?	Using high temperatures to speed up reactions	Minimising toxic reagents used in a synthesis	Maximisation of atom economy	Minimising the use of solvents	Using high temperatures to speed up reactions
20	Which of the following is not a priority in green chemical development?	Optimising the overall yield of a drug	Optimising the activity of a drug	Developing a cheap synthetic route	Optimising the purity of a drug	Developing a cheap synthetic route
21	Green chemistry aims to?	Design chemical products and process that maximize profits	Design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances	Design chemical products and processes that work most efficiently	Utilize non-renewable energy	Design safer chemical products and processes that reduce or eliminate the use and generation of hazardous substances
22	Green chemists reduce risk by?	Reducing the hazard inherent in a chemical product or process	Minimizing the use of all chemicals	Inventing technologies that will clean up toxic sites	Developing recycled products	Reducing the hazard inherent in a chemical product or process
23	Which of the following is a challenge for green chemists?	Awareness of the benefits of green chemistry	Developing chemicals that are recyclable	Training for cleaning up chemical spills	Knowing when to reduce and eliminate hazardous waste	Knowing when to reduce and eliminate hazardous waste

24	Business benefits of green chemistry include?	Reduced costs associated with waste treatment and disposal	Innovating 'greener' products to entice customers	Greater compliance with environmental legislation	All of the above	All of the above
25	What is the U.S. Presidential Green Chemistry Challenge Award?	An award related to recycling	An award for industry only	The only chemistry award given by the President	Challenges companies to become fuel efficient	The only chemistry award given by the President
26	The first listed of the 12 Principles of Green Chemistry is?	Prevent waste	Catalysis	Atom economy	Benign solvents	Prevent waste
27	Green chemistry synthesis could also involve which of the following?	High temperature	Dichloromethane	Fossil fuels	Microwave	Microwave
28	This word is synonymous with green chemistry and also means harmless, or gentle and not life threatening?	) Sustainable	Benign	User friendly	Greenness	Benign
29	Bio-polymers exemplify Green Chemistry Principle # 10, which is?	Catalysis	Prevent waste	Benign solvents & auxiliaries	Design for degradation	Design for degradation
30	The use of solar power is covered within Green Chemistry Principle #6, which is?	Atom economy	Design for energy efficiency	Design benign chemicals	Less hazardous synthesis	Design for energy efficiency
31	An example of green chemistry is?	Recycled carpet	A product made on Earth Day	A sublimation reaction	Bio-plastics	Bio-plastics
32	Biodiesel is an example of which of the 12 Principles of Green Chemistry?	Waste prevention	Use of renewable feedstocks	Use of catalysis	Safer solvents	Use of renewable feedstocks
33	Green chemistry can reduce all but which of the	Cost	Risk & Hazard	Awareness	Waste	Awareness

	following?					
34	Which of the following gases is not a green house gas?	CO	O3	CH4	H2O vapour	CO
35	The consequences of global warming may be	increase in average temperature of the earth	melting of Himalayan Glaciers.	increased biochemical oxygen demand.	eutrophication.	increase in average temperature of the earth
36	The formation of ethene from the dehydration of ethanol can best be described as	an addition reaction	an elimination reaction	an oxidation reaction	a substitution reaction	an elimination reaction
37	What is the major driver for focussing on solvents when addressing the 'greenness' of a process?	They are petroleum derived	They are serious pollutants	They are toxic	they make up the largest component (by mass) of a process	they make up the largest component (by mass) of a process
38	Heart of green chemistry is	to maximize the waste products formation	to minimize the waste products formation	to increase the toxic materials	to increase toxic materials and waste products formation	to minimize the waste products formation
39	Among them which is green solvent	benzene	dichloro methane	super critical water	duetrated water	super critical water
40	Green chemistry synthesis could also involve which of the following?	High temperature	Dichloromethane	Fossil fuels	Microwave	Microwave
41	Solvent doesn't used in the reaction is called	Elimination reaction	Substitution reactions	Addition reaction	Solvent less reaction	solventless reaction
42	The following is often referred to as the universal solvent and is a preferred green solvent?	Water	Methanol	Ethyl acetate	Benzene	Water
43	The Neat reaction takes place	In the absence of solvent	In the absence of a solid support	In the absence of a catalyst	In presence of a solvent	In the absence of solvent
44	Liquids with a wide	Solid supports	organic catalysts	organic solvents	Ionic liquids	Ionic liquids

	temperature range and no vapour pressure					
45	What gives ionic liquids their low melting point?	Low molecular weight	No ionic bonding	High lattice energy	Large ions and shape mismatch between them	Large ions and shape mismatch between them
46	Solvents used for cleaning electronic circuit boards are	chlorofluorocarbons	carbons	fluorides	grease	chlorofluorocarbons
47	Which of the following is the greenest solvent?	Formaldehyde	benzene	Ethanol	water	Water
48	Benzene, a _______ substance, is an important industrial solvent used in the production of pharmaceuticals, plastics, and dyes?	Odorless	Non-flammable	Biodegradable	Carcinogenic	Carcinogenic
49	which one is an excellent ‘green’ solvent as well as a greenhouse gas?	Methanol	CFCs	Carbon monoxide	Carbon dioxide	Carbon dioxide
50	Among them which is green solvent	benzene	dichloro methane	super critical water	duetrated water	super critical water
51	Which of the following reaction gives 100% atom economy	clemmenson reduction	elimination reaction	diels alder reaction	aldol condensation	diels alder reaction
52	Addition reactions give	90% atom economy	75% atom economy	50% atom economy	100% atom economy	100% atom economy
53	Diels alder reaction is a	[3+1] cycloaddition	[4+2] cycloaddition	[2+2] cycloaddition	[2+2] cycloaddition	[4+2] cycloaddition
54	Diels alder reaction is a	4π-electron system	2π-electron system	6π-electron system	3π-electron system	4π-electron system
55	Atom economy is higher in	Addition reactions	Elimination reactions	Substitution reactions	Free radical substitutions	Addition reactions

56	Atom economy is higher in	Rearrangement reactions	Elimination reactions	Substitution reactions	Free radical substitutions	Rearrangement reactions
57	Atom economy is lower in	Rearrangement reactions	Elimination reactions	Addition reactions	Free radical reactions	Elimination reactions
58	Atom economy is lower in	Rearrangement reactions	Substitution reactions	Addition reactions	Free radical reactions	Substitution reactions
59	Limonene is obtained from orange peel using	Liquid carbon dioxide as the solvent	Ionic liquids	Supercritical carbondioxide	Fluorous solvents	Liquid carbon dioxide as the solvent
60	Caffein is obtained from tea using	Liquid carbon dioxide as the solvent	Ionic liquids	Supercritical carbondioxide	Fluorous solvents	Supercritical carbondioxide

UNIT II

Energy requirements for reactions – alternative sources of energy: use of microwaves and ultrasonic energy. Selection of starting materials; avoidance of unnecessary derivatization – careful use of blocking/protecting groups. Use of catalytic reagents (wherever possible) in preference to stoichiometric reagents; catalysis and green chemistry, comparison of heterogeneous and homogeneous catalysis, biocatalysis, asymmetric catalysis and photo catalysis. Prevention of chemical accidents designing greener processes, inherent safer design, principle of ISD "What you don't have cannot harm you", greener alternative to Bhopal Gas Tragedy (safer route to carcarbaryl) and Flixiborough accident (saferroute to cyclohexanol) subdivision of ISD, minimization, simplification, substitution, moderation and limitation. Strengthening/ development of analytical techniques to prevent and minimize thegeneration of hazardous substances in chemical processes.

UNIT II

Energy requirements for reactions – alternative sources of energy: use of microwaves and ultrasonic energy.

Energy Requirements for Synthesis

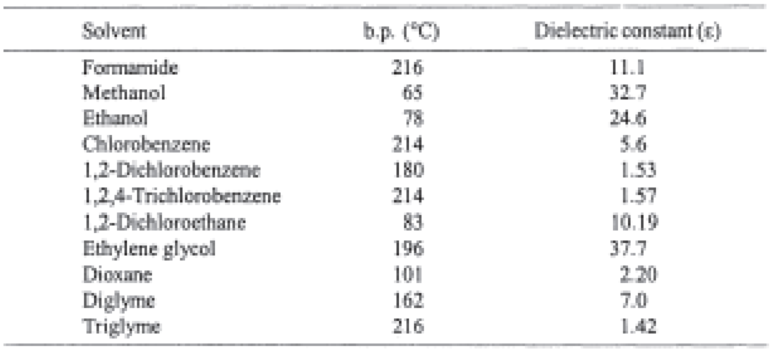
In any chemical synthesis, the energy requirements should be kept to a minimum. For example, if the starting material and the reagents are soluble in a particular solvent, the reaction mixture has to be heated to reflux for the required time or until the reaction is complete. In such a case, time required for completion should be minimum, so that bare minimum amount of energy is required. Use of a catalyst has the great advantage of lowering the energy requirement of a reaction.

In case the reaction is exothermic, sometimes extensive cooling is required. This adds to the overall cost. If the final product is impure, it has to be purified by distillation, recrystallisation or ultrafiltration. All these steps involve the use of energy. By designing the process such that there is no need for separation or purification, the final energy requirements can be kept at the bare minimum. Energy to a reaction can be supplied by photochemical means, microwave or sonication

Microwave Induced Green Synthesis

Normally microwaves have wavelengths between 1 cm and 1 m (frequencies of 30 GHz to 300 Hz). These are similar to frequencies of radar and telecommunications. In order to avoid any interference with these systems, the frequency of radiation that can be emitted by household and industrial microwave oven is regulated, most of the appliances operate at a fixed frequency of 2.45 GHz. The microwaves, as we know, are used for heating purposes. The mechanism of how energy is given to a substance which is subjected to microwave irradiation is complex. One view is that microwave reactions involve selective absorption of electromagnetic waves by polar molecules, non-polar molecules being inert to microwaves. When molecules with a pennanent dipole are submitted to an electric field, they become aligned and as the field oscillates their orientation changes, this rapid reorientation produces intense internal heating. The main difference between classical heating and microwave heating,lies in core and homogenous heating associated with microwaves, whereas classical heating is all about heat transfer by preheated molecules. The preferred reaction-vessel for microwave induced organic reaction, is a tall beaker (particularly for small scale reactions in the laboratory), loosely covered and the capacity ofthe beaker should be much greater than the volume of the reaction mixture. Alternatively, teflon and polystyrene containers can be used. These materials are transparent to microwaves. Metallic containers should not be used as reaction vessels. In microwave induced organic reactions, the reactions can be carried out in a solvent medium or on a solid support in which no solvent is used. For reactions in a solvent medium, the choice of the solvent is very important.

The solvent to be used must have a dipole moment so as to absorb microwaves and a boiling point at least 20-30 °C higher than the desired reaction temperature. An excellent solvent in a domestic microwave oven is N ,N –dimethylfonnarnide (DMF) (b.p. 160 ° C, E = 36.7). The solvent can retain water fonned in a reaction, thus, obviating the need for water separation. Some other solvents of choice are given as follows:



Solvent	b.p. (°C)	Dielectric constant (ε)
Formamide	216	11.1
Methanol	65	32.7
Ethanol	78	24.6
Chlorobenzene	214	5.6
1,2-Dichlorobenzene	180	1.53
1,2,4-Trichlorobenzene	214	1.57
1,2-Dichloroethane	83	10.19
Ethylene glycol	196	37.7
Dioxane	101	2.20
Diglyme	162	7.0
Triglyme	216	1.42

Hydrocarbon solvents, for example, hexane (I> = 1.9), benzene (E = 2.3), toluene (I> = 2.4) and xylene are unsuitable because ofless dipole moment and also because these solvents absorb microwave radiations poorly. However, addition of small amounts of alcohol or water to these solvents can lead to dramatic coupling effects. Liquids which do not have a dipole moment cannot be heated by microwaves. By adding a small amount of a dipolar liquid to a miscible non-dipolar liquid, the mixture will rapidly achieve a uniform temperature under irradiation.

Microwaves may be considered as a more efficient source of heating than conventional steam (or oil heated vessels), since the energy is directly imparted to the reaction medium rather than through the walls of a reaction vessel. In fact, the rapid heating capability of the microwave leads to considerable saving in dissolution or the reaction time. The smaller volume of solvent required contributes to saving in cost and diminishes the waste disposal problem Microwave procedures are limitedS by the presence of solvents which reach their boiling points within a very short time

(- 1 min) of exposure to microwave. Consequently, high pressures are developed, leading to damage to the vessels material or the microwave oven itself and may occasionally lead to explosion.

Well-designed industrial microwave ovens are available now. Consideration of safety aspects coupled with the limitations of the solvents imposed by microwave heating, has led to many reactions being carried out in water or more commonly under solvent free conditions. This is a major green advantage of microwave reactions. It is believed that due to high polarity and non-volatility, ionic liquids (see also Chapter 14) might be ideal for carrying out high temperature reactions efficiently, since temperatures of over 200°C can be readily attainable.

Applications

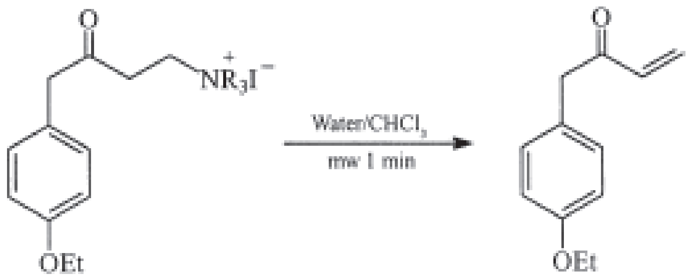
It is possible to carry out a number of microwave organic synthesis. These syntheses are grouped in the following three categories:

(i) Microwave-assisted reactions in water.
(ii) Microwave-assisted reactions in organic solvents.
(iii) Microwave solvent-free reactions (solid state reactions).
Some microwave assisted organic synthesis are:

Microwave Assisted Reactions in Water

Hofmann Elimination

In this method, normally quaternary ammonium salts are heated at high temperature and the yield of the product is low. Use of microwave irradiation has led to high-yielding synthesis of a thermally unstable Hofmann elimination product. In this water-chloroform system is used.

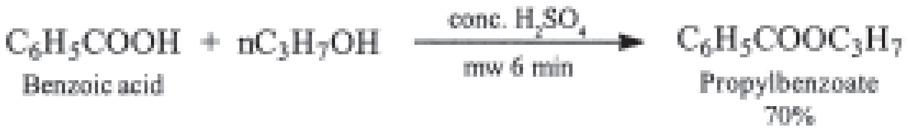


Microwave-Assisted Reactions in Organic Solvents

This includes those microwave induced reactions in which one or both the reactants (if liquid) act as a solvent and also those reactions in which organic solvent is used to assist the reaction.

Esterification: Reaction of Carboxylic Acid and Alcohol

A mixture of benzoic acid and n-propanol on heating in a microwave oven for 6 min in presence of catalytic amount of cone. sulphuric acid gives propylbenzoate.



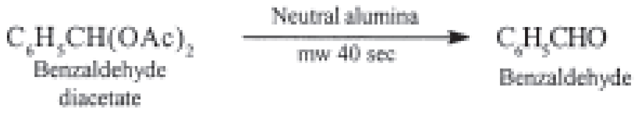
$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + nC_3H_7OH \xrightarrow[\text{mw 6 min}]{\text{conc. } H_2SO_4} \underset{\substack{\text{Propylbenzoate}\\ 70\%}}{C_6H_5COOC_3H_7}$$

Microwave Solvent Free Reactions (Solid State Reactions)

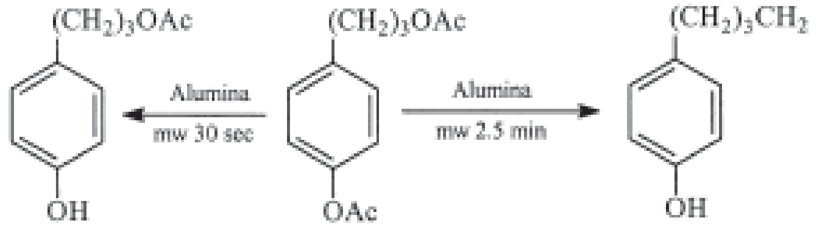
Application of microwave irradiation in organic reactions has added a new dimension to solid phase synthesis. By the use of this technique, it is now possible to carry out reactions without the use of toxic or other solvents, which is one of the main problems associated with green synthesis. In these, the reactants are dissolved in a suitable solvent like water, alcohol, methylene chloride etc. and the solution stirred with a suitable adsorbent or solid support like silica gel, alumina or phyllosilicate (Mn+ -montomorillonite). After stirring, the solvent is removed *in vacuo* and the dried solid support on which the reactants have been adsorbed are used for carrying out the reaction under microwave irradiation. Following are some of the important applications of solid support synthesis.

Deacetylation

Aldehydes , phenols and alcohols are protected by acetylation. After the reaction, the deacetylation of the product is carried out usually under acidic or basic conditions; the process takes long time and the yields are low. Use of microwave irradiation reduces the time of deacetylation and the yields are good. Some examples are as follows:



$$\underset{\substack{\text{Benzaldehyde}\\ \text{diacetate}}}{C_6H_5CH(OAc)_2} \xrightarrow[\text{mw 40 sec}]{\text{Neutral alumina}} \underset{\text{Benzaldehyde}}{C_6H_5CHO}$$



Ultrasound Assisted Green Synthesis

The word 'ultrasound' has become common knowledge due to the widespread use of ultrasound scanning equipments in medical applications. Ultrasound refers to sound waves having frequencies higher than those to which the human ear can respond *(fl*, > 16 KHz) (Hz = Hertz = cycles per second). High frequency ultrasound waves are used in medical equipments. The ultrasound frequencies ofintetest for chemical reactions (about 20-100 KHz) are much lower than those used for medical applications, but the power used is higher. The ultrasound is generated with the help of an instrument having an ultrasonic transducer, a device by which electrical or mechanical energy can be converted into sound energy. The most commonly used are the electromechanical transducers which convert energy into sound - they are mostly made of quartz and are commonly based on the piezoelectric effect.

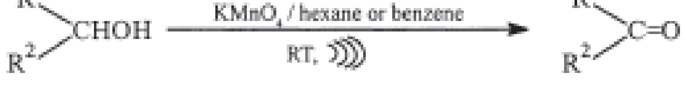
When equal and opposite electrical charges are applied to opposite faces of a crystal of quartz, expansion or contraction occurs. Application of rapidly reversing charges sets up a vibration that emits ultrasonic waves called the *piezoelectric effect.* In modern ultrasonic equipments, the piezoelectric transducers are made from ceramic impregnated barium titanate. Such devices convert over 95% of the electrical energy into ultrasound. In practice, the devices only have an optimum operating frequency.

When a sound wave, propagated by a series of compression and refraction cycles, pass through a liquid medium, it causes the molecules to oscillate around their mean position. During the compression cycle, the average distance between the molecules is reduced and during refraction, the average distance between the molecules is increased. In the refraction cycle, under appropriate conditions, the attractive forces of the molecules of the liquid may be overcome, causing formation of bubbles. In case the internal forces are great enough to ensure collapse of these bubbles, very high local temperature (around 5000°C) and pressure (over 1000 bar) may be created. It is this very high temperature' and pressure that initiate chemical reactions.

Most of the reactions/syntheses reported are carried out at room temperature unless otherwise specified. The symbol))) is used for reactions carried out on exposure to ultrasound.

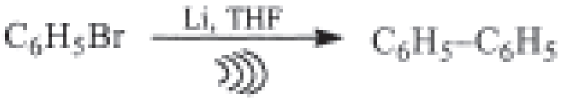
Oxidation

The oxidation of alcohols by solid potassium permanganate in hexane or benzene is enhanced considerably by sonication.



Coupling Reactions

Homocoupling of organometallic generated *in situ* by the reaction of alkyl, aryl of vinyl halides with lithium in THF takes place on sonication. No reaction takes place in absence of ultrasound.



Designing a Green Synthesis

In any synthesis of a target molecule, the starting materials that are made to react with a reagent under appropriate conditions. Before coming to a final decision, consider all the possible methods that can give the desired product. The same product can also be obtained by modifying the conditions. The method of choice should not use toxic starting materials and should eliminate by-products and wastes. Following are some of the important considerations.

Choice of Starting Materials

It is very important to choose the appropriate starting materials. The synthetic pathway will depend on this. Also consider the hazards that may be faced by the workers (chemists carrying out the reaction and also the shippers who transport these) handling the starting materials.
Till now, most syntheses make use of petrochemicals (made from petroleum), which are non-renewable. Petroleum refining also requires considerable amounts of energy. It is therefore important to reduce the use of petrochemicals by using alternative starting materials, which may be of agricultural biological origin. For example, some of the agricultural products such as corn, potatoes, soya and molasses are transformed through a variety of processes into products like textiles, nylon etc. Some of the materials that have biological origin (obtained from biomass) are: butadiene, pentane, pentene, benzene, toluene, xylene, phenolics, aldehydes, resorcinol, acetic acid, peracetic acid, acrylic acid, methyl aryl ethers, sorbitol, mannitol, glucose, gluconic acid, 5-hydroxymethyl furfural, furfural, levulinic acid, furan, tetrahydrofuran, furfuryl alcohol etc.

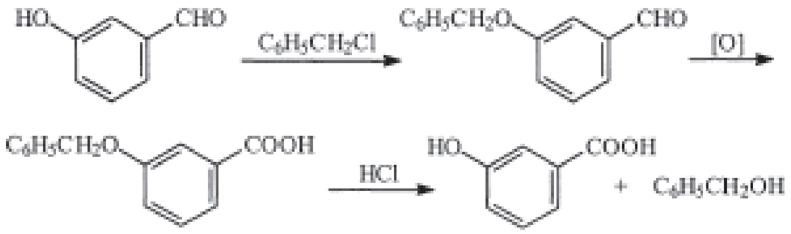
Choice of Reagents
Selection of the right reagent for a reaction is made on the basis of efficiency, availability and its effect on environment. The selection of a particular reagent versus another reagent for the same transformation can effect the nature of by-products, percentage yield etc.

Choice of Catalysts

Certain reactions proceed much faster and at a lower temperature with the use of catalysts. Heavy metal catalysts should be avoided as they cause environmental problems and are toxic in nature. Use of visible light to carry out the required chemical transformation should be explored. Certain biocatalysts (enzymes) can also be used for various steps

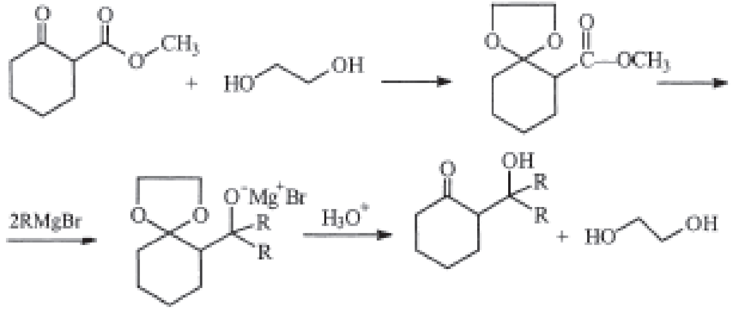
Use of Protecting Groups

In case an organic molecule contains two reactive groups and you want to use only one of these groups, the other group has to be protected, the desired reaction completed and the protecting group removed. For example



Reactions of this type are common in the synthesis of fine chemicals, pharmaceuticals, pesticides etc. In the above protection, benzyl chloride (a known hazard) and the waste generated after deprotection should be handled carefully.

Another reaction involving protection of a keto function by using 1,2- ethanediol is as follows



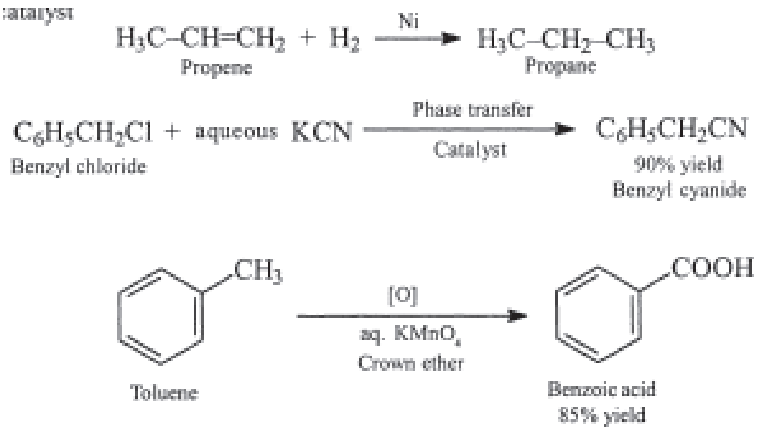
Thus, we see that the protecting groups that are needed to solve a chemoselectivity problem should be added to the reaction in stoichiometric amounts only and removed after the reaction is complete. Since these protecting groups are not incorporated into the final product, their use makes a reaction less atom-economical. In other words the use of protective group should be avoided whenever possible. Though atom-economy is a valuable criteria in evaluating a particular synthesis as 'green', other aspects of efficiency must also be considered.

Use of Catalyst

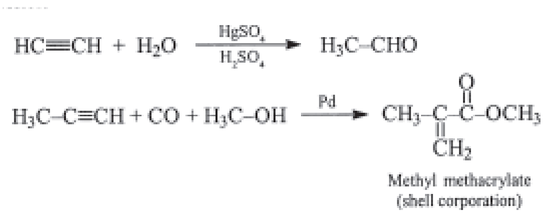
It is well known that use of a catalyst facilitates transformation without the catalyst being consumed in the reaction and without being incorporated in the final product. Therefore, use of catalyst should be preferred whenever possible.

Some of the advantages are:

(i) Better yields. Hydrogenation or reduction of olefins in presence of nickel catalyst

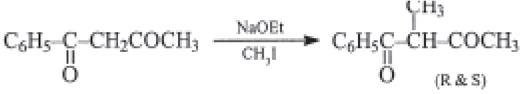


(ii) The reaction becomes feasible in those cases where no reaction is normally possible



(iii) Selectivity enhancement

Selectivity in C-methylation versus O-methylation



In addition to the above mentioned beneficial use of catalysts, there is significant advantage in the energy requirement. With advances in the selectivity of catalysts, certain reactions in green synthesis have become very convenient. A special advantage of the use of catalysts is better utilisation of starting materials and minimum waste product formation.

Some of the major advances in chemistry especially industrial chemistry, over the past decade have been in the area of catalysts. Through the use of catalyst, chemists have found ways of removing the need for large quantities of reagents that would otherwise have been needed to carry out the transformations and ultimately would have contributed to the waste stream.

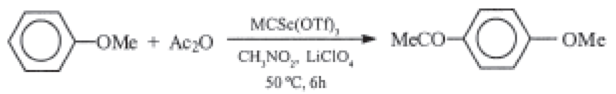
Catalysts playa major role in establishing the economic strength of the chemical industry and the clean technology revolution in the industry will provide new opportunities for catalysis and catalytic processes. Following are some different types of catalysts used.

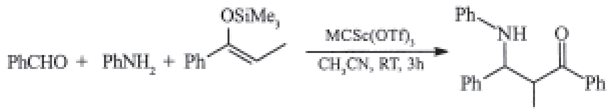
Acid Catalysts

The traditional catalyst hydrogen fluoride, an extremely corrosive, hazardous and toxic chemical used in the production oflinear alkylbenzenes (LAB's), has been successfully replaced by a solid acid catalyst, viz. fluorided silica-alumina catalyst, which does not require special material of construction (of the container), involves lower operating costs and obviates the need for an acid scrubbing system and waste disposal of calcium fluoride.·

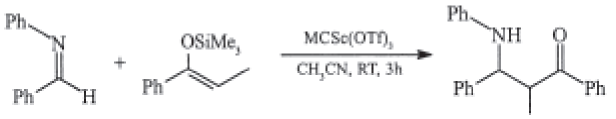
Microencapsulated Lewis acids have replaced traditional corrosive monomeric Lewis acids in the reactions like Michael, Friedel Crafts, Mannich, Imino aldo reactions

Scheme 1



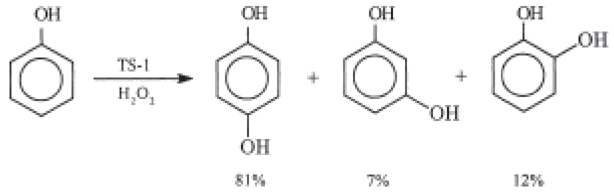


Scheme 3



Oxidation Catalysts

A large number of supported reagents have been used in the liquid phase partial oxidation of organic substrates.13•14 There has been considerable success in the use of molecular sieves (titanium and vanadium) in commercial unitsY The most important application oftitanium silicates (TS-I) is the hydroxylation of phenol, giving mixtures of hydroquinone and catechol. The process is clean, giving excellent conversion to product with very little waste.



Basic Catalysts

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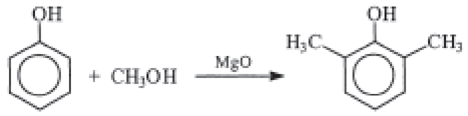
In contrast to the areas of heterogeneous oxidation catalysis and solid acid catalysis, the use of solid base catalysis in liquid phase reactions has not met the same level of breakthrough.
The industrial applications of basic catalysts are in the alkylation of phenol, side chain alkylation and isomerisation reactions



Besides what has been stated above, the following catalysts/catalytic processes find wide applications in industry.

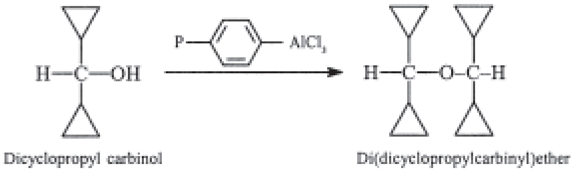
1. Biocatalysis: The most important conversions in the context of green chemistry is with the help of enzymes or biocatalysts.
2. Phase transfer catalysis and crown ethers: These find numerous applications in organic synthesis in industry and in the laboratories.
3. Photocatalysis: A large number of conversions/syntheses have been carried out photolytically.

Polymer Supported Catalysts

The conventional catalyst which is normally used in the homogenous phase, is linked to a polymer backbone and is used in this form to catalyse different reactions. Following are some of the polymer supported catalysts and their applications.

Polystyrene-aluminium Chloride

It is used to prepare ethers from alcohols. Thus, dicyclopropyl carbinol on treatment with polystyrene-Alel3 produces die dicyclo-propylcarbinyl) ether in high yield



Biocatalysts in Organic Synthesis

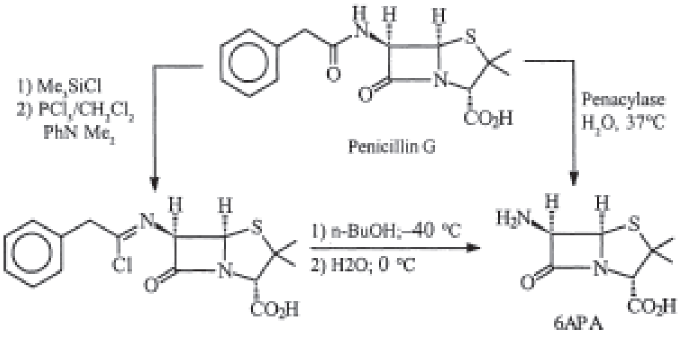
The most important conversions in the context of green chemistry is with the help of enzymes. Enzymes are also referred to as biocatalysts and the transformations are referred to as biocatalytic conversions. Enzymes are now easily available and are an important tool in organic synthesis. The earliest biocatalytic conversion known to mankind is the manufacture of ethyl alcohol from molasses, the mother liquor left after the crystallisation of cane sugar from concentrated cane juice. This transformation is brought about by the enzyme 'invertase' which converts sucrose into glucose and fructose and finally by the enzyme zymase which converts glucose and fructose into ethyl alcohol. It is well known that most of the antibiotics have been prepared using enzymes (enzymatic fermentation).

The biocatalytic conversions have many advantages in relevance to green chemistry. Some of these are given below:

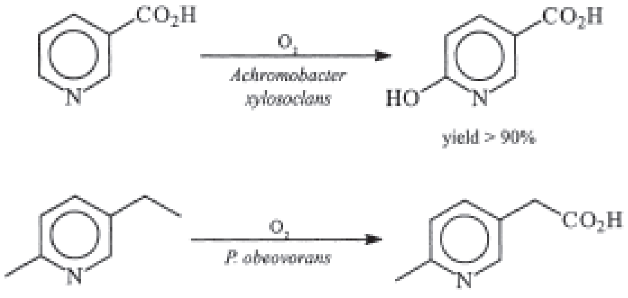
- Most of the reactions are performed in aqueous medium at ambient temperature and pressure.
- The biocatalytic conversions normally involve only one step.
- Protection and deprotection of functional groups is not necessary.
- The reactions are fast reactions.
- The conversions are stereospecific.

One of the most common examples is the biocatalytic conversion of Penicillin into 6-APA by the enzyme 'Penacylase' (one step process). However, the chemical conversion requires a number of steps .
A special advantage of the biochemical reactions is that they are chemoselective, regioselective and stereoselective. Also, some of the biochemical conversions are generally not possible by conventional chemical means. Two such examples in heterocyclic compounds are given in (Scheme 2). I A number of diverse reactions are possible by biocatalytic processes, which are catalysed by enzymes. The major six classes of enzymes and the type of reactions they catalyse are discussed as follows:

1. Oxidoreductases: These enzymes catalyse oxidation-reduction reactions. This class includes oxidases (direct oxidation with molecular oxygen) and dehydrogenases (which catalyse the removal of hydrogen from one substrate and pass it on to a second substrate).



Scheme 1



Scheme 2

2. Transferases: These enzymes catalyse the transfer of various functional groups, e.g. transaminase.

3. Hydrolases: This group of enzymes catalyse hydrolytic reactions, e.g. penteases (proteins), esterases (esters) etc.

4. Lyases: These are of two types, one which catalyses addition to double bond and the other which catalyses removal of groups and leaves double bond. Both addition and eliminations of small molecules are on Sp3_hybridized carbon.

5. Isomerases: These catalyse various types of isomerisation, e.g. racemases, epimerases etc.
6. Ligases: These catalyse the formation or cleavage of sp3-hybridized carbon.

As already stated the enzymes are specific in their action. This specificity of enzymes may be manifested in one of the three ways:
(i) An enzyme may catalyse a particular type of reaction, e.g. esterases hydrolyses only esters. Such enzymes are called reaction specific. Alternatively, an enzyme may be specific for a particular class of compounds. These enzymes are referred to as substrate specific, e.g., urease hydrolyses only urea and phosphatases hydrolyse only phosphate esters.

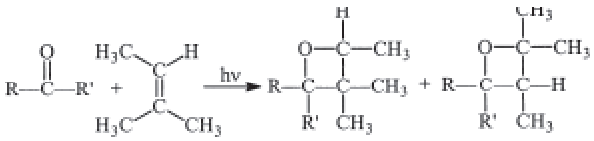
(ii) An enzyme may exhibit kinetic specificity. For example, esterases hydrolyse all esters but at different rates.

(iii) An enzyme may be stereospecific. For example, maltase hydrolyses aglycosides but not J3-glycosides. On the other hand emulsin hydrolyses the J3-glycosides but not the a-glycosides. It should be noted, that a given enzyme could exhibit more than one specificities.

Photochemical Reactions

The importance of photochemical reactions can hardly be overemphasized. The earliest known photochemical reaction is the photosynthesis of sugars by plants using sunlight, CO2 and Hp in presence of chlorophyll. Some of the common examples of routine photochemical reactions are:

(i) Photochemical cyc1oaddition of carbonyl compounds and olefins (PatemoBuchi reaction) to give four membered ether rings



(ii) Photo fries rearrangements. The phenolic esters in solution on photolysis give a mixture of 0- and p-acylphenols.

Designing of Manufacturing **Plants**

The importance of prevention of accidents in manufacturing units cannot be over emphasised. A number of accidents have been found to occur in industrial units. The gas tragedy in Bhopal (December 1984) and several other places has resulted not only in loss of thousands of human lives but also rendered many persons disabled for the rest of their lives. The hazards posed by toxicity, explosions, fire etc. must be looked into and the manufacturing plants should be so designed to eliminate the possibility of accidents during operation.

Strengthening of Analytical Techniques

Analytical techniques should be so designed that they require minimum usage of chemicals, like recycling of some unreacted reagent (chemical) for the completion of a particular reaction. Further, placement of accurate sensors to monitor the generation of hazardous by-products during chemical reaction is also advantageous.

On the 3rd of December 1984, 40 tonnes of toxic gases escaped from the Union Carbide pesticide plant in Bhopal, India. The result was catastrophic. 3,000 people— men, women, and children— were dead within the hour; after 72 hours the death toll had tripled. Over 22,000 have died to date from gas-related afflictions, and permanent injuries run into the hundreds of thousands.

The local ecosystem is likewise suffering; water and soil are laden with toxins that are hundreds of times more prevalent than can be safely absorbed by humans and local wildlife. The Bhopal Gas Disaster highlights the environmental and human costs of laissez-faire industry.

Preventing Environmental Disasters

While natural disasters are largely unpredictable, environmental disasters are caused directly or indirectly by human behavior. Chemical disasters, like the one in Bhopal, are preventable if risks are identified and addressed early on.

It will take the combined effort of competent authorities, private sector and society to prevent tragic environmental events from happening. Some measures include: Developing policies to ensure that industries operate in accordance with technical and safety standards and allocating resources for risk assessment and monitoring. Most of all, it’s important to adhere to environmental norms. Taking environmental safety and public health risks seriously, and promoting do-no-harm industrial development can make a big difference.

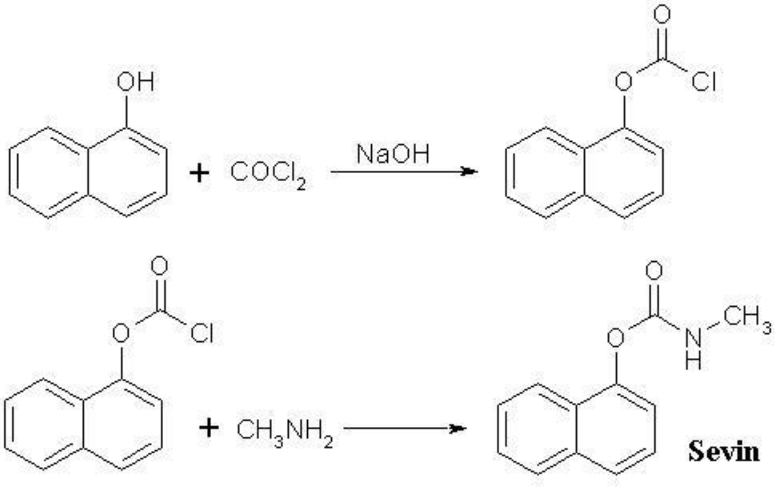
There is a clear need to promote clean development that innovatively addresses potential negative impacts on the environment. To prevent future environmental disasters, all sectors could also do more to integrate environmental emergency preparedness and response activities into strategies and sustainable development programs. These measures could make a big difference in people’s health and well-being, and avoid future tragedies.

Introduction

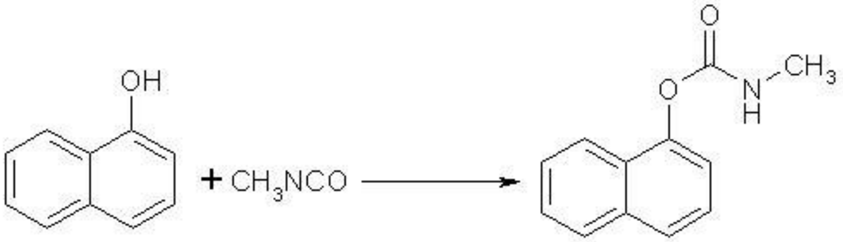
Carbaryl is a wide-spectrum carbamate insecticide which controls over 100 species of insects on citrus, fruit, cotton, forests, lawns, nuts, ornamentals, shade trees, and other crops, as well as on poultry, livestock and pets. It is also used as a molluscicide and an acaricide. Carbaryl works whether it is ingested into the stomach of the pest or absorbed through direct contact. The chemical name for carbaryl is 1- naphthol N-methylcarbamate. Carbaryl is formulated as a solid which varies from colorless to white to gray, depending on the purity of the compound. The crystals are odorless. This chemical is stable to heat, light and acids under storage conditions. It is non-corrosive to metals, packaging materials, or application equipment. It is found in all types of formulations including baits, dusts, wettable powder, granules, oil, molassas, aqueous dispersions and suspensions.

Routes of Sevin synthesis:

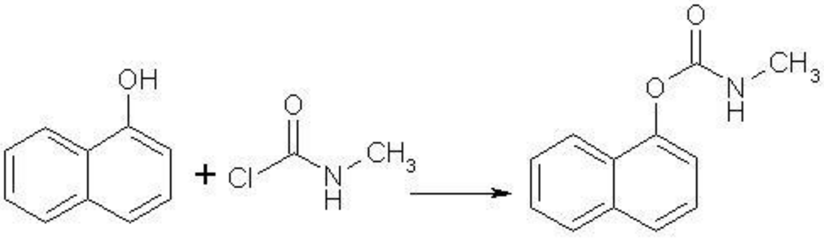
1) With using naphtol-1 and phosgene:



2) With using naphtol-1 and methyl isocyanate:

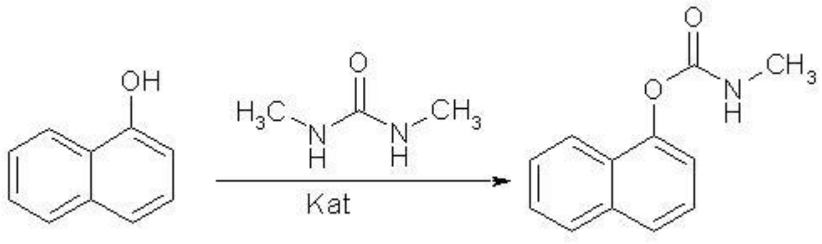


3) With using naphtol-1 and methylcarbamoyl chloride:



In these routes of synthesis of Carbaryl highly toxic substances such as phosgene, methyl isocyanate and methylcarbamoyl chloride are used.

A new and cost-effective approach to Sevin synthesis without using of toxic reagents:



The **Flixborough disaster** was an explosion at a chemical plant close to the village of Flixborough, North Lincolnshire, England on Saturday, 1 June 1974. It killed 28 people and seriously injured 36 out of a total of 72 people on site at the time. The casualty figures could have been much higher, if the explosion had occurred on a weekday, when the main office area would have been occupied. A contemporary campaigner on process safety wrote "the shock waves rattled the confidence of every chemical engineer in the country".

The disaster involved (and may well have been caused by) a hasty modification. There was no on-site senior manager with mechanical engineering expertise (virtually all the plant management had chemical engineering qualifications); mechanical engineering issues with the modification were overlooked by the managers who approved it, nor was the severity of the potential consequences of its failure appreciated.

The chemical works, owned by Nypro UK (a joint venture between Dutch State Mines (DSM) and the British National Coal Board (NCB)) had originally produced fertiliser from by-products of the coke ovens of a nearby steelworks. Since 1967, it had instead produced caprolactam, a chemical used in the manufacture of nylon 6. The caprolactam was produced from cyclohexanone. This was originally produced by hydrogenation of phenol, but in 1972 additional capacity was added, built to a DSM design in which hot liquid cyclohexane was partially oxidised by compressed air. The plant was intended to produce 70,000 tpa (tons per annum) of caprolactam but was reaching a rate of only 47,000 tpa in early 1974. Government controls on the price of caprolactam put further financial pressure on the plant.[2]

It was a failure of this plant that led to the disaster. A major leak of liquid from the reactor circuit caused the rapid formation of a large cloud of flammable hydrocarbon. When this met an ignition source (probably a furnace at a nearby hydrogen production plant) there was a massive fuel-air explosion. The plantcontrol room collapsed, killing all 18 occupants. Nine other site workers were killed, and a delivery driver died of a heart attack in his cab. Fires started on-site which were still burning ten days later. Around 1,000 buildings within a mile radius of the site (in Flixborough itself and in the neighbouring villages.

The plant was re-built but cyclohexanone was now produced by hydrogenation of phenol (Nypro proposed to produce the hydrogen from LPG; in the absence of timely advice from the Health and Safety Executive (HSE) planning permission for storage of 1200 te LPG at Flixborough was initially granted subject to HSE approval, but HSE objected); as a result of a subsequent collapse in the price of nylon it closed down a few years later. The site was demolished in 1981, although the administration block still remains. The site today is home to the Flixborough Industrial Estate, occupied by various businesses and Glanford Power Station.

The foundations of properties severely damaged by the blast and subsequently demolished can be found on land between the estate and the village, on the route known as Stather Road. A memorial to those who died was erected in front of offices at the rebuilt site in 1977. Cast in bronze, it showed mallards alighting on water. When the plant was closed, the statue was moved to the pond at the parish church in Flixborough. During the early hours of New Year's Day 1984, the sculpture was stolen. It has never been recovered but the plinth it stood on, with a plaque listing all those who died that day, can still be found outside the church.

The cyclohexane oxidation process is still operated in much the same plant design in the Far East

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Green Chemistry

UNIT II

S.No	Question	a	b	c	d	Answer
1.	The audible frequency range of ultrasounds	less than 16KHZ	greater than 16KHZ	equal to 16 KHZ	16MHZ	greater than 16KHZ
2.	Exampes for Microwave-assisted reactions in water	Hofmann Elimination	*Reaction of Carboxylic Acid and Alcohol*	Deacetylation	oxidation of alcohols by solid potassium permanganate	Hofmann Elimination
3.	Example for Microwave-Assisted Reactions in Organic Solvents	Hofmann Elimination	Reaction of Carboxylic Acid and Alcohol	Deacetylation	oxidation of alcohols by solid potassium permanganate	Reaction of Carboxylic Acid and Alcohol
4.	Example for microwave assisted solvent free reaction	Hofmann Elimination	*Reaction of Carboxylic Acid and Alcohol*	Deacetylation	oxidation of alcohols by solid potassium permanganate	Deacetylation
5.	Example for an ultrasound assisted reaction	Hofmann Elimination	*Reaction of Carboxylic Acid and Alcohol*	Deacetylation	oxidation of alcohols by solid potassium permanganate	oxidation of alcohols by solid potassium permanganate
6.	Hofmann Elimination reaction is an example for	Microwave-Assisted Reactions in	microwave assisted solvent free	Microwave-assisted reactions in water	ultrasound assisted reaction	Microwave-assisted reactions in water

		Organic Solvents	reaction			
7.	*Reaction of Carboxylic Acid and Alcohol is an example for*	Microwave-Assisted Reactions in Organic Solvents	microwave assisted solvent free reaction	Microwave-assisted reactions in water	ultrasound assisted reaction	Microwave-Assisted Reactions in Organic Solvents
8.	Deacetylation reaction is an example for	Microwave-Assisted Reactions in Organic Solvents	microwave assisted solvent free reaction	Microwave-assisted reactions in water	ultrasound assisted reaction	microwave assisted solvent free
9.	oxidation of alcohols by solid potassium permanganate	Microwave-Assisted Reactions in Organic Solvents	microwave assisted solvent free reaction	Microwave-assisted reactions in water	ultrasound assisted reaction	ultrasound assisted reaction
10	quaternary ammonium salts are heated at high temperature to yield α – keto alkenes. This is	Hofmann Elimination	esterification	Deacetylation	oxidation of alcohols by solid potassium permanganate	Hofmann Elimination
11	benzoic acid and n-propanol on heating in a microwave oven in presence of sulphuric acid to give propyl benzoate. This is	Hofmann Elimination	esterification	Deacetylation	oxidation of alcohols by solid potassium permanganate	esterification
12	solid support like silica gel, alumina or phyllosilicate are used in	Hofmann Elimination	esterification	Deacetylation reactions	oxidation of alcohols by solid potassium permanganate	Deacetylation reactions
13	solid support like silica gel, alumina or phyllosilicate are used in	Microwave-Assisted Reactions in Organic Solvents	microwave assisted solvent free reaction	Microwave-assisted reactions in water	ultrasound assisted reaction	microwave assisted solvent free reactions
14	Example for deacylation reaction is	benzoic acid and n-propanol on heating in a microwave oven in presence of sulphuric acid to	quaternary ammonium salts are heated at high temperature to	Benzaldehyde diacetate is converted into benzaldehyde in	Benzaldehyde is converted inti benzaldehyde diacetata in a	Benzaldehyde diacetate is converted into benzaldehyde in

		give propyl benzoate.	yield α – keto alkenes.	presence of neutral alimuna in microwave oven	microwave oven	presence of neutral alimuna in microwave oven
15	microwaves have wavelengths between	1cm and 1m	1m and 1 dm	400 nm and 700 nm	less than 16KHZ	1cm and 1m
16	The frequencies of microwaves are between	30GHz and 300 Hz	less than 16KHZ	20 KHz and 100 KHz	30GHZ and 100GHZ	30GHz and 300 Hz
17	household and industrial microwave oven is regulated, at a fixed frequency of	16KHz	2.45 GHz.	30 KHz	100 MHz and 400 MHz	2.45 GHz.
18	microwave reactions involve selective absorption of electromagnetic waves by	Polar molecules	Non polar molecules	Symmetrical hydrocarbons	Ethane	Polar molecules
19	The container which can be used in a microwave oven is	Teflon	Ordinary glass	plastic	fiber	Teflon
20	The container which can be used in a microwave oven is	Teflon containers	Ordinary glass containers	Plastic containers	Fiber containers	Teflon containers
21	The container which can be used in a microwave oven is	polystyrene containers	Ordinary glass containers	Plastic containers	Fiber containers	polystyrene containers
22	Which cannot be used as a container in an microwave oven	Teflon	Polystyrene container	Ceramic containers	Metallic containers	Metallic containers
23	In Microwave-Assisted Reactions in Organic Solvents The solvent should have	volatility	Boiling point less than the reaction temperature	Dipole moment	Specific gravity	Dipole moment
24	In Microwave-Assisted Reactions in Organic Solvents The solvent should have	volatility	Boiling point 20 degrees higher than the reaction temperature	Dipole moment	Specific gravity	Boiling point 20 degrees higher than the reaction temperature
25	Which solvent can be used in	n-hexane	Petroleum ether	N,N-dimethyl	n-octane	N,N-dimethyl

	microwave assisted reactions			formamide		formamide
26	Which is not a suitable solvent for a microwave assisted reaction	benzene	N,N-dimethyl formamide	ethanol	dichloromethane	benzene
27	Why benzene cannot be used as a solvent in MW assisted reactions, because	It is a polar molecule	Do not have a dipole moment	It is an assymetric molecule	It do nt has specific gravity	Do not have a dipole moment
28	In designing a green synthesis, the starting materials should be	Hazardous substances	Non renewable substances	Renewable materials	Flammable solvents	Renewable materials
29	Which is not an advantage in using a catalyst for a reaction	Better yields	reaction becomes feasible in those cases where no reaction is normally possible	Selectivity enhancement	The reaction takes place slowly	The reaction takes place slowly
30	The traditional catalyst hydrogen fluoride has been replaced by	fluorided silica-alumina catalyst	Lewis acids	Lewis bases	Oxidative catalysts	fluorided silica-alumina catalyst
31	The traditional catalyst Lewis acids has been replaced by	fluorided silica-alumina catalyst	Encapsulated Lewis acids	Lewis bases	Oxidative catalysts	Encapsulated Lewis acids
32	Ultrasound waves are produced by	Change in dipole moment	Piezoelectric effect	Seeback effect	Change in optical density	Piezoelectric effect
33	A device by which electrical or mechanical energy can be converted into sound energy is called.	Cathode ray emitter	ultrasonic transducer	magnetometer	cytometer	ultrasonic transducer
34	The catalyst used in biocatalysis is	Enzyme	Light	Basic catalysts	Microencapsulated lewis acids	Enzyme
35	The catalyst used in photocatalysis is	Enzyme	Light	Basic catalysts	Microencapsulated lewis acids	Light
36	The catalyst used in	Enzyme	Light	Basic catalysts	Microencapsulated	Basic catalysts

	alkylation of phenol, side chain alkylation				lewis acids	
37	In greener reaction conditions the catalyst used in the reactions like Michael, Friedel Crafts, Mannich, Imino aldo reactions	Enzyme	Light	Basic catalysts	Microencapsulated lewis acids	Microencapsulated lewis acids
38	Microencapsulated lewis acids are used as catalyst in	Michael, Friedel Crafts, Mannich, Imino aldo reactions	alkylation of phenol, side chain alkylation	Photocatalysis reactions	biocatalysis	Michael, Friedel Crafts, Mannich, Imino aldo reactions
39	Basic catalysts are used in	Michael, Friedel Crafts, Mannich, Imino aldo reactions	alkylation of phenol, side chain alkylation	Photocatalysis reactions	biocatalysis	alkylation of phenol, side chain alkylation
40	Light is used as a catalyst in	Michael, Friedel Crafts, Mannich, Imino aldo reactions	alkylation of phenol, side chain alkylation	Photocatalysis reactions	biocatalysis	Photocatalysis reactions
41	Enzymes are used as catalysts in	Michael, Friedel Crafts, Mannich, Imino aldo reactions	alkylation of phenol, side chain alkylation	Photocatalysis reactions	biocatalysis	biocatalysis
42	The enzyme which is used to converts sucrose into glucose and fructose	Invertase	zymase	pencylase	ligase	Invertase

43	The enzyme which is used to converts glucose and fructose into ethanol	Invertase	zymase	'Penacylase	ligase	zymase
44	The enzyme used to convert Penicillin into 6-APA	Invertase	zymase	'Penacylase	ligase	'Penacylase
45	Which reactions are chemoselective, regioselective and stereoselective	Michael, Friedel Crafts, Mannich, Imino aldo reactions	alkylation of phenol, side chain alkylation	Photocatalysis reactions	biocatalysis	biocatalysis
46	Enzymes which catalyse oxidation-reduction reactions	Oxidoreductases	Transferases	Hydrolases	Isomerases	Oxidoreductases
47	enzymes catalyse the transfer of various functional groups	Oxidoreductases	Transferases	Hydrolases	Isomerases	Transferases
48	enzymes catalyse hydrolytic reactions	Oxidoreductases	Transferases	Hydrolases	Isomerases	Hydrolases
49	catalyses addition to double bond	Oxidoreductases	Transferases	Hydrolases	ligases	ligases
50	Oxidoreductases	Enzymes which catalyse oxidation-reduction reactions	enzymes catalyse the transfer of various functional groups	enzymes catalyse hydrolytic reactions	catalyses addition to double bond	Enzymes which catalyse oxidation-reduction reactions
51	Transferases	Enzymes which catalyse oxidation-reduction reactions	enzymes catalyse the transfer of various functional groups	enzymes catalyse hydrolytic reactions	catalyses addition to double bond	enzymes catalyse the transfer of various functional groups
52	Hydrolases	Enzymes which catalyse oxidation-reduction reactions	enzymes catalyse the transfer of various functional groups	enzymes catalyse hydrolytic reactions	catalyses addition to double bond	enzymes catalyse hydrolytic reactions

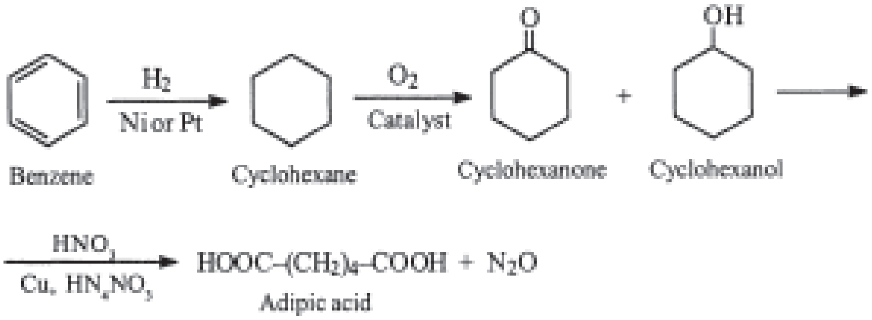
53	Ligases are	Enzymes which catalyse oxidation-reduction reactions	enzymes catalyse the transfer of various functional groups	enzymes catalyse hydrolytic reactions	catalyses addition to double bond	catalyses addition to double bond
54	**The toxic gases escaped from the Union Carbide pesticide plant in Bhopal, India**	Methyl cyanide	Hydrogen sulphide	Carbon monoxide	Sulphur dioxide	Methyl cyanide
55	The insecticide produced in **Union Carbide pesticide plant in Bhopal**	Carbaryl	DDT	Malathion	Copper sulphate	Carbaryl
56	The chemical name for carbaryl is	1- naphthol N-methylcarbamate	Methyl cyanide	Malathion	Copper sulphate	1- naphthol N-methylcarbamate
57	The compound produced in **Flixborough**	caprolactam was produced from cyclohexanone	Carbaryl	Malathion	Copper sulphate	caprolactam was produced from cyclohexanone
58	PatemoBuchi Reaction is a	Photochemical reaction	Biocatalytic reaction	Basic catalytic reaction	Acid catalytic reaction	Photochemical reaction
59	Example for a Photochemical reaction	PatemoBuchi Reaction	Michael addition	Hoffmann elimination	Clemenson reduction	PatemoBuchi Reaction
60	Enzymes which catalyse various types of isomerisation	Oxidoreductases	Transferases	Hydrolases	Isomerases	Isomerases

UNIT III
Examples of Green Synthesis/ Reactions and some real world cases

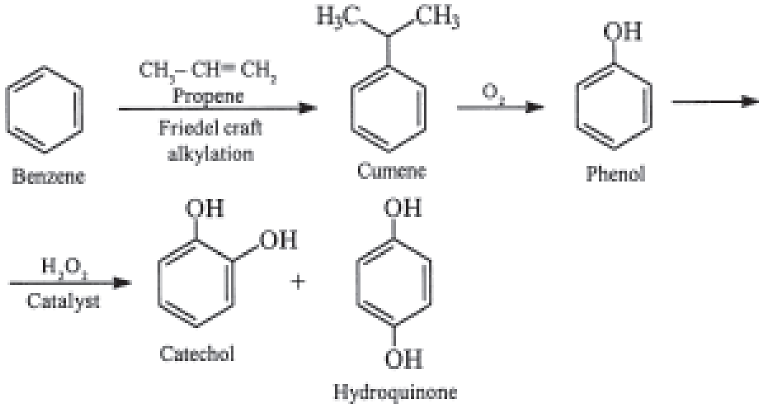
1. Green Synthesis of the following compounds: adipic acid, catechol, disodiumimino diacetate (alternative to Strecker synthesis)
2. Microwave assisted reactions in water: Hofmann Elimination, methyl benzoate to benzoic acid, oxidation of toluene and alcohols; microwave assisted reactions in organic solvents Diels-Alder reaction and Decarboxylation reaction
3. Ultrasound assisted reactions: sonochemical Simmons-Smith Reaction (Ultrasonic alternative to Iodine)
4 Surfactants for carbon dioxide – replacing smog producing and ozone depleting solvents with CO_2 for precision cleaning and dry cleaning of garments.
5 Designing of Environmentally safe marine antifoulant.

Synthesis of Adipic Acid, Catechol and 3-Dehydroshikimic Acid (a Potential Replacement for BHT)

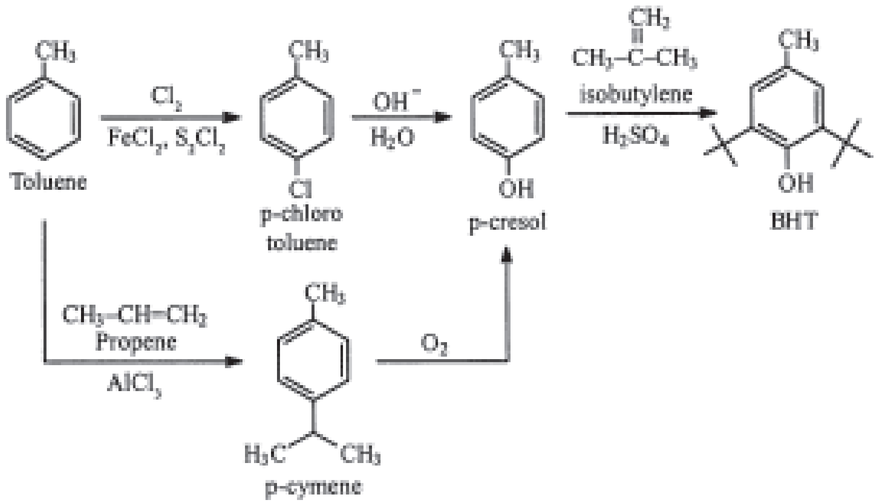
Adipic acid is required in large quantities (about 1 billion kg a year) for the synthesis of nylon, plasticizers and lubricants. Conventionally, adipic acid is made from benzene



Like adipic acid, catechol is also manufactured using benzene as the starting material. The procedure is given. As seen, both adipic acid and catechol are obtained from benzene, which causes environmental and health problem. Also, benzene is produced from non-renewable source. In addition, in the synthesis of adipic acid, nitrous oxide is generated as a byproduct, which contributes to the greenhouse effect as well as destruction of the ozone layer.

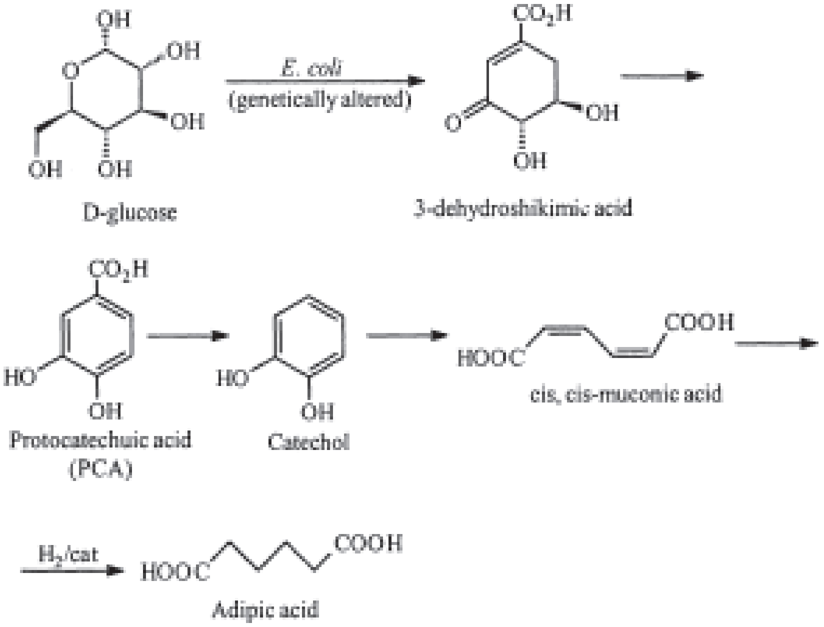


BHT is obtained from toluene (which unlike benzene is not carcinogenic but is toxic in nature) as shown



Scheme 4. Conventional synthesis of BHT

BHT (a potential replacement for BHT) has been developed by John W. Frost and Karen M. Draths starting with glucose and using a biocatalyst (genetically altered *E. coli* bacteria).

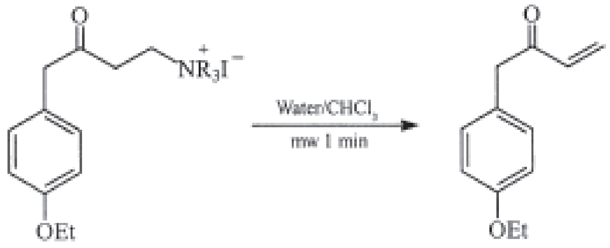


The above environmentally benign synthesis of catechol and adipic acid uses D-glucose (a non-toxic and a renuable resource) as the starting material. Also the synthesis is conducted in water instead of organic solvents. The reaction can also be used to stop at either catechol stage or at the adipic acid stage by using another genetically altered *E. coli*. It may be appropriate to say that in the above synthesis, use of unmodified *E. coli* gives the amino acids, L-phenylalanine, L-tyrosine and L-tryptophan via the formation of shikimic acid from dehydroshikimic acid

Microwave Assisted Reactions in Water

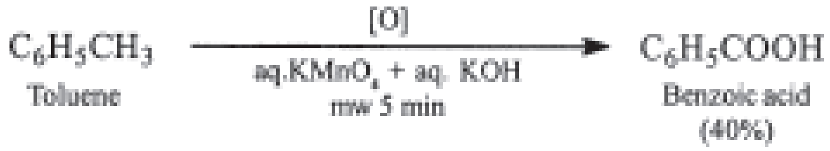
Hofmann Elimination

In this method, normally quaternary ammonium salts are heated at high temperature and the yield of the product is low. Use of microwave irradiation has led to high-yielding synthesis of a thermally unstable Hofmann elimination product. In this water-chloroform system is used.



Oxidation of Toluene

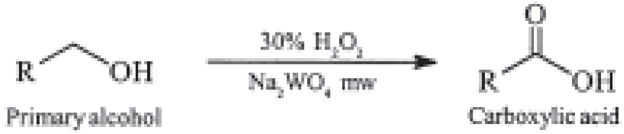
Oxidation of toluene with KMn04 under normal conditions ofrefluxing takes 10-12 hr compared to reaction in microwave conditions5, which takes only 5 min and the yield is 40%.

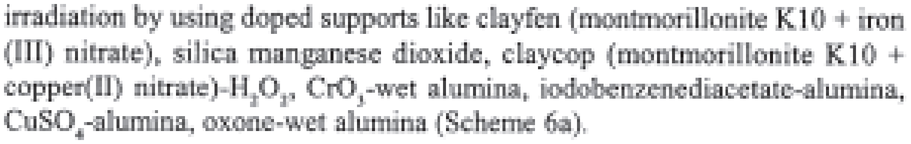


$$C_6H_5CH_3 \xrightarrow[\text{aq.KMnO}_4 + \text{aq. KOH, mw 5 min}]{[O]} C_6H_5COOH$$

Oxidation 0f Alcohols

A number of primary alcohols can be oxidised to the corresponding carboxylic acid using sodium tungstate as catalyst in 30% aqueous hydrogen peroxide.



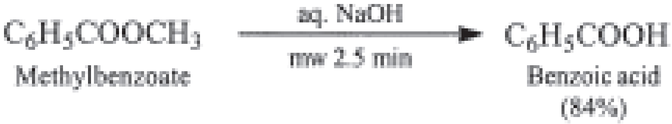


irradiation by using doped supports like clayfen (montmorillonite K10 + iron (III) nitrate), silica manganese dioxide, claycop (montmorillonite K10 + copper(II) nitrate)-H_2O_2, CrO_3-wet alumina, iodobenzenediacetate-alumina, $CuSO_4$-alumina, oxone-wet alumina (Scheme 6a).

R, R$_1$ = various aromatic, aliphatic and heterocyclic groups

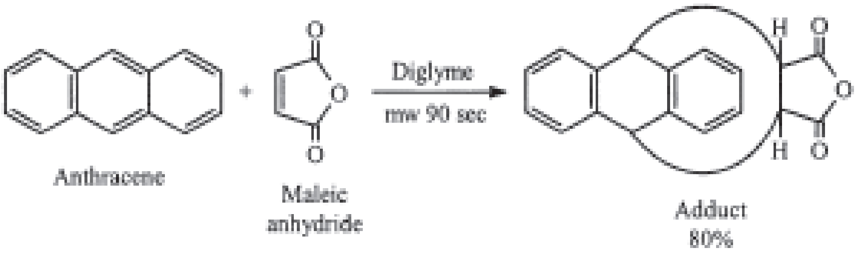
Hydrolysis of Methylbenzoate to Benzoic Acid (Saponification)

Saponification of methylbenzoate in aqueous sodium hydroxide under microwave conditions (2.5 min) gives5 84% yield of the benzoic acid



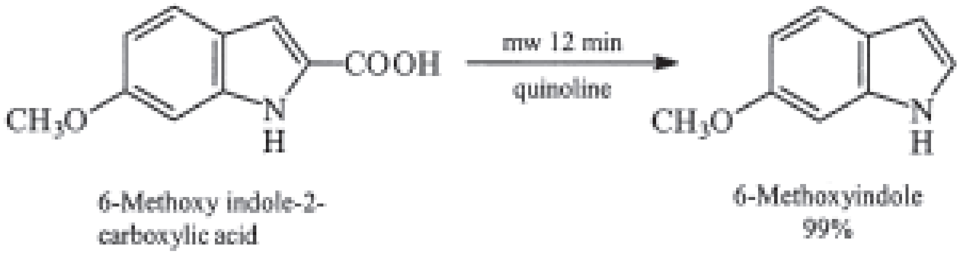
Diels Alder Reaction

The reaction involves 1,4-addition of an alkene (e.g., maleic anhydride) to a conjugated diene (e.g. anthracene) to form an adduct of six membered ring. Under usual conditions '1 the reaction requires a reflux period of 90 min. However, under microwave conditions3,12 diglyme is used as a solvent and 80% yield of the adduct is obtained in 90 sec.



Decarboxylation

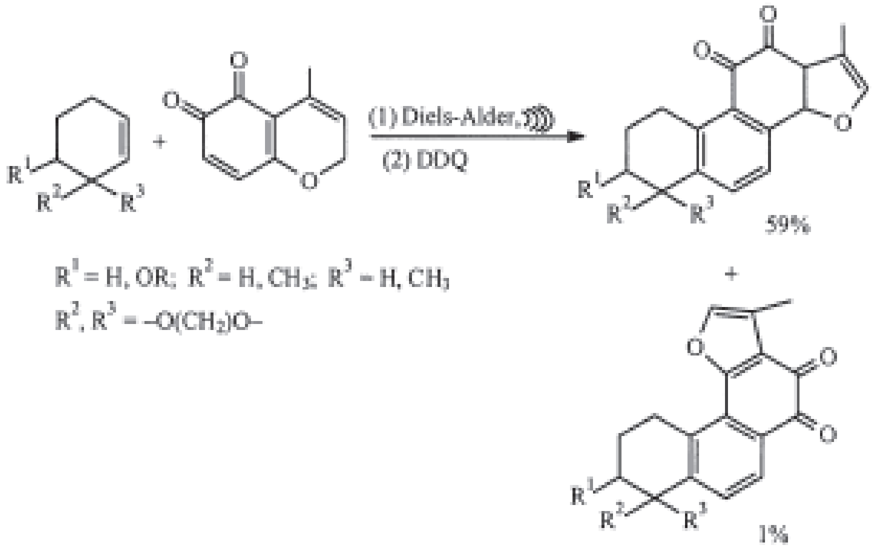
Conventional decarboxylation of carboxylic acids involve refluxing in quinoline in presence of copper chromite and the yields are low. However, in the presence of microwaves, decarboxylation takes place in much shorter time



Simmons-Smith Reaction

In this reaction, sonochemically activated zinc and methylene iodide are used. The generated carbene adds on to an olefinic bond to give 91 % yield of the cyclopropane derivative compared (Scheme 25) to 51 % yield by the normal route.

The' above method can be scaled Up41 and has several advantages. The reagent used, ZnlCH2I2 is known as Simmons-Smith reagent. Ketones on reaction with Simmons-Smith reagent results in methylenation of carbonyl group (Scheme 26). Normally such methylenation of carbonyl group requires complex reagents. It can now be accomplished by sonication.



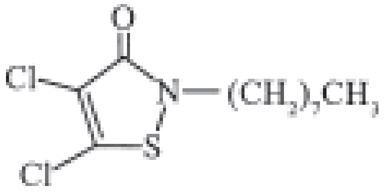
Scheme 24

Scheme 25

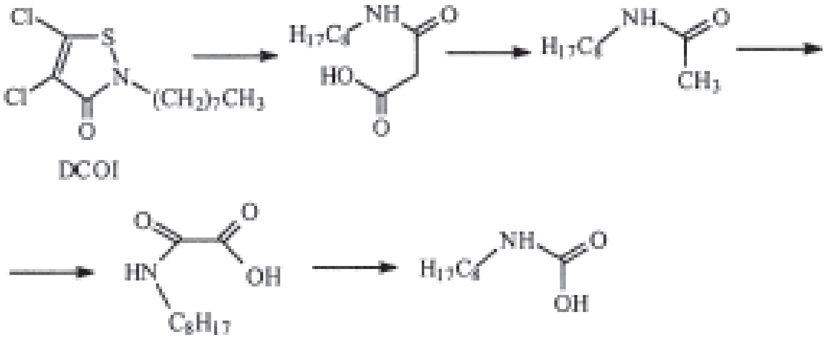
R = R' = alkyl
R = alkyl, R' = H

An Environmentally Safe Marine Antifoulant

The antifouling agents are used on boat hulls to reduce the build up of marine organisms (such as barnacles, algae, plants and diatoms). A build up of these organism causes additional costs involved in increased fuel consumption and cleaning time. Tributyltin (TBT) compounds were earlier used as antifoulant agents. One of the main drawbacks was their persistence in the environment and bioaccumulation in various nontargent marine organisms. Rohm and Haas has developed the use of 4,5-dichloro-2-n-octyl-4- isothiazolin-3-one (DCOI) as an antifouling agent



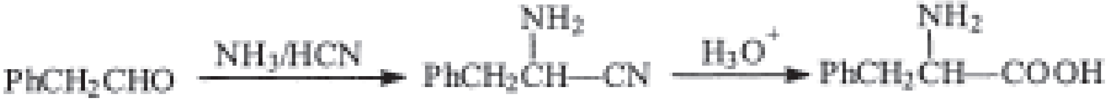
Unlike tributyltinoxide (TBTO), the DCOI is far less persistent in marine environments. Also in the case of DCOI, the product of the metabolism are non toxic



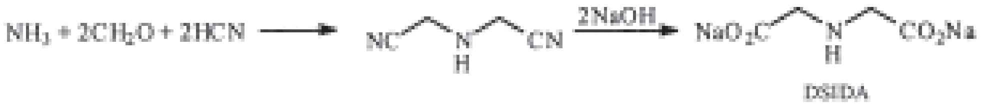
Metabolic products of DCOI

Strecker Synthesis

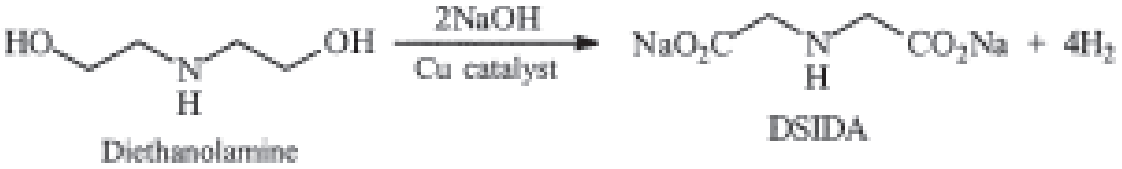
This method is used for the synthesis of amino acids by the reaction of an aldehyde with ammonia followed by reaction with HCN to give a-aminonitrile, which on hydrolysis give the corresponding amino acid



The a-aminonitrile can also be obtained by the treatment of the aldehydes with HCN followed by reaction of the formed cyanohydrin with ammonia. This method is known as Erlenmeyer modification. 84 A more convenient route is to treat the aldehyde in one step with ammonium chloride and sodium cyanide (this mixture is equivalent to ammonium cyanide, which in tum dissociate into ammonia and HCN). This procedure is referred to as the Zelinsky-Stadnikott modification.85 The final step is the hydrolysis ofthe intermediate a-arninonitrile under acidic or basic conditions. Using strecker synthesis, disodium iminodiacetate (DSIDA) an intermediate for the manufacture is Monsantos' Roundup (herbicide) was synthesized.



In the above synthesis hydrogen cyanide, a hazardous chemical is used and this requires special handling to minimise the risk to workers and the environment. An alternative green synthesis of DSIDA was developed by Monsanto.



The new method avoids the use of HCN and H*CHO* and is safer to operate.

Carbon Dioxide: An Alternative Solvent

- Preferable to VOCs and Halogenated Organic Compounds

- Nonflammable, nontoxic, and chemically unreactive
- Available as a cheaply recovered byproduct from the production of ammonia and from natural gas wells
- The used carbon dioxide can easily be recovered, purified, and reused

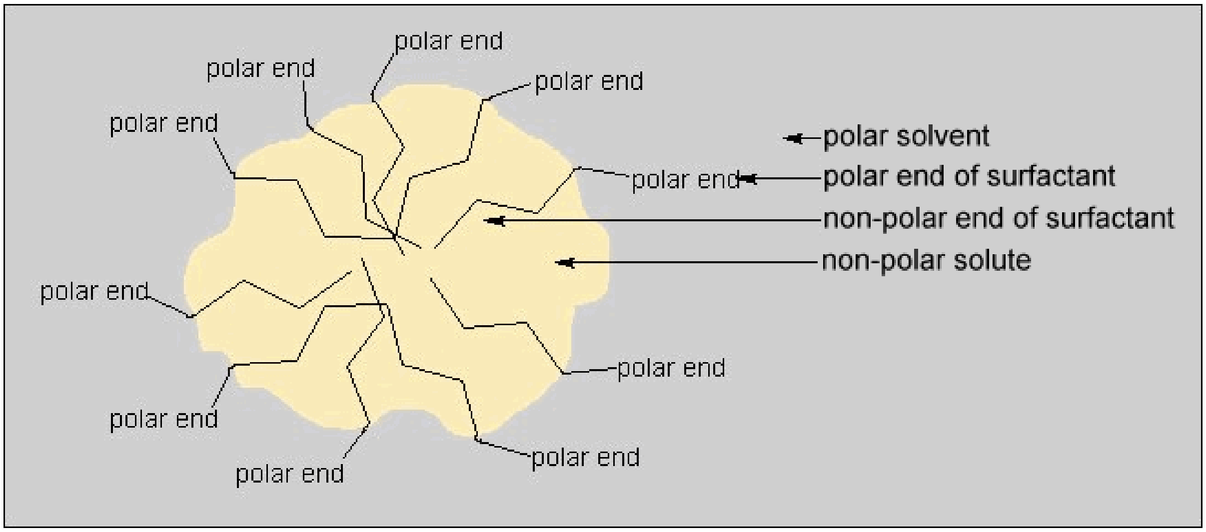
Solubility of Substances in CO2

- Carbon dioxide a non polar molecule since the dipoles of the two bonds cancel one another.
- Carbon dioxide will dissolve smaller non polar molecules ¬ hydrocarbons having less than 20 carbon atoms ¬ other organic molecules such as aldehydes, esters, and ketones
- But it will not dissolve larger molecules such as oils, waxes, grease, polymers, and proteins, or polar molecules.

Surfactants

- A molecule that contains a polar portion and a non polar portion.
- A surfactant can interact with both polar and non polar molecules.
- A surfactant increases the solubility of the otherwise insoluble substances.
- In water, surfactant molecules tend to cluster into a spherical geometry ¬ non polar ends on the inside of the sphere ¬ polar ends on the outside, These clusters are called micelles

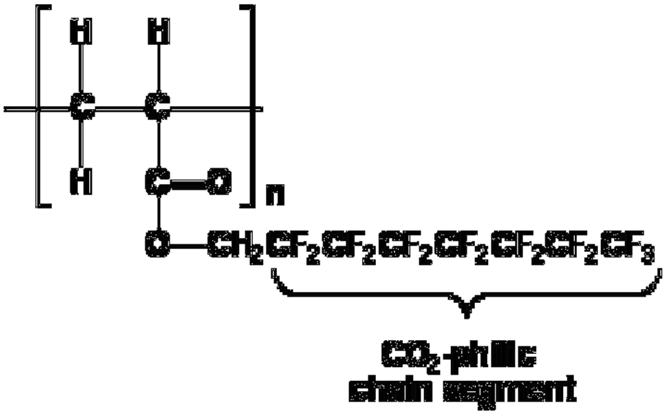
Micelle Structure of a Surfactant



A Surfactant for Liquid or Supercritical Fluid CO_2

- Must have both CO_2 -philic (CO_2 loving) and CO_2 -phobic functionality.

- In 1994, Joseph M. DeSimone of the University of North Carolina and North Carolina State University published his discovery that polymers such as that shown below are soluble in liquid or supercritical CO2



Polymers

- Molecule with a high molar mass (typically 10,000 to 10 6)

- Polystyrene is an example:

- n is the number of times the structure in brackets repeats itself (on average)

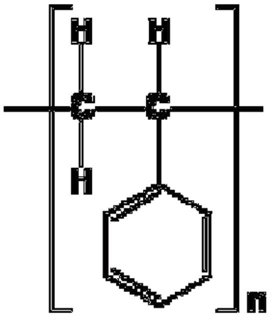
- n is called the number average degree of polymerization and is usually ≥1000

Copolymers

• A copolymer contains two different types of repeat units within the same polymer chain.

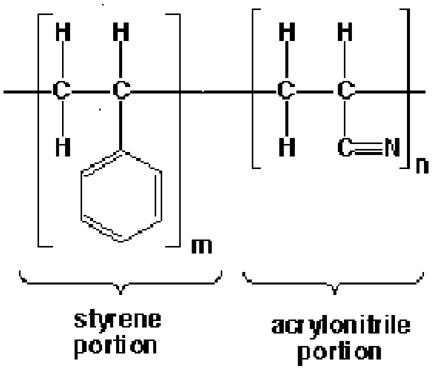
• A copolymer is not a blend of two different polymers, but instead the two monomers are covalently bonded along the length of the chain.

• Example of a copolymer of styrene and acrylonitrile:

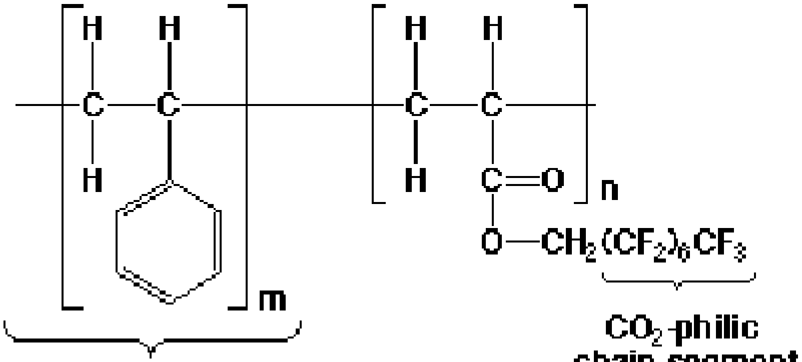


Possible Copolymer Sequencing Arrangements Using ‘S’ to represent the styrene monomers and ‘A’ to represent the acrylonitrile monomers: •Random Copolymer SASASAASASSAS •Block Copolymer SSSSSSAAAAAAA •Alternating Copolymer SASASASASASASA

Block Copolymers are Used to make a Surfactant for CO2 •



DeSimone synthesized copolymers w O2 -philic portion.

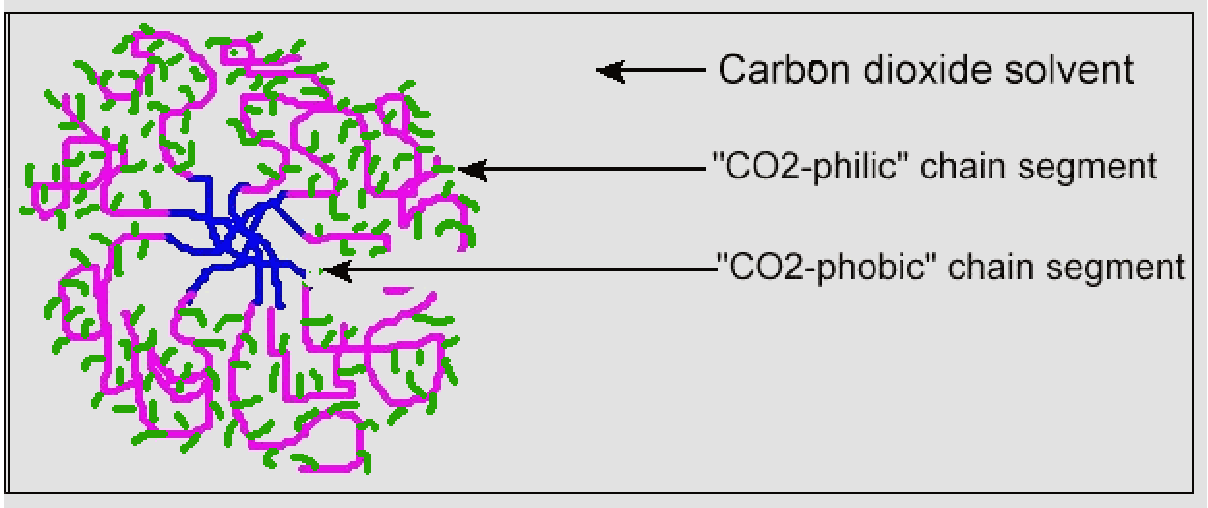


Current Use of CO2 Surfactants--Green Chemistry in ACTION • The

dry cleaning industry typically uses the solvent perchloroethylene (PERC), as the cleaning agent.

- 344 million lb of PERC were produced in the United States in 1998.
- The dry cleaning industry uses approximately 50% of the PERC produced each year ~ 172 million pounds of the solvent.

Mischell structure of co2 surfactant



Current Use of CO_2 Surfactants--Green Chemistry in ACTION

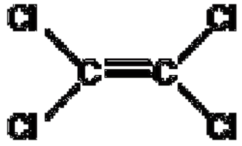
- EPA has classified PERC as a groundwater contaminant and a potential human health hazard.
- PERC is a suspected human carcinogen and a known rodent carcinogen.
- Breathing PERC for short periods of time can adversely affect the central nervous system.

- These effects are not likely to occur though at levels of PERC that are normally found in the environment, but people who work in the dry cleaning industry have the greatest risk for exposure.

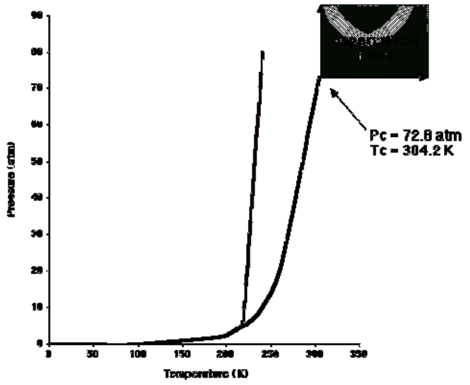
- Micell Technologies, a company founded in 1995, has made the CO_2 surfactant technology available commercially.

- Micell'sMicareô system is a commercial washing machine that utilizes CO_2 and a CO_2 surfactant instead of PERC, thereby eliminating the need for PERC.

- The franchise, Hangers, uses this technology.



Supercritical CO_2



The application on supercritical carbon dioxide (sc-CO2) as an alternative solvent to traditional organic ones, despite of its several desirable characteristics, is often hindered because CO2 is non-polar, and only dissolves small and apolar molecules. One way to overcome such limitation face to polar chemical species is to introduce specially-designed surfactants in the system. The sc-CO2-suitable surfactants are molecules composed of a CO2-philic part (generally containing a perfluorocarbon chain) and a CO2-phobic part (capable of solubilizing polar compounds). The first observations of aggregation of surfactants in sc-CO2 was has opened an intense research interest for surfactants capable of solubilizing polar substances in sc-CO2]. However, it is a well known that perfluorinated compounds, despite of high solubilities in scCO2, are persistent organic pollutants. So, since observations that oxygenated compounds could serve as substitutes for fluorinated compounds , new compounds has been synthesized and tested as potential amphiphiles to be used in sc-CO2 media.

Carbon dioxide is a component of the atmosphere and is essential to life. However, it is widely recognised that the increase in atmospheric CO2 levels due to industrial activity is the main cause of climate change. Ways of using the excess CO2 are thus being sought and one idea is that, under the right conditions, it could be used industrially as a solvent.

Benefits can be realised if CO2 gas is pressurised to condense it to form a liquid. If exhaust gas CO2 were liquefied then perhaps it might find use as an industrial solvent; this article explores the possibilities for such applications. In fact, CO2 can also be produced in a very special form, a supercritical fluid, which has unique properties that are beneficial for many industrial applications. However, it can be seen that if CO2 could be trapped and used in liquid (supercritical) form then it could solve many of the problems that contribute towards

The advantages of using supercritical fluids over normal liquid solvents can be realised once it is appreciated that solvent strength and density can be varied over a very wide range. This allows fine control over all physical properties such as viscosity, density, solubility parameter, dielectric constant and diffusivity though only modest changes in the temperature and pressure. Since the 1950s, the use of supercritical CO2 (scCO2) as a solvent has been investigated by academia and industry.

Although this ‘green’ scCO2 solvent has many desirable properties, technically speaking it is a very ‘weak’ solvent: the polarity, dielectric constant and dipole moment are less than that of most conventional organic solvents. Consequently, high-molecular-weight polymers, proteins and polar molecules are only sparingly soluble or even insoluble in scCO2. One effective way to make scCO2 able to dissolve high-molecularweight or polar compounds is by using suitable additives, or surfactants, to produce nanometresized domains in the scCO2 by forming micelles or microemulsions (Figure 1). The problem is the naturally very low solubilities of readily available surfactants with scCO2. Therefore, during the last two decades, many research groups have tried to design new surfactants compatible with scCO2.

To date, the most effective compounds for this purpose contain high levels of fluorine in the molecules, which is needed to boost the solubility in scCO2 (Eastoe et al., 2006a). Unfortunately, fluorinated surfactants are not a good way to solve the problem, being both expensive and environmentally harmful. Some efforts have been made to investigate fluorine-free surfactants (Eastoe et al., 2006b) for CO2. The significance is that these surfactants are generally cheaper and less environmentally hazardous than the fluorinebearing analogues There is currently great interest in designing and understanding the nature of fluorine-free CO2-compatible hydrocarbon surfactants. Research has shown that branched and methylated surfactants and those with a ‘stubby’ molecular shape, can be used to stabilise water-in-CO2 (w/c) microemulsions (Figure 1), presumably because of higher solvation and lower intermolecular interactions. With the underlying philosophy and strategy previously explored, some success has been achieved at the University of Bristol with new CO2-philic hydrocarbon surfactants, including highly branched and oxygenated surfactants (Table 1) (Eastoe et al., 2006a; 2006b). The special aspects of the chemical structures that give rise to high solubility in scCO2 are described later in this chapter.

CO2-soluble micelles and water-in-CO2 (w/c) microemulsions

Solubility is very important for potential applications in the food and pharmaceutical industries, where health and safety legislation places severe restrictions on solvents that can be used. By addition of a soap-like surfactant toscCO2, the resulting formation of microemulsions helps to overcome these limitations of solubility in scCO2, making it possible to dissolve highly polar, ionic and also high-molecular-weight species in the internal domains formed (Figure 1). A very useful feature of w/c microemulsions is the creation of polar water pool domains inside the bulk CO2 (Figure 1). These domains (~2–5nm, also called reverse micelles) act as pools for dissolving polar molecules. Addition of these surfactants can change scCO2 from being rather a weak solvent into a very useful ‘universal solvent’. One other important problem to overcome is the low viscosity of scCO2. Since interesting and potentially valuable applications are envisaged for scCO2 as a fluid for enhanced oil recovery (McHugh and Krukonis, 1994), where high viscosities are essential, ways must be found to enhance its viscosity. This can only be achieved by designing CO2-soluble additives that can serve as viscosity modifiers, such as surfactants and polymers. A microemulsion is a thermodynamically stable dispersion of two immiscible liquids (such as oil/ water or scCO2/water) stabilised by surfactants. Surfactants adsorb at the fluid–fluid interface and reduce the interfacial tension via a balance of hydrophilic and hydrophobic interactions. The unique properties and chemical structures of surfactants enable them to form spherical aggregates by using hydrophilic parts known as head groups, while hydrophobic parts called tails interact with the non-polar solvent (as discussed later, this surfactant–solvent interaction is very important for solubility). As mentioned above, these surfactant aggregates in microemulsions are also called reverse micelles (Figure 1). Microemulsions and reverse micelles have the remarkable property of solubilising polar compounds such as water by providing stable microenvironments in the background scCO2 medium (Eastoe et al., 2006a). Systems of this kind thus have the potential to enhance solubility in scCO2. As such, w/c microemulsions are ideal candidates as universal solvents for use in fields such as pharmaceutical, food and cosmetic industries. Although there are some promising indications concerning the aggregation of cholesterol in scCO2, early studies on a great number of commercial surfactant–water–scCO2 systems have, disappointingly, not found any evidence for micelle formation (Eastoe et al., 2006a). Based on these findings, it was concluded that most commercially available ionic and non-ionic surfactants are almost entirely ineffective for w/c microemulsions. The main factor contributing to this is poor interactions of the surfactants of this type with scCO2, limiting the ability to stabilise the necessary micellar association structures. Because of these problems, it was necessary to design and synthesise highly scCO2-soluble surfactant molecules, which were fluorine-bearing fluorosurfactants (Hoefling, Enick and Beckman, 1991). This breakthrough proved that modification by inserting fluorinated groups into the surfactant alkyl chains provides favourable interactions between the tails and the external scCO2 solvent medium. In fact, it is known that fluorine-bearing organic compounds are much more soluble in scCO2 than molecules that contain carbon and hydrogen only. The most effective compounds reported so far for stabilisation of w/c microemulsions are partially or fully fluorinated surfactants (Table 3) (Eastoe et al., 2006a), particularly fluorinated analogues of the commercially available common hydrocarbon compound AOT (see Table 1 for molecular structure and chemical name). Although these fluorinated surfactants are very successful in scCO2, their environmental and biological persistence and their expense have prevented use in commercial applications. Thus, less expensive, biodegradable and more economical CO2-philic surfactants are needed and this is the subject of the following section.

Design of hydrocarbon CO2-philic surfactants

Research efforts continued and it become apparent that, in order to advance the field, a basic understanding of solvation of the surfactant tails by CO2 was needed. The first spectroscopic evidence for specific CO2–surfactant interactions was obtained by Dardin, DeSimone and Samulski (1998). The results showed that favourable van der Waals intermolecular interactions take place between fluorinated surfactants and CO2, highlighting the importance of specific tail–fluid interactions. Even though arguments about the exact nature of the interactions between CO2 and fluorosurfactants continue, favourable interactions between surfactant tails and CO2 are understood to be the key factor in designing new surfactants for CO2.Liu et al. (2001) investigated the solubility of the hydrocarbon (fluorine-free) surfactant Dynol- 604 in scCO2 and microemulsion formation. (The molecular structure of Dynol-604 is a trade secret.) The results showed that Dynol-604 can dissolve in CO2 up to 5wt%. Water loading to generate reverse micelles in CO2–Dynol-604 mixtures was achieved up to 0.6wt% of added water by controlling pressure and temperature. The solubility and water-loading in scCO2 of the non-fluorinated Ls-36 and Ls-45 surfactants (Table 4) were studied by the same group. Comparing surfactant structures, Ls-36 has three hydrophilic ethylene oxide (EO) groups and six hydrophobic propylene oxide (PO) groups, whereas Ls-45 has four EO groups and five PO groups. The results showed that both surfactants are quite soluble in CO2, at approximately 4wt% (pressure 19–22MPa and temperature 37–47°C). Raveendran and Wallen (2002) reported that the specially modified acylated (Ac) sugars α- and β-1,2,3,4,6-pentaacetyl-D-glucose and β-1,2,3,4,6-pentaacetyl-D-galactose (Table 4) exhibit high solubilities in scCO2. The strategy for enhancing solubility involves using carbonyl groups in the Ac parts of the adapted solutes. The high solubility was attributed to Lewis acid–Lewis base interactions between CO2 and the CO2-philic sugars, with the carbonyl groups providing Lewis base functionality (Eastoe et al., 2006a).

Specific beneficial interactions between CO2 and the carbonyl groups were confirmed by spectroscopic studies. The finding demonstrates favourable interactions betweenCO2 and acetylated groups, especially the pendent carbonyl parts. The design of efficient hydrocarbon CO2-philic surfactants can be achieved using the template of AOT (Table 1), a common commercially available surfactant that is frequently used for reverse micelle formation in a variety of organic solvents (Eastoe et al., 2006a). Unfortunately, normal AOT is incompatible with CO2, but by subtle modifications of the alkyl tails it can be coerced to dissolve in CO2 (Eastoe et al., 2001). This class of surfactants can be readily synthesised from inexpensive, commercially available reagents by a well-documented two-step reaction. The major rationale in designing hydrocarbon surfactants is to increase the density of the terminal CO2-philic methyl groups. This is the region where CO2 comes into intimate contact with surfactant molecules, and optimising the surfactant–CO2 solvent intermolecular interactions in this 'chain tip' region is now known to be of key importance for generating CO2-soluble surfactants. Based on this approach, the twin-tailed, branched, hydrocarbon-based ionic surfactant AOT4 (Table 1) was designed and synthesised, and it was found to have good CO2 compatibility and to form dry reverse micelles in pure CO2 (50MPa, 33°C) (Eastoe et al., 2001). The results revealed that molecular structures with branched and pendent methyl groups (chain tips) serve to boost compatibility in scCO2.Furthermore, the methylation of chain tips and addition of carbonyl functional groups in the surfactant (Eastoe et al., 2006b) successfully lead to CO2 solubility with another new tri-chain hydrocarbon surfactant, TC14 (Table 1) (Hollamby et al., 2009). The tri-chain TC14 exhibited good compatibility with CO2 resulting in homogeneous, optically transparent solutions under mild conditions (15MPa, 25°C). Compared with the di-chain analogue AOT4, the introduction of third surfactant chain has a dramatic improvement on surfactant–CO2 solvent intermolecular interactions, allowing the formation of reverse micelles in CO2 (Hollamby et al., 2009). Significantly, the addition of a third surfactant chain also improves the spacefilling efficiency of the surfactant tails, which is expected to favour formation of reverse micelles by providing better separation between CO2 and water across the interface (Mohamed et al., 2010). There are two main considerations if CO2-philic surfactants are to be commercialised: l the minimisation of raw material costs; l the reduction of working pressure, thereby reducing engineering demands on processing rigs and plant. Clearly, these are both of great importance for applications involving high volumes of scCO2. At current market prices and using scientific (notbulk) suppliers, the raw costs for di-CF4, the leading CO2-philic fluorosurfactant(Table 3), can be estimated at US$220 per gram. In contrast, the hydrocarbon analogues, loaded with terminal methyl groups, are much cheaper at around US$1 per gram for AOT4 and US$6 per gram for TC14.

KARPAGAM ACADEMY OF HIGHER EDUCATION

CLASS: III B.Sc CHEMISTRY COURSE NAME: GREEN CHEMISTRY

COURSE CODE: 16CHU603A UNIT: III (**Green Synthesis and real world cases**) BATCH:2018-2020

Green Chemistry

UNIT III

S.No	Question	a	b	c	d	Answer
1.	Adipic acid is used to prepare	Nylon	terylene	bakelite	plastic	Nylon
2.	Conventionally adipic acid is prepared from	Toluene	benzene	napthalene	anthracene	Benzene
3.	Conventionally catechol is prepared from	Toluene	benzene	napthalene	anthracene	Benzene
4.	In the preparation of adipic acid from benzene it also produces a green house gas	Nitrous oxide	Carbon monoxide	carbondioxide	chlorofluorocarbons	Nitrous oxide
5.	BHT is obtained from	Toluene	benzene	napthalene	anthracene	Toluene
6.	Starting with glucose and using a biocatalyst ---- can be prepared	Adipic acid	Catechol	nylon	terylene	Adipic acid
7.	Glucose is converted into adipic acid using a biocatalyst	Genetically modified E.Coli	Genetically modified S.aures	ligase	transferase	Genetically modified E.Coli
8.	In the environmentally benign synthesis of catechol, the starting material is	D-glucose	fructose	Sucrose	corn	D-glucose
9.	In the environmentally benign synthesis of adipic acid, the starting material is	D-glucose	fructose	Sucrose	corn	D-glucose
10.	Example for Hofmann	quaternary	Reaction of alcohol	Introduction of	Conversion of	quaternary

	Elimination reaction	ammonium salts are heated at high temperature	with an acid	aldehyde group into a aromatic ring	amides to amines	ammonium salts are heated at high temperature
11.	In the benign Hoffmann elimination reaction the quarternaryammonium salt is converted in to alkenes. The conditions used is	Water/Chloroform; MW 1 min,	Chloroform/alcohol MW 1 min	Water/DMF MW 1 min,	Water/DMSO MW 1 min,	Water/Chloroform; MW 1 min
12.	When toluene is oxidised with potassium permanganate, the product is	Benzoic acid	Benzyl alcohol	Phenyl cyanide	Phenyl isocyanide	Benzoic acid
13.	The reagent used to convert toluene into benzoic acid is	Hydrogen/Nickel	Palladium/sulphuric acid	potassium permanganate	Ferric chloride/aluminium chloride	potassium permanganate
14.	Oxidation of toluene with KMn04 under normal conditions of refluxing takes	5 min	10-12 hrs	Instantaneously	Reaction wont take place	10-12 hrs
15.	Oxidation of toluene with KMn04 under micro waves conditions of refluxing takes	5 min	10-12 hrs	Instantaneously	Reaction wont take place	5 min.
16.	A number of primary alcohols can be oxidised to the corresponding carboxylic acid under microwave conditions using	Hydrogen peroxide and sodium tungstate	Palladium/sulphuric acid	potassium permanganate	Ferric chloride/aluminium chloride	Hydrogen peroxide and sodium tungstate
17.	Saponification of methylbenzoate in aqueous sodium hydroxide under microwave conditions gives	Benzoic acid	Acetic acid	Methanoic acid	Benzyl alcohol	Benzoic acid
18.	Saponification of methylbenzoate in aqueous sodium hydroxide under microwave conditions gives benzoic acid. The time required	2.5 min	10-12 hrs	24 hrs	Reaction wont take place	2.5 min

	is					
19.	The reaction involving 1,4-addition of an alkene to a conjugated diene is called	Friedel crafts reaction	Riemer Tieman reaction	Diels-Alder Reaction	Hoffmann elimination	Diels-Alder Reaction
20.	The reaction involving addition of maleic anhydride to a anthracene to form an adduct of six membered ring	Friedel crafts reaction	Riemer Tieman reaction	Diels-Alder Reaction	Hoffmann elimination	Diels-Alder Reaction
21.	The reaction involving addition of maleic anhydride to a anthracene to form an adduct of six membered ring under normal conditions required	90 sec	No reaction	24 hrs	90 min	90 min
22.	The reaction involving addition of maleic anhydride to a anthracene to form an adduct of six membered ring under microwave conditions required	90 sec	No reaction	24 hrs	90 min	90 sec
23.	In the reaction involving addition of maleic anhydride to a anthracene to form an adduct of six membered ring under microwave conditions, the solvent used is	chloroform	water	DMF	diglyme	diglyme
24.	The reagent used for decarboxylation of carboxylic acids	quinoline in presence of copper chromite	Potassium dichromate	Potassium permanganate	Acetic acid	quinoline in presence of copper chromite
25.	6-methoxyindole carboxylic acid on decarboxylation gives	indole carboxylic acid	6-methoxyindole	methoxy carboxylic acid	No reaction	6-methoxyindole
26.	Conversion of an an alkene to form a cyclopropane using ultrasound waves is called	Simmon-Smith reaction	Riemer Tieman reaction	Diels-Alder Reaction	Hoffmann elimination	Simmon-Smith reaction
27.	In the Conversion of an an alkene to cyclopropane by	Sonochemicaaly activated Zn and	Cu/methylene iodide	quinoline in presence of	Potassium permanganate	Sonochemicaaly activated Zn and

	Simmon-Smith reaction the reagent used is	methelene iodide		copper chromite		methelene iodide
28.	Sonochemicaaly activated Zn and methelene iodide is used as a reagent in	Simmon-Smith reaction	Riemer Tieman reaction	Diels-Alder Reaction	Hoffmann elimination	Simmon-Smith reaction
29.	An organozinc carbenoid is involved in	Simmon-Smith reaction	Riemer Tieman reaction	Diels-Alder Reaction	Hoffmann elimination	Simmon-Smith reaction
30.	The antifouling agents are used on boat hulls to reduce the build up of	Marine organisms	bacteria	virus	musquitoes	Marine organisms
31.	Marine organisms include	barnacles, algae, plants	bacteria	virus	musquitoes	barnacles, algae, plants
32.	An example for conventional antifouling agent is	Tributyltinoxide (TBT)	4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI)	Methyl acetate	phenols	Tributyltin (TBT)
33.	An example for a greener antifouling agent is	Tributyltinoxide (TBT)	4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI)	Methyl acetate	phenols	4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI)
34.	The antifouling agent developed by Rohm and Haas	Tributyltinoxide (TBT)	4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI)	Methyl acetate	phenols	4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOI)
35.	The drawback of Tributyltinoxide (TBT) as an antifouling agent is	It is volatile in nature	It is not stable	persistence in the environment and bioaccumulation	It is biodegradable	persistence in the environment and bioaccumulation
36.	A method used for the synthesis of amino acids is	Strecker synthesis	Diels-Alder Reaction	Hoffmann elimination	Simmon-Smith reaction	Strecker synthesis
37.	the reaction of an aldehyde with ammonia followed by reaction with HCN to give a-	Strecker synthesis	Diels-Alder Reaction	Hoffmann elimination	Simmon-Smith reaction	Strecker synthesis

	aminonitrile, which on hydrolysis give the corresponding amino acid is called					
38.	Strecker synthesis is	Used for the synthesis of aminoacids	Synthesis of anti fouling agents	Synthesis of phenol using MW cnditions	Synthesis of adipic acid	Used for the synthesis of aminoacids
39.	The α-aminonitrile can be obtained by the treatment of the aldehydes with HCN followed by reaction with ammonia is	Strecker synthesis	Erlenmeyer modification	Zelinsky-Stadnikott modification	Monsantos' Roundup	Erlenmeyer modification
40.	to treat the aldehyde in one step with ammonium chloride and sodium cyanide to amino acids is	Strecker synthesis	Erlenmeyer modification	Zelinsky-Stadnikott modification	Monsantos' Roundup	Erlenmeyer modification
41.	Strecker synthesis is	the reaction of an aldehyde with ammonia followed by reaction with HCN to give a-aminonitrile, which on hydrolysis give the corresponding amino acid	The α-aminonitrile can be obtained by the treatment of the aldehydes with HCN followed by reaction with ammonia	to treat the aldehyde in one step with ammonium chloride and sodium cyanide to amino acids	disodium iminodiacetate (DSIDA) an intermediate to form an herbecide	the reaction of an aldehyde with ammonia followed by reaction with HCN to give a-aminonitrile, which on hydrolysis give the corresponding amino acid
42.	Erlenmeyer modification for synthesis of amino acids involve	the reaction of an aldehyde with ammonia followed by reaction with HCN to give a-aminonitrile, which on hydrolysis give the corresponding amino acid	The α-aminonitrile can be obtained by the treatment of the aldehydes with HCN followed by reaction with ammonia	to treat the aldehyde in one step with ammonium chloride and sodium cyanide to amino acids	disodium iminodiacetate (DSIDA) an intermediate to form an herbecide	The α-aminonitrile can be obtained by the treatment of the aldehydes with HCN followed by reaction with ammonia

43.		the reaction of an aldehyde with ammonia followed by reaction with HCN to give a-aminonitrile, which on hydrolysis give the corresponding amino acid	The α-aminonitrile can be obtained by the treatment of the aldehydes with HCN followed by reaction with ammonia	to treat the aldehyde in one step with ammonium chloride and sodium cyanide to amino acids	disodium iminodiacetate (DSIDA) an intermediate to form an herbecide	to treat the aldehyde in one step with ammonium chloride and sodium cyanide to amino acids
44.	Monsantos' Roundup is related to	the reaction of an aldehyde with ammonia followed by reaction with HCN to give a-aminonitrile, which on hydrolysis give the corresponding amino acid	The α-aminonitrile can be obtained by the treatment of the aldehydes with HCN followed by reaction with ammonia	to treat the aldehyde in one step with ammonium chloride and sodium cyanide to amino acids	Conversion of disodium iminodiacetate (DSIDA) an intermediate to form an herbecide	Conversion of disodium iminodiacetate (DSIDA) an intermediate to form an herbecide
45.	As an alternative synthesis of DSIDA Monsantos' company used	Diethanolamine and sodium hydroxide in presence of copper catalyst	HCN as a raw material	Benzaldehyde and actophenone	quinoline in presence of copper chromite	Diethanolamine and sodium hydroxide in presence of copper catalyst
46.	In the conventional synthesis of DSIDA Monsantos' company used	Diethanolamine and sodium hydroxide in presence of copper catalyst	HCN and HCHO as a raw material	Benzaldehyde and actophenone	quinoline in presence of copper chromite	HCN and HCHO as a raw material
47.	Carbon dioxide is	Nonflammable, nontoxic, and chemically unreactive	Flammable gas	Toxic gas	Highly reactive gas	Nonflammable, nontoxic, and chemically unreactive

48.	Carbon dioxide is	byproduct from the production of ammonia and from natural gas wells	Flammable gas	Toxic gas	Highly reactive gas	byproduct from the production of ammonia and from natural gas wells
49.	Carbon dioxide is	can easily be recovered, purified, and reused	Flammable gas	Toxic gas	Highly reactive gas	can easily be recovered, purified, and reused
50.	Which is not true with respect to carbon dioxide	can easily be recovered, purified, and reused	byproduct from the production of ammonia and from natural gas wells	Nonflammable, nontoxic, and chemically unreactive	Highly reactive gas	Highly reactive gas
51.	Carbon dioxide is a	Polar molecule	Positively charged molecule	Non polar molecule	Zwitterionic molecule	Non polar molecule
52.	Carbon dioxide will dissolve	smaller non polar molecules	smaller polar molecules	larger polar molecules	Only amino acids	smaller non polar molecules
53.	Carbon dioxide will dissolve	smaller polar molecules	larger polar molecules	Only amino acids	hydrocarbons having less than 20 carbon atoms	hydrocarbons having less than 20 carbon atoms
54.	Carbon dioxide will dissolve	smaller polar molecules	larger polar molecules	Only amino acids	organic molecules such as aldehydes, esters, and ketones	organic molecules such as aldehydes, esters, and ketones
55.	Which is not true about carbon dioxide	organic molecules such as aldehydes, esters, and ketones	hydrocarbons having less than 20 carbon atoms	smaller non polar molecules	Polymer molecules	Polymer molecules
56.	A surfactant can interact with	Polar molecules	Non polar molecules	both polar and non polar molecules	Neutral molecules	both polar and non polar molecules
57.	Surfactants contains a	Polar portion	Non-polar portion	Polar and non-polar	neutral	Polar and non-polar

				portions		portions
58.	In water, surfactant molecules tend to cluster into a	Octahedral geometry	spherical geometry	Squareplanar geometry	Linear geometry	spherical geometry
59.	In water, surfactant molecules forms micelles in which	non polar ends on the inside of the sphere	polar ends on the outside	non polar ends on the inside of the sphere and polar ends on the outside	Surfactants are neutral molecules	non polar ends on the inside of the sphere and polar ends on the outside
60.	Are Used to make a Surfactant for CO2	Blocked copolymers	Soap molecules	detergents	Amino acids	Blocked copolymers

UNIT IV

1. Rightfit pigment: synthetic azopigments to replace toxic organic and inorganic pigments.
2 An efficient, green synthesis of a compostable and widely applicable plastic (polylactic acid) made from corn.
3 Healthier fats and oil by Green Chemistry: Enzymatic interesterification for production of no Trans-Fats and Oils
4 Development of Fully Recyclable Carpet: Cradle to Cradle Carpeting

Rightfit pigments

Innovation and Benefits:

Rightfit azo pigments contain calcium, strontium, or barium; they replace conventional heavy-metal-based pigments containing lead, hexavalent chromium, or cadmium. Because of their low potential toxicity and very low migration, most of the Rightfit azo pigments have received U.S. Food and Drug Administration (FDA) and Canadian Health Protection Branch (HPB) approval for indirect food contact applications. By 2004, Engelhard expects to have replaced all 6.5 million pounds of its heavy-metal-based pigments with Rightfit pigments.

Summary of Technology:

Historically, pigments based on lead, chromium(VI), and cadmium have served the red, orange, and yellow color market. When the U.S. EPA began regulating heavy metals, however, color formulators typically turned to high-performance organic pigments to replace heavy-metal-based pigments. Although high-performance pigments meet performance requirements, they do so at the expense of the following:

(1) Their higher cost often acts as a deterrent to reformulation;

(2) Their production uses large volumes of organic solvents;

(3) Some require large quantities of polyphosphoric acid, resulting in phosphates in the

effluent; and

(4) Some are based on dichlorobenzidine or polychlorinated phenyls.

Engelhard has developed a wide range of environmentally friendly Rightfit azo pigments that contain calcium, strontium, or sometimes barium instead of heavy metals. True to their name, the Rightfit pigments have the right environmental impact, right color space, right performance characteristics, and right cost-to-performance value. Since 1995, when Engelhard produced 6.5 million pounds of pigments containing heavy metals, it has been transitioning to Rightfit azo pigments.

In 2002, Engelhard produced only 1.2 million pounds of heavy-metal pigments; they expect to phase them out completely in 2004.

1. Rightfit pigments eliminate the risk to human health and the environment from exposure to heavy metals such as cadmium, chromium(VI), and lead used in the manufacture of cadmium and chrome yellow pigments.
2. They are expected to have very low potential toxicity based on toxicity studies, physical properties, and structural similarities to many widely used food colorants.
3. Because they have low potential toxicity and very low migration, most of the Rightfit pigments have been approved both by the U.S. Food and Drug Administration (FDA) and the Canadian Health Protection Branch (HPB) for indirect food contact applications.
4. In addition, these pigments are manufactured in aqueous medium, eliminating exposure to the polychlorinated intermediates and organic solvents associated with the manufacture of traditional high-performance pigments.

Rightfit pigments have additional benefits, such as

1. Good dispersibility,
2. Improved dimensional stability,
3. Improved heat stability, and
4. Improved color strength.
5. Their higher color strength achieves the same color values using less pigment.

6. Rightfit pigments also cover a wide color range from purple to green-shade yellow color.
7. Being closely related chemically, these pigments are mutually compatible, so two or more can combine to achieve any desired intermediate color shade.

Rightfit pigments meet the essential performance characteristics at significantly lower cost than high-performance organic pigments. Thus, formulators get the right performance properties at the right cost, resulting in a steadily increasing market for these pigments. Rightfit pigments provide environmentally friendly, value-added color to packaging used in the food, beverage, petroleum product, detergent, and other household durable goods markets.

Achievements by Engelhard Corporation

- Engelhard Corporation has a ‘Safety First’ oriented culture where any project irrespective of its importance is put on hold until all safety concerns are addressed.
- The Beachwood R & D site has an enviable record of more than 3.6 million man hours and over 19 years without a lost time accident with more than 4 years without a recordable injury.
- During the monthly safety meetings the safety at work as well as outside of work is emphasized.

Environmental Achievements

- 1976 Developed three-way auto emission catalyst
- (This technology has since eliminated 500 million tons of CO and 50 million tons of NOx)
- 1982 Received U.S. and United nations “Award of the Decade” for environmental innovation and achievement
- Early 1990s Commercialized DPX (diesel particulate filter) technology
- Mid 1990s Developed organic yellow pigments to replace lead chromate pigments in traffic markings
- 2004 Earned the Presidential Green Chemistry Challenge Award for RightfitOrganic Pigments. These pigments are produced in Engelhard Louisville plant
- 2005 Earned the GPEC 2005 New Technologies Material Processing Award from the Society of Plastics Engineers “For Development of Heat Stable and Migration Resistant AZO Pigments in a Wide Range of Colors to Replace Pigments Based on Lead Chromium (VI) and Cadmium”

Presidential Green Chemistry Challenge Awards

- Presidential Green Chemistry Challenge Awards Program provides national recognition for outstanding chemical technologies that incorporate the principles of green chemistry into design, manufacture, and use, and that have been or can be utilized by industry to achieve its pollution prevention goals. Five winners are typically honored each year, one in each of the following categories

Key Issues

- Traditionally heavy metal based pigments have been used for coloration in plastics and coatings
- High cost of High Performance Pigments acts as impediment in replacement of heavy metal pigments with these organic pigments.
- Polychlorinated intermediates and organic solvents are used in the manufacture of many High Performance Pigments.
- Engelhard has developed a wide range of environmentally friendly Rightfitted organic pigments with the objective of replacing heavy metal pigments in some niche markets at significant cost savings compared to currently available High Performance Pigments

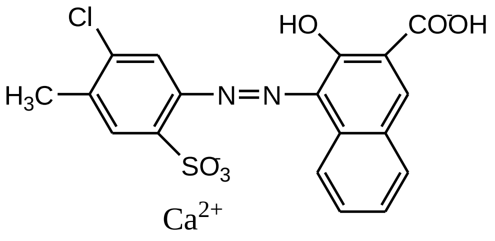
Rightfit Pigments: Environmental Impact

- Eliminate exposure to heavy metals such as cadmium, chromium(VI) and lead used in the manufacture of cadmium and chrome yellowpigments.
- Eliminate exposure to heavy metals such as cadmium, chromium(VI) and lead used in the manufacture of cadmium and chrome yellow pigments.
- Aqueous manufacturing processes.
- Not bioaccumulative: very low octanol/water partition coefficients.
- Resistant to migration in both aqueous and fatty solvents.
- Structurally related to widely used foodcolorants.
- Until recently the formulators replacing heavy metal based pigments typically turned to high performance organic pigments. While these pigments function well, their higher cost often acts as a deterrent to reformulate. The Engelhard Rightfit pigments meet the essential performance characteristics at significantly lower cost than high performance pigments. As a result, formulators get the right performance properties at the right cost/performance level.

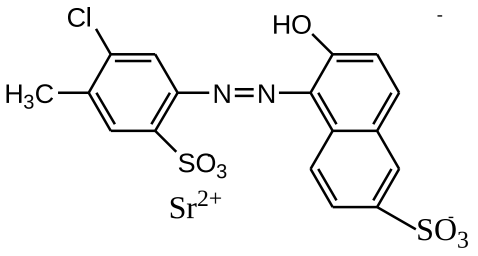
Key Technologies Applied

- Modification of Chemical Structure
- Mixed Crystal Formation
- Selection of Appropriate Laking Metal
- Selective Metallization
- Generation of Desired Crystal Form
- Appropriate Surface Treatment

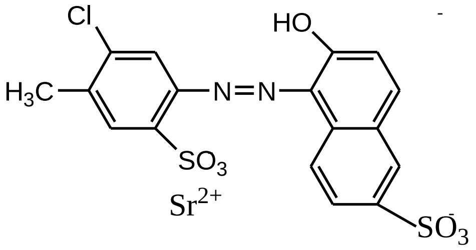
Technology- Modification of Chemical Structure



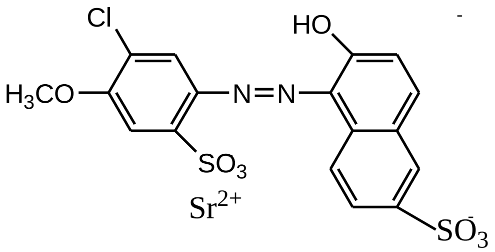
Pigment Red; Heat stability 238°C



Redfit Scarlet; Heat stability 289°C

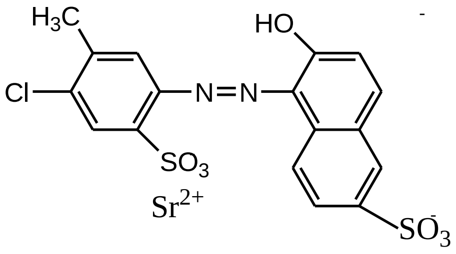


Yellow shade red; Heat stability 289°C

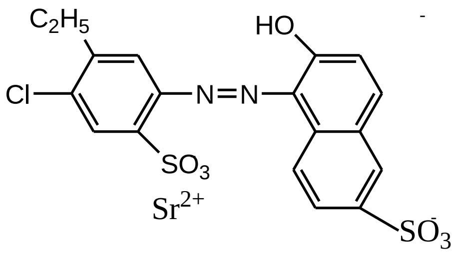


Blue shade red; Heat stability 315°C

Technology- Mixed Crystal Formation



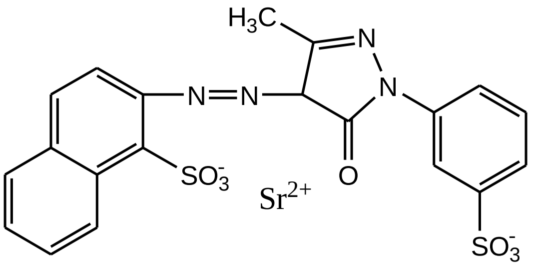
Hue angle 31.7



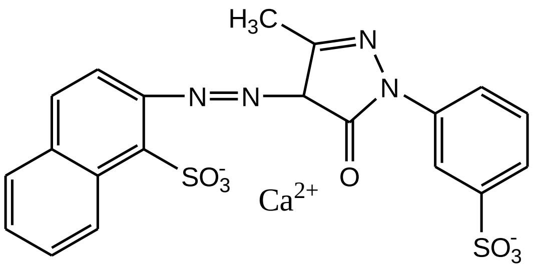
Hue angle 23.3

Mixed crystal 1:1; Hue angle 25.8

Technology-Selection of Appropriate Laking Metal

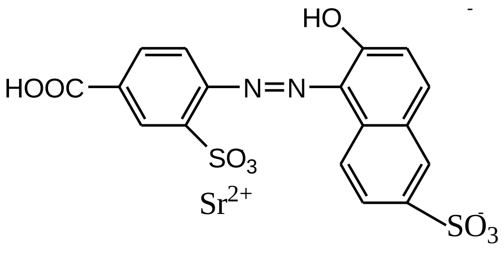


Reddish Yellow; Hue amgle 69.5

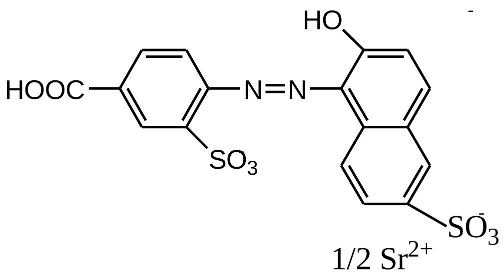


Very Reddish Yellow; Hue amgle 63.5

Technology-Selective Laking

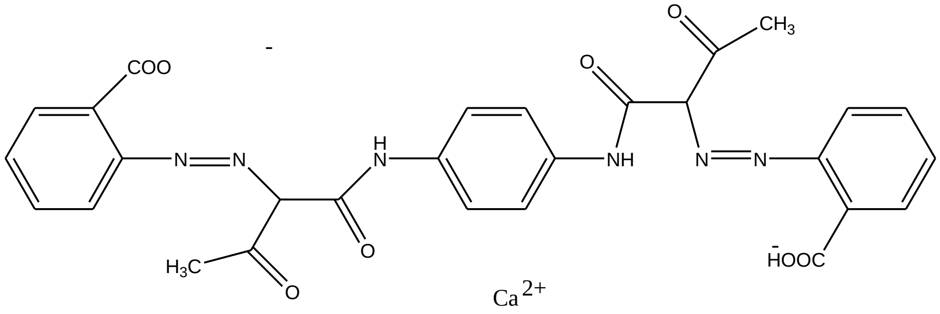


Medium red



Brillant orange

Technology-Generation of Desired Crystal Form



	Hue Angle	Apparent strength
Crystal form A (desired)	91.8	8.74
Crystal form B	101.0	4.49
Crystal Form C	95.7	2.68

Technology-Appropriate Surface Treatment

Appropriate surface treatment helps in dispersibility of the pigment in the application medium. The treatment is selected based on the application as well as the chemical structure of the pigment.

Intelluctual property rights

For the Rightfit Pigments, Engelhard has been granted ten US Patents with two additional US Patents pending

Historically, pigments containing lead molybdate ($PbMoO_4$), lead chromate ($PbCrO_4$), cadmium sulfoselenide (CdSe/CdS), and related heavy-metal-based compounds have served as the pigments of choice for the red, orange, and yellow color market, according to Amrit P. Bindra, Engelhard's manager of color research and development. The blue and green colorneeds are met by phthalocyanine blue and green pigments at reasonable cost and don't pose environmental concerns.

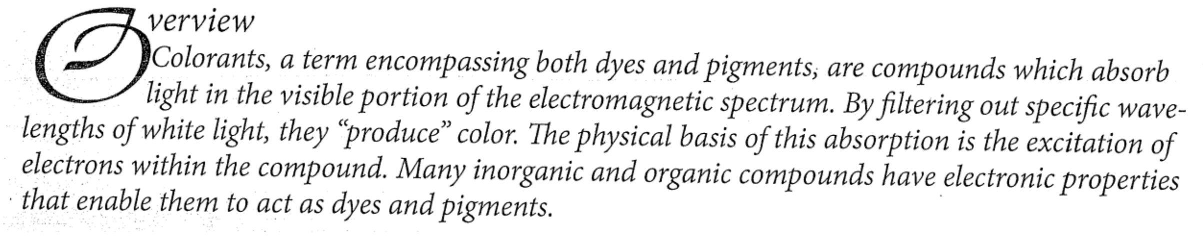
When EPA began regulating heavy metals in the 1970s, color formulators started turning to organic pigments such as dichlorobenzidines, isoindolinones, and quinacridones. Although these organic pigments meet performance requirements, they are relatively expensive and their manufacture requires large volumes of organic solvent. In addition, polyphosphoric acid is sometimes used to make some of these compounds, which leads to environmentally harmful phosphates in the plant effluent. Some of the pigments also contain polychlorinated aromatics.

In the mid-1990s, Engelhard began a program to develop environmentally friendlier and lower cost azo pigments to meet new EPA requirements, "Commonly available azo pigments have limited heat stability and are not suitable for most plastic applications," "But identified appropriate substituents on the starting amine and other reactants that were conducive to heat stability and were reactive in aqueous systems."

The azo compounds contain a –N=N– bridge that links two aromatic groups, such as a substituted phenyl and a substituted naphthyl. The compounds generally are synthesized by reaction of aniline or other amines with nitrous acid, followed by coupling to a second nucleophilic aromatic compound. The azo compounds are highly colored because the nitrogen bridge extends the π conjugation of the aromatic ring systems, resulting in strong absorption in the visible region.

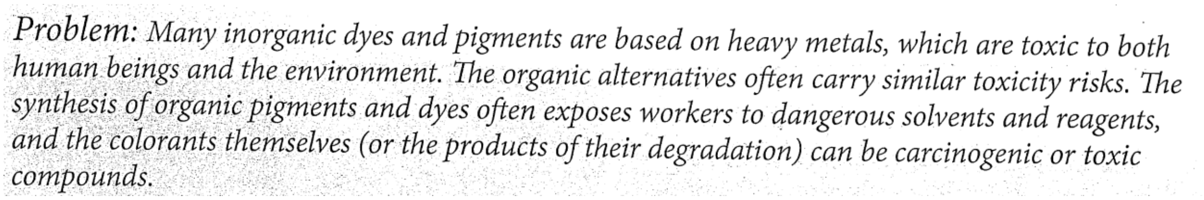
Because of their solubility, azo dyes undergo N=N cleavage, resulting in generation of aromatic amines that in some cases are toxic, Bindra noted. The azo pigments, on the other hand, are virtually insoluble and are unlikely to undergo N=N cleavage. Therefore, they have a lower demonstrated toxicity, he said. Engelhard scientists engineered the Rightfit pigments by placing carboxylic acid or sulfonic acid substituents on the aromatic groups on both sides of the bridge, so that even if cleavage did occur, the cleaved components would not be bioaccumulative.

The choice of alkyl, alkoxy, or halogen substituent groups on the aromatic rings in addition to the acid groups leads to azo pigments of nearly every color shade, he said. Using another approach, desired shades can be obtained by producing mixed crystals of two or more pigments. "These pigments provide brilliant colors with high color strength and good heat stability for applications in plastics,".

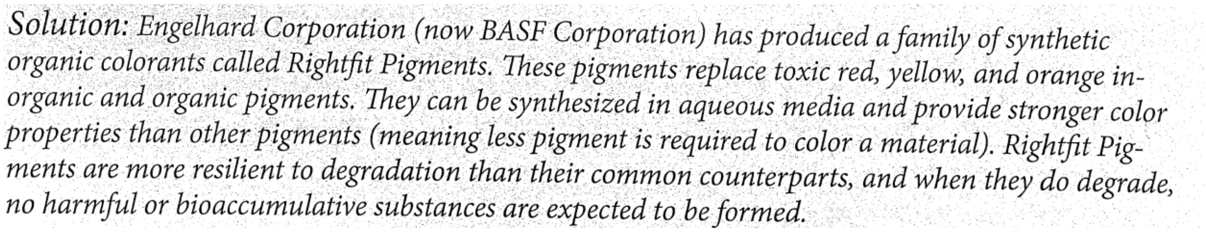


Overview

Colorants, a term encompassing both dyes and pigments, are compounds which absorb light in the visible portion of the electromagnetic spectrum. By filtering out specific wavelengths of white light, they "produce" color. The physical basis of this absorption is the excitation of electrons within the compound. Many inorganic and organic compounds have electronic properties that enable them to act as dyes and pigments.



Problem: Many inorganic dyes and pigments are based on heavy metals, which are toxic to both human beings and the environment. The organic alternatives often carry similar toxicity risks. The synthesis of organic pigments and dyes often exposes workers to dangerous solvents and reagents, and the colorants themselves (or the products of their degradation) can be carcinogenic or toxic compounds.



Solution: Engelhard Corporation (now BASF Corporation) has produced a family of synthetic organic colorants called Rightfit Pigments. These pigments replace toxic red, yellow, and orange inorganic and organic pigments. They can be synthesized in aqueous media and provide stronger color properties than other pigments (meaning less pigment is required to color a material). Rightfit Pigments are more resilient to degradation than their common counterparts, and when they do degrade, no harmful or bioaccumulative substances are expected to be formed.

Many heavy metals such chromium, cadmium and lead are used extensively in inorganic pigments.

Chronic exposure to these metals is believed to cause physical damage (lesions and ulcers), neurological disorders and some cancers.

95% of the pigments available worldwide contain heavy metls.

While consumer exposure to these toxic pigments is a cause for alarm, high levels of exposure to which employees in the manufacturing facilities are subjected can be an even greater concern.

Chromium is considered to be a lung carcinogen, irritant on the respiratory tract, and cause ulcers on the mucous membrane of the lungs and on skin.

Exposure to cadmium causes cancer and birth defects, can damage kidney and skeletal system. Ingestion of cadmium based paints can be fatal.

Lead is dangerous to children and can go in by inhalation or ingestion. It damages nervous system and excess of lead can led to fatal. In adults it affects the reproductive system.

Pigments: colourant compounds that are insoluble in the media they are intended to colour. To make a pigment, a soluble colorant is often bound to a metal ion making it insoluble. All inorganic colorants are pigments.

Dyes are colorant molecules that are at least partially soluble in their intended substrate.

Green synthesis of plastic (poly lactic acid) made from corn.

Today, polymers and materials used for food packaging consist of a variety of petrochemical-based polymers, metals, glass, paper, and board, or combinations hereof. The durability and degradability of packaging materials are two contradictory subjects; the 1st is desirable for packaging stability and protection for its contents during shelf life and the 2nd for its rapid degradation in the environment.

Advantages of petrochemical-based polymers, which encouraged industries to use them are: (a) low cost and high-speed production;
(b) high mechanical performance;
(c) good barrier properties; and
(d) good heat sealability.

On the other hand, several disadvantages include:
(a) declining oil and gas resources;
(b) increasing oil and gas prices during recent decades;
(c) environmental concerns for their degradation or incineration and global warming;
(d) uneconomical costs and cross-contaminations in their recycling; and
(e) consumer toxicity risks about their monomers or oligomers migrating to edible materials

Mechanical recycling (segregated plastics, mixed plastics), biological recycling (sewage, compost, soil), and energy recovery (incineration, pyrolysis) are 3 alternative ways for plastics waste management, with each having some advantages and disadvantages as to economical, processing, and technological aspects.

The above-mentioned concerns are negligible for biopolymers concerning the biodegradation process that takes place in nature. Biodegradation is defined as the degradation of a polymer in natural environments that includes changes in chemical structure, loss of mechanical and structural properties, and finally, changing into other compounds like water, carbon dioxide, minerals, and intermediate products like biomass and humic materials. The natural environments contain chemical, biological, and physical forces with impinging factors like temperature, humidity, pH, O_2 presence, and so on, which determine the rate and products of the biodegradation process.

Biopolymers are produced from natural resources and crude oil. Four categories of biopolymers are recognized:

(a) Extracted directly from natural raw materials, such as polysaccharides like starch and cellulose; proteins like gelatin, casein, and silk; and marine prokaryotes;

(b) Produced by chemical synthesis from bio-derived monomers such as poly-lactic acid (PLA), also known as poly(lactic acid) in the literature;

(c) Produced by microorganisms or genetically modified bacteria such as polyhydroxyalkanoates (PHA), polyhydroxybutyrate (PHB), hydroxyl-valerate (PHV), bacterial cellulose, xanthan, and pullan; and

(d) Produced from crude oil like aliphatic and aromatic polyesters, polyvinyl alcohol, and modifiedpolyolefins, which are sensitive to temperature and light.

It is highly impossible to avoid products made from synthetic plastics. In many cases, these strong, long-lasting materials have replaced natural substances such as wood and metal in a variety of applications. The marketing of cheap plastic items to the general public has led to the popularity of “single use” items that can be simply thrown away without any cleanup on the part of the consumer.

This being the situation what problem we face

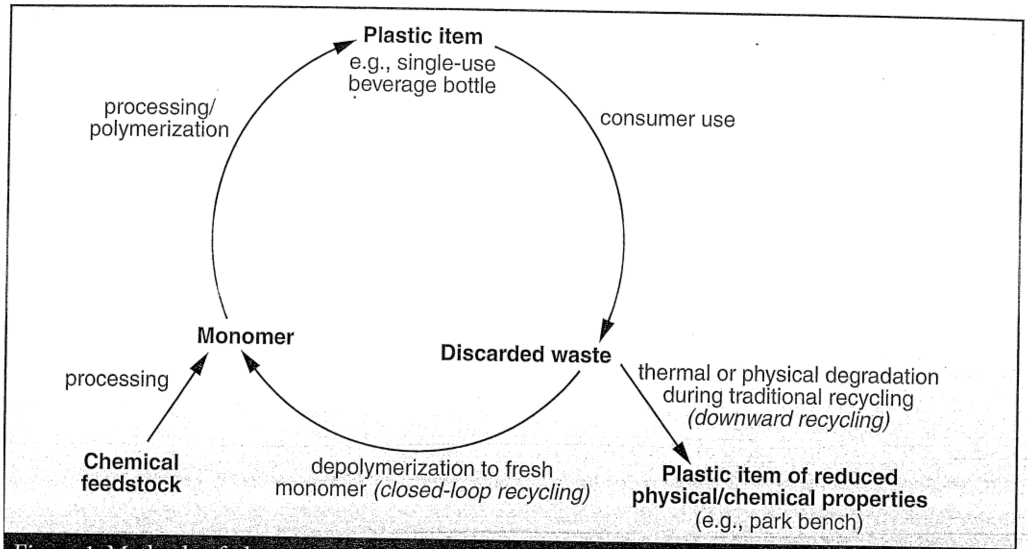
Almost all plastic products made today are made from crude oil which is a non-renewable source that is quickly being depleted. Eventhough some people encourage us to reuse and recycle plastic commodities, these practice will not permanently solve the problem generated by plastic waste. Many plastic items are designed for “single use” means which cannot be reused, while the physical process of recycling often degrades the quality of the second generation plastic.

Neither reusing or recycling is always beneficial as we are led to believe. Due to contamination many plastic items such as plastic food wrap and diapers simply cannot be reused, while the process of recycling often thermally or mechanically degrades polymer molecules leading to a reduction in their physical properties. For example polystyrene commonly used as a packing material undergoes 34% reduction in impact strength after three rounds of recycling.

Because of such issues as contamination and thermal degradation, most plastic products are downward recycled into a product with inferior quality. For example a plastic drink bottle that is recycled does not return to a consumer as a fresh drink bottle, but rather as an item such as plastic chair or plastic pots. Downward recycling prevents the bottle from entering the landfill, but fresh monomer is still required to create a new bottle.

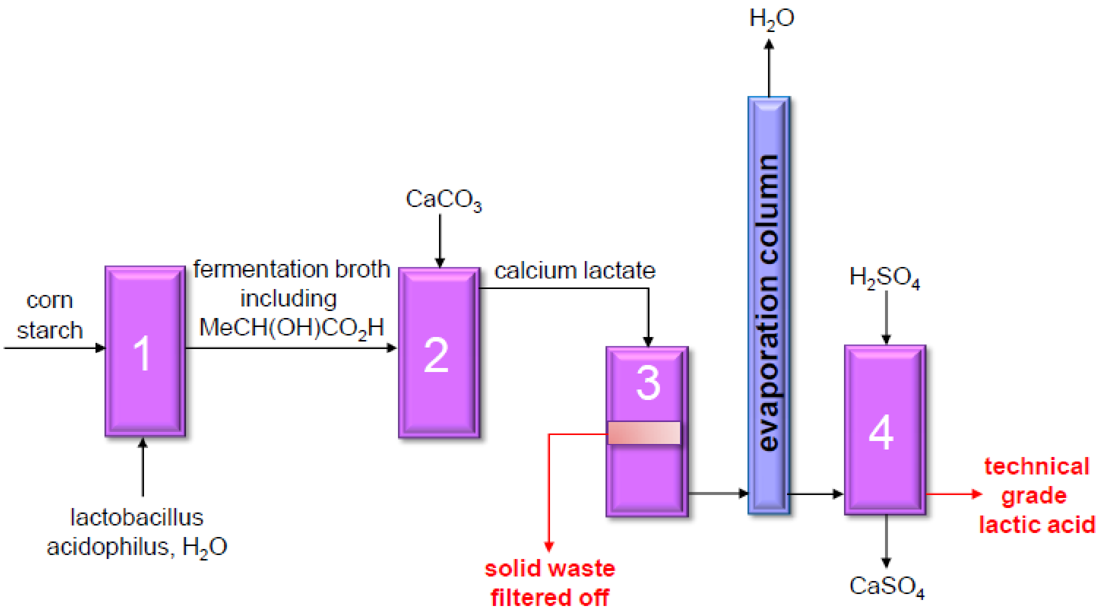
So what will the solution

‘Polylactic acid’ is a plastic made from the starch found naturally in plants. It can be used in many applications, including packaging, fabrics, and biomedical implants. The material is fully compostable and can be recycled back into pure starting materials to make virgin polylactic acid. Nature works LLC has developed a method for producing polylactic acid from corn. This synthesis uses a renewable resource to produce the monomer and also avoids using the organic solvents common to most synthesis of petrochemical based polymers.



Methods of recycling.

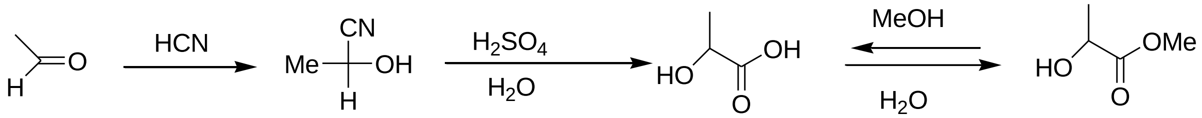
Biosynthesis from starch
Reactor 1: fermentation; 2: salt formation; 3: filtration; 4: hydrolysis



Poly(lactic acid) or **polylactic acid** or **polylactide** (**PLA**) is a biodegradable and bioactive thermoplastic aliphatic polyester derived from renewable resources, such as corn starch.There are several industrial routes to usable (i.e. high molecular weight) PLA. Two main monomers are used: lactic acid, and the cyclic di-ester, lactide.

Chemical synthesis of lactic acid

Lactic acid can also be synthesised from acetaldehyde.



The advantages of this synthetic method is that

1. all the reactions involved are fast and high yielding reactions
2. MeOH generated in final step is recycled
3. Produces high purity lactic acid (99%)

The disadvantages are

1. HCN is highly toxic; acetaldehyde and MeOH are also toxic
2. Waste stream of Ammonium sulphate is produced(but can be used as a fertilizer)
3. Several energy intensive distillations required.

Biochemical Process

The advantages are 1. Renewable feedstock 2. Uses non-hazardous materials

The disadvantages are

1. Slow process (every cycle takes 4-6 days)
2. Quantity of product per reactor volume is low

3. Evaporation is required (due to low salt concentration)
4. Technical grade lactic acid(85 % purity) produced. In order to produce high purity product, the material has to undergo the methanol transesterification process.
5. Waste stream of $CaSO_4$ produced and very large quantities of waste water.

PLA Production

Lactic acid (2-hydroxy propionic acid), the single monomer of PLA, is produced via fermentation or chemical synthesis. Its two optically active configurations, the L(+) and D(−) stereoisomers are produced by bacterial (homofermentative and heterofermentative) fermentation of carbohydrates. Industrial lactic acid production utilizes the lactic fermentation process rather than synthesis because the synthetic routes have many major limitations.

1. Limited capacity due to the dependency on a by-product of another process,
2. Inability to make only the desirable L-lactic acid stereoisomer, and
3. High manufacturing costs.

The homofermentative method is preferably used for industrial production because its pathways lead to greater yields of lactic acid and to lower levels of by-products. The general process consists of

a. Using species of the *Lactobacillus* genus such as *Lactobacillus delbrueckii, L.amylophilus, L. bulgaricus, and L. leichmanii,*
b. pH range of 5.4 to 6.4,
c. Temperature range of 38 to 42 °C, and
d. Low oxygen concentration.

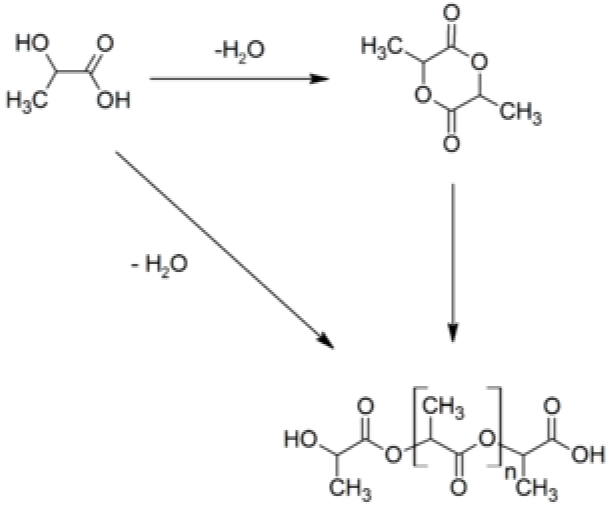
Generally, pure L-lactic acid is used for PLA production.

The most common route to PLA is the ring-opening polymerization of lactide with various metal catalysts(typically tin octoate) in solution, in the melt, or as a suspension. The metal-catalyzed reaction tends to cause racemization of the PLA, reducing its stereoregularity compared to the starting material (usually corn starch).

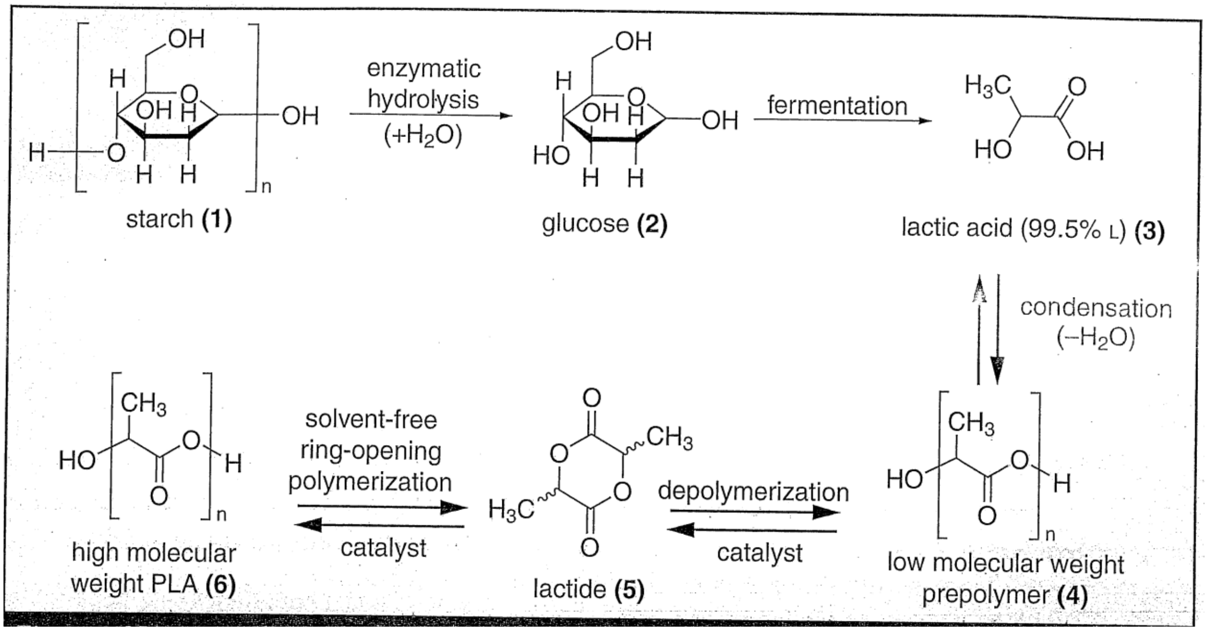
Another route to PLA is the direct condensation of lactic acid monomers. This process needs to be carried out at less than 200 °C; above that temperature, the entropically favoured lactide monomer is generated.

This reaction generates one equivalent of water for every condensation (esterification) step, and that is undesirable because water causes chain-transfer leading to low molecular weight material. The direct condensation is thus performed in a stepwise fashion, where lactic acid is first oligomerized to PLA oligomers. Thereafter, polycondensation is done in the melt or as a solution, where short oligomeric units are combined to give a high molecular weight polymer strand.

Water removal by application of a vacuum or by azeotropic distillation is crucial to favour polycondensation over transesterification. Molecular weights of 130 kDa can be obtained this way. Even higher molecular weights can be attained by carefully crystallizing the crude polymer from the melt. Carboxylic acid and alcohol end groups are thus concentrated in the amorphous region of the solid polymer, and so they can react. Molecular weights of 128–152 kDa are obtainable thus.



NatureWorks exclusively uses corn starch as raw material for lactic acid production via lactic fermentation. Many studies have been conducted to find other sources of carbohydrates for lactic acid production. The use of a specific carbohydrate feedstock depends on its price, availability, and purity. Some agricultural by-products, which are potential substrates for lactic acid production include, cassava starch, lignocellulose/hemicellulose hydrolysates, cottonseed hulls, Jerusalem artichokes, corn cobs, corn stalks, beet molasses, wheat bran, rye flour, sweet sorghum, sugarcane press mud, cassava, barley starch, cellulose, carrot processing waste, molasses spent wash, corn fiberhydrolysates, and potato starch.



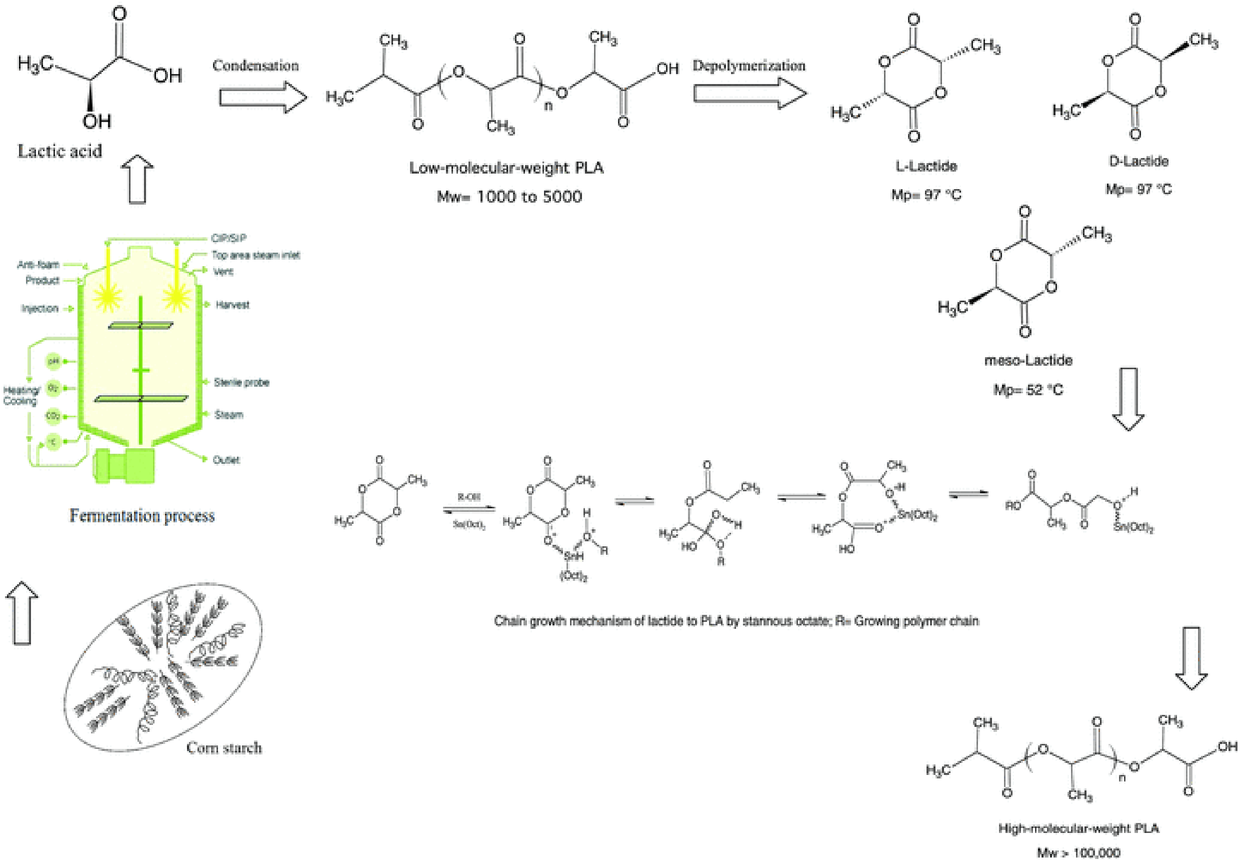
Production of PLA from starch

Other sources of carbohydrate for lactic acid production include kitchen wastes, fish meal wastes, and paper sludge. By using kitchen wastes, concerns about waste management in crowded cities could be automatically eased. Additionally, some parts of carbohydrates from wastes will return to the production cycle of lactic acid and, as a result, decrease a large amount of corn consumption. By using other carbohydrate sources rather than corn, the criticisms and debates about utilizing a food source as packaging material will be defused.

Producing high molecular weight PLA polymers by direct polycondensation in an azeotropic solution and also application of some catalysts is more practicable. The azeotropic solution helps to decrease the distillation pressures and facilitates PLA separation from the solvent by application of molecular sieves.

Lactide purification is accomplished by vacuum-distillation of high temperatures. After the vacuum-distillation of L-lactide, high molecular weight PLA with a controlled optical and crystal purity is formed by ring-opening polymerization. Ring-opening polymerization of lactide can be carried out in melt or solution by cationic, anionic, and coordination mechanisms, depending on the initiator utilized. The most considered active initiator for the L-lactide ring-opening polymerization is stannous octoate (bis 2-ethyl hexanoate, $SnOct_2$), which causes a low degree of racemization at high temperature. It has a low toxicity and is accepted by FDA.

Figure 1 shows PLA production steps by ring-opening polymerization using stannous octoate as an initiator.



Current production steps for PLA.

New ideas for decreasing PLA final price and making production processes more eco-friendly, in comparison to earlier production process, include

1. Usage of crop residue (stems, straw, husks, and leaves) from corn or, potentially, other crops, and use of unfermentable residues as a heat source,
2. Substituting some part of electricity energy by wind power energy.

These approaches decrease the consumption of fossil fuels and corn starch as raw materials and also diminish polluting air, water, and waste emissions to the environment.

One of the most positive points of PLA production in comparison with the other hydrocarbon-based polymers is the decrease of CO_2 emission. Carbon dioxide is believed to be the most important contributor to global climate change and its warming. Because, carbon dioxide is absorbed from air when corn is grown, use of PLA has the potential to emit fewer greenhouse gases compared to competitive hydrocarbon-based polymers.

PLA or poly-lactide was discovered in 1932 by Carothers (at DuPont). He was only able to produce a low molecular weight PLA by heating lactic acid under vacuum while removing the condensed water. The problem at that time was to increase the molecular weight of the products; and, finally, by ring-opening polymerization of the lactide, high-molecular weight PLA was synthesized. PLA was 1st used in combination with polyglycolic acid (PGA) as suture material and sold under the name Vicryl in the U.S.A. in 1974.

In comparison to other biopolymers, the production of PLA has numerous advantages including:
(a) production of the lactide monomer from lactic acid, which is produced by fermentation of a renewable agricultural source corn;
(b) fixation of significant quantities of carbon dioxide via corn (maize) production by the corn plant;
(c) significant energy savings;
(d) the ability to recycle back to lactic acid by hydrolysis or alcoholysis;

(e) the capability of producing hybrid paper-plastic packaging that is compostable;

(f) reduction of landfill volumes;

(g) improvement of the agricultural economy; and

(h) the all-important ability to tailor physical properties through material modifications

Briefly, PLA is based on agricultural (crop growing), biological (fermentation), and chemical (polymerization) sciences and technologies.

Healthier fats and oil by Green Chemistry: Enzymatic interesterification for production of no Trans-Fats and Oils

POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What are the requirements for an ideal greener antifoulants.
2. What is the chemical name and structure active ingredient in Sea-Nine 211.
3. What is the innovatin and benefit of *Designing an Environmentally Safe Marine Antifoulant by* Rohm and Haas's discovery of Sea-Nine 211.
4. What are the innovations and benefits of the Rightfit pigments.
5. Summarise the benefits of the rightfit pigments.
6. What are the key environmental issues lyeing behind the usage of conventional clours and pigments.
7. Explain the environmental impact of the Rightfit pigments.

PART C (8 Mark Questions)

1. The environmental significance of Rohm and Haas's discovery of Sea-Nine 211 was recognized with a Presidential Green Chemistry Challenge Award in 1996. Look up the three focus areas for this award and determine which focus area this case best fits into.
2. List out any two of the twelve principles of green chemistry that are addressed by the green chemistry developed by Rohm and Haas's discovery of Sea-Nine 211.
3. Explain the summary of the technology developed by Rohm and Haas's discovery of Sea-Nine 211.
4. Summarise the technology developed by the Right fit pigments in developing their materials.
5. Explain with suitable examples the key technologies followed by Rightfit pigments.

Green Chemistry

UNIT IV

S.No	Question	a	b	c	d	Answer
1.	Rightfit azo pigments contain	Calcium	lead	cadmium	hexavalent chromium	Calcium
2.	Rightfit azo pigments contain	Barium	lead	cadmium	hexavalent chromium	Barium
3.	The metal present in Rightfit azo pigments	Strontium	lead	cadmium	hexavalent chromium	Strontium
4.	The metal not present in Rightfit azo pigments	Strontium	Barium	Calcium	hexavalent chromium	hexavalent chromium
5.	The metal not present in Rightfit azo pigments	Strontium	Barium	Calcium	cadmium	cadmium
6.	The metal not present in Rightfit azo pigments	Strontium	Barium	Calcium	lead	lead
7.	Rightfit azo pigments contain	Alkali metals	Alkaline earth metals like Ca, Ba, Sr	Transition metals	Non metals	Alkaline earth metals like Ca, Ba, Sr
8.	Rightfit azo pigments are preferred due to	low potential toxicity	High penentration power through skin	High toxicity	High voltality	low potential toxicity
9.	Rightfit azo pigments are preferred due to	low penentration power through skin	High penentration power through skin	High toxicity	High voltality	low penentration power through skin
10.	The disadvantage of high-performance organic pigments is	higher cost	Their production uses smaller volumes of organic solvents	less quantities of polyphosphoric acid is used, resulting in less phosphates in	Do not have dichlorobenzidine or polychlorinated phenyls moieties	higher cost

				the effluent		
11.	The disadvantage of high-performance organic pigments is	low cost	Their production uses larger volumes of organic solvents	less quantities of polyphosphoric acid is used, resulting in less phosphates in the effluent	Do not have dichlorobenzidine or polychlorinated phenyls moieties	Their production uses larger volumes of organic solvents
12.	The disadvantage of high-performance organic pigments is	low cost	Their production uses smaller volumes of organic solvents	larger quantities of polyphosphoric acid is used, resulting in more phosphates in the effluent	Do not have dichlorobenzidine or polychlorinated phenyls moieties	larger quantities of polyphosphoric acid is used, resulting in more phosphates in the effluent
13.	The disadvantage of high-performance organic pigments is	low cost	Their production uses smaller volumes of organic solvents	smaller quantities of polyphosphoric acid is used, resulting in less phosphates in the effluent	have dichlorobenzidine or polychlorinated phenyls moieties	have dichlorobenzidine or polychlorinated phenyls moieties
14.	Which is not applicable to Rightfit pigments	right environmental impact	right color space	right performance characteristics	Causes pollution	Causes pollution
15.	Which is not applicable to Rightfit pigments	right environmental impact	No color space	right performance characteristics	right cost-to-performance value	No color space
16.	Which is not applicable to Rightfit pigments	right environmental impact	Right color space	Don’t have right performance characteristics	right cost-to-performance value	Don’t have right performance characteristics
17.	Which is not applicable to Rightfit pigments	right environmental impact	Right color space	right performance characteristics	cost-to-performance value is not acceptable	cost-to-performance value is not acceptable
18.	Which is not true with Rightfit pigments	Poor dispersibility,	Improved dimensional stability	Improved heat stability	Improved color strength	Poor dispersibility,
19.	Which is not true with Rightfit pigments	Good dispersibility,	poor dimensional stability	Improved heat stability	Improved color strength	poor dimensional stability

20.	Which is not true with Rightfit pigments	Good dispersibility,	Improved dimensional stability	poor heat stability	Improved color strength	poor heat stability
21.	Which is not true with Rightfit pigments	Good dispersibility,	Improved dimensional stability	Improved heat stability	No color strength	No color strength
22.	Dis Advantages of petrochemical-based polymers	low cost and high-speed production	high mechanical performance	good barrier properties	declining oil and gas resources	declining oil and gas resources
23.	Dis Advantages of petrochemical-based polymers	low cost and high-speed production	high mechanical performance	good barrier properties	increasing oil and gas prices	increasing oil and gas prices
24.	Dis Advantages of petrochemical-based polymers	low cost and high-speed production	high mechanical performance	good barrier properties	environmental concerns for their degradation or incineration and global warming	environmental concerns for their degradation or incineration and global warming
25.	Dis Advantages of petrochemical-based polymers	low cost and high-speed production	high mechanical performance	good barrier properties	consumer toxicity risks	consumer toxicity risks
26.	Dis Advantages of petrochemical-based polymers	low cost and high-speed production	high mechanical performance	good barrier properties	uneconomical costs and cross-contaminations in their recycling	uneconomical costs and cross-contaminations in their recycling
27.	Advantages of petrochemical-based polymers	low cost and high-speed production	uneconomical costs and cross-contaminations in their recycling	consumer toxicity risks	increasing oil and gas prices	low cost and high-speed production
28.	Advantages of petrochemical-based polymers	high mechanical performance	uneconomical costs and cross-contaminations in their recycling	consumer toxicity risks	increasing oil and gas prices	high mechanical performance
29.	Advantages of petrochemical-based polymers	low cost and high-speed production	uneconomical costs and cross-contaminations in their recycling	consumer toxicity risks	increasing oil and gas prices	low cost and high-speed production

30.	Advantages of petrochemical-based polymers	good barrier properties	uneconomical costs and cross-contaminations in their recycling	consumer toxicity risks	increasing oil and gas prices	good barrier properties
31.	Advantages of petrochemical-based polymers	good heat sealability	uneconomical costs and cross-contaminations in their recycling	consumer toxicity risks	increasing oil and gas prices	good heat sealability
32.	Which is a plastics waste management	Polymerization	Photocatalysis	copolymerization	Mechanical recycling	Mechanical recycling
33.	Which is a plastics waste management	Polymerization	Photocatalysis	copolymerization	biological recycling	biological recycling
34.	Which is a plastics waste management	Polymerization	Photocatalysis	copolymerization	energy recovery	energy recovery
35.	segregated plastics, mixed plastics can be subjected to	Mechanical recycling	biological recycling	energy recovery	Chemical recycling	Mechanical recycling
36.	sewage, compost, soil can be subjected to	Mechanical recycling	biological recycling	energy recovery	Chemical recycling	biological recycling
37.	incineration, pyrolysis belongs to	Mechanical recycling	biological recycling	energy recovery	Chemical recycling	energy recovery
38.	Mechanical recycling can be followed for	segregated plastics, mixed plastics	sewage, compost, soil	incineration, pyrolysis	Carbondioxide and water	segregated plastics, mixed plastics
39.	biological recycling applied to	segregated plastics, mixed plastics	sewage, compost, soil	incineration, pyrolysis	Carbondioxide and water	sewage, compost, soil
40.	energy recovery applied to	segregated plastics, mixed plastics	sewage, compost, soil	incineration, pyrolysis	Carbondioxide and water	energy recovery
41.	poly-lactic acid is prepared from	Corn	Petrochemicals	Green house gases	explosives	Corn
42.	The biopolymer which is Extracted directly from natural raw materials	Starch	Polylactic acid	polyhydroxybutyrate	polyesters	Starch
43.	The biopolymer which is Extracted directly from natural	Silk	Polylactic acid	polyhydroxybutyrate	polyesters	silk

	raw materials					
44.	The biopolymer which is Produced by chemical synthesis from bio-derived monomers	Starch	Polylactic acid	polyhydroxybutyrate	polyesters	Polylactic acid
45.	The biopolymer which is Produced by microorganisms	Starch	Polylactic acid	polyhydroxybutyrate	polyesters	polyhydroxybutyrate
46.	The biopolymer which is Produced from crude oil	Starch	Polylactic acid	polyhydroxybutyrate	polyesters	polyesters
47.	Starch is a biopolymer	which is Extracted directly from natural raw materials	Produced by chemical synthesis from bio-derived monomers	Produced by microorganisms	Produced from crude oil	which is Extracted directly from natural raw materials
48.	Polylactic acid is a polymer	which is Extracted directly from natural raw materials	Produced by chemical synthesis from bio-derived monomers	Produced by microorganisms	Produced from crude oil	Produced by chemical synthesis from bio-derived monomers
49.	Polyhydroxybutyrate is a polymer	which is Extracted directly from natural raw materials	Produced by chemical synthesis from bio-derived monomers	Produced by microorganisms	Produced from crude oil	Produced by microorganisms
50.	Polyester is a polymer	which is Extracted directly from natural raw materials	Produced by chemical synthesis from bio-derived monomers	Produced by microorganisms	Produced from crude oil	Produced from crude oil
51.	In commonly used carpets the polymer used as a backing material is	Poly vinyl chloride	Poly lactic acid	Rightfit polymers	polyhydroxybutyrate	Poly vinyl chloride
52.	Close-looped recycling is not possible in carpers made up of	Poly vinyl chloride	Poly lactic acid	Rightfit polymers	polyhydroxybutyrate	Poly vinyl chloride
53.	Environmentally friendly carpet is made from	Poly vinyl chloride	Poly lactic acid	Rightfit polymers	Polyolefin backing	Polyolefin backing
54.	Environmentally friendly	Poly vinyl chloride	Poly lactic acid	Rightfit polymers	Nylon-6 fibers	Nylong-6 fibers

	carpet is made from					
55.	Consumption of space for landfilling happens with	Polyvinyl chloride carpets	Poly lactic acid	Rightfit polymers	Polyoefin carpets	Polyvinyl chloride carpets
56.	Which is used as a plasticizer in the synthesis of PVC	Phthalates	vinylchloride	Polyolefins	Nylon 6-fibers	Phthalates
57.	Which acts as a face fiber in environmental friendly carpets	Phthalates	vinylchloride	Polyolefins	Nylon 6-fibers	Nylon 6-fibers
58.	The carpet made up of polyolefin backing layer and nylon-6 as face fiber	Allows Close loop recycling	Is Health hazards to workers	Is More heavier than PVC made carpets	Uses calcium carbonate as filler	Allows Close loop recycling
59.	The filler used in PVC backing carpets	Calcium carbonate	Vinyl chloride	Nylon-6	Fly ash	Calcium carbonate
60.	The filler used in poleolefin backing carpets	Calcium carbonate	Vinyl chloride	Nylon-6	Fly ash	Fly ash

UNIT V

Future Trends in Green Chemistry

Oxidation reagents and catalysts; Biomimetic, multifunctional reagents; Combinatorial green chemistry; Proliferation of solventless reactions; co crystal controlled solid state synthesis(C_2S_3); Green chemistry in sustainable development.

In the last decade Green Chemistry and Green Engineering have advanced for a great variety of research and technology fields providing cutting-edge research and practical applications for a wide spectrum of chemical products and technological innovations. The most important research and technological fields of GC and GE include solutions. Among other things, reduction of global warming and use of CO2 as a raw material for chemical synthesis, microwave, electrochemical and ultrasound synthetic methods, solvent free reactions (or water as a solvent), phytoremediation, waste management and wastewater, eco-friendly dyes and pigments, innovative food products, catalysis and biocatalysis, biopolymer technology, renewable materials, renewable energy sources, etc.

Although there are many fields of innovation for GC and GE products we list below some of the areas.

a. Biocatalysis and biotransformations processes for practical synthetic reactions

b. Directed evolution. New enzymes for organic synthesis

c. Green chemistry and synthetic processes in the pharmaceutical industry

d. Hydrogen production via catalytic splitting of water

e. Green and renewable energy sources

f. Green chemistry and agricultural technologies benign to environment

g. Green chemistry. Multicomponent reactions

h. Green flow chemistry and continuous processes in chemical industry

i. Green chemistry and biodegradable polymers

j. Green chemistry and organic solar cells

k. Solvent and solvent selection in industrial synthesis

Except for the above, there are also numerous other technological; fields of Green Chemistry and Green Engineering that have been advanced in the last years. Already, some these innovative inventions have been applied and improved sustainability, reduced environmental pollution and released less hazardous chemical products.

Oxidation Reagents and Catalysts: Though there is notable advancement in oxidation chemistry, but it is still one of the most polluting chemical technology. Oxidative transformations, as we know are the basis of necessary functionalization of fundamental molecules. It is the oxidation procedures that allows petroleum based feed stocks to become chemical products, which are the starting materials of numerous chemical industries.

Over the years, in the past many of the oxidation reagents and catalysts comprise of toxic substances like heavy metals (e.g. chromium). These substances have been used in large amounts for the manufacture of billions of kilograms of petrochemicals. All these processes have lead to the release of huge quantities of these metals into the environment. Further these toxic substances affects the human health.

During the past 2-3 decades, considerable attention has been directed towards the development of green chemistry techniques that will be environmentally benign and will also bring economic benefits to the industries. The oxidation techniques to be developed will need catalysts so that there is high turnover rates. Even if some heavy metals / transition metals have to be used, attempt should be made to use some of the most innocuous metals e.g. iron etc. The objective of green oxidation chemistry will, of course be to use and generation of non-hazardous substances, with maximum efficiency of atom incorporation.

Biomimetic, Multifunctional Reagents: In the human system, there is thousands of reactions going on due to which the body survives. The scientists are trying to understand the mechanism that the biological systems used to carry out their functions. The chemists approach is to biomimic such reactions in the laboratory. In case of synthetic chemists, most of the transformations are carried with the help of catalysts e.g. oxidation, reduction and methylation. However, biological systems often carry out several manipulations with the same reagent. These manipulations many include activation, conformation and other transformations. In the laboratory, it has now been possible to carry out biochemical oxidations, biochemical reductions and enzyme catalyed hydrolytic process. Different types of enzymes e.g. hydrolase, Lyases, isomerases, Ligases, transferases, oxidoreductases are available.

The biocatalytic conversions have many advantage in relevance to green chemistry. Some of these are –

- Most of the reactions are performed in aqueous medium at ambient temperature and pressure.
- The biocatalytic transformations normally involve only one step.
- Protection and deprotection of functional group in not necessary.
- The biocatalytic reactions are fast and the conversion are stereospecific.

Combinatorial Green Chemistry:

Combinatorial chemistry is a practice of being able to make a large number of chemical compounds rapidly on a small scale through reaction matrices. This practice is used on a large scale in the pharmaceutical sector. The pharmaceutical company identifies lead compound, which has considerable promise (as far as its biological activity is concerned) then the company would proceed in making a large number of derivatives of the lead compound and test their efficacy. In this way, the potential of a compound will be optimized. The combinatorial chemistry has enabled large number of substances to be made and screened for their activities without having any adverse effect on the environment. This approach is very useful to assess the biodegradability of the products. For example, if a company has struck on a biodegradable pesticide, the combinatorial approach will be helpful to make large number of other compounds, which will have the required pesticidal activity along with biodegradability.

4. Proliferation of Solventless Reactions: A large number of reactions occur in solid phase without the use of solvents are not harmful to the environment. In fact, a number of solventless reactions occur more efficiently with more selectivity compared to reactions carried out using solvents. Such reactions are simple to handle, reduce pollution and are comparatively cheaper to operate.

5. Non Covalent Derivatization: Any chemical synthesis involving formation and breaking of covalent bonds. The philosophy of making and breaking covalent bond must change. Infact, without bond making, physical / chemical properties can be modified and performance measured. Through the formation of dynamic complexation (which temporarily allow modification of the chemical structure) the properties of the molecules can be changed for in a short period of time to carry out a particular function. In this case no waste will be generated if full derivatization were implemented.

Green Chemistry in Sustainable Development:

Green chemistry can play a vital role sustainable development. Green chemistry as we know is environmentally benign synthesis. Chemical manufacturing is the source of many useful and enjoyable products, which has not only improved the quality of life of the people but also increased their life expectancy. Some of these products include antibiotics and other medicines, plastics, gasoline and other fuels, agricultural chemicals like fertilizers and pesticides, and a variety of synthetic fabrics including nylon, rayon and polyester. All these products are made by chemical industrial processes, which are mainly responsible for pollution of the environment. This in fact, green chemistry works toward sustainability by – Making chemical products that do not harm either the environment or our health.

- Using industrial processes that reduce or eliminate hazardous chemicals.
- Designing more efficient processes that minimize the production of waste materials.
- Using the most appropriate starting materials, reagents and catalysts.
- New products designed should be biodegradable.
- The waste products should be recycled as far as possible.

Directed Evolution', Green Chemistry and Biocatalysis

In 2016 the biochemical engineer Frances Arnold (CALTECH) received the Millennium Technology Prize (1 million Euros, awarded by Technology Academy Finland, Helsinki) in recognition of her discoveries and research on the field of ‗**directed evolut**ion', which mimics natural evolution to create new and better proteins (enzymes for biocatalysis) in the laboratory. This technology have solved many important synthetic industrial problems, often replacing less efficient synthetic methods and sometimes harmful technologies. Thanks to directed evolution, sustainable development and clean technology (biocatalysis) become available in many fields of chemical industry.

The 'Bionic Leaf'. Sunlight Splits Water and Bacteria Produce from Hydrogen Liquid Fuels

Hydrogen generated from solar-driven water-splitting has the potential to be a clean, sustainable and abundant energy source. Inspired by natural photosynthesis, artificial solar water-splitting devices are now being designed and tested for efficiency. Although sunlight-driven water splitting is a promising process to sustainable hydrogen (H2) production as fuel, widespread implementation is hampered by the expense of the photovoltaic and photoelectrochemical apparatus. Various catalysts and integrated systems have been used for the production of hydrogen from water.33,34 International teams of researchers have succeeded to increase the efficiency for direct solar water splitting with a tandem solar cell whose surfaces have been selectively modified with as new record of 14% efficiency.

At present there is in use of new generation of hydrogen fuel cell vehicles with zero emissions. The H2 car runs on compressed hydrogen fed into a fuel cell "stack" that produces electricity to power the vehicle. A fuel cell can be used in combination with an electric motor to drive a vehicle – quietly, powerfully and cleanly. Great attention has been focused on hydrogen as a potential energy vector and on the use of water-splitting technology as a clean and renewable means to generate hydrogen using solar energy. Numerous attempts have been made to develop photo-catalysts that work not only under UV light but also under visible-light illumination to efficiently utilize solar energy. Some potential sources of hydrogen are electrical, thermal, biochemical, photonic, electro-thermal, photo-thermal, photo-electric, photo-biochemical, and thermal-biochemical. Such forms of energy can be derived from renewable sources, and from energy recovery processes for hydrogen production purposes.

The Idea of the 'Bionic Leaf 2.0' for Photochemical Use of Sunlight

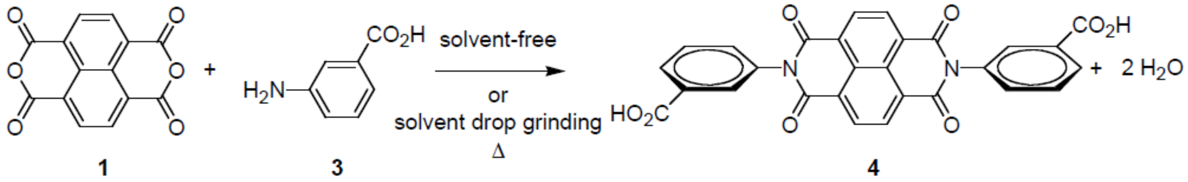
In the last decade new research activities introduced the idea of ―bionic leaf‖ for the efficient splitting of water by photochemical use of sunlight. This research started in the University of Harvard (Massachusetts, USA) and the goal has always been to harness sunlight and use it to create liquid fuel rather than electricity that must then be stored in a battery. The experimental set was designed to use solar power to separate oxygen atoms in water from hydrogen, which is then converted into isopropyl alcohol by bacteria. But prior efforts had used a nickelmolybdenum-zinc (NiMoZn) catalyst and the resulting reactive oxygen species (reactive oxygen species, ROS) would destroy the bacteria‘s DNA.

Green Biocatalysis for the Pharmaceutical Industry

Aftrer an initial lag phase the pharmaceutical industry embraced Green Chemistry from the beginning for economic and prestige purposes with emphasis in greener synthetic methods, less solvents and environmental protection. In the last decades biocatalysis has established itself as a scalable and green technology for the production of a broad range of pharmaceutical compounds and intermediates. Biocatalysts employed on large scale in pharmaceutical synthesis deliver cost- and quality- advantages to the pharmaceutical industry. To this respect there are many discoveries of innovative biocatalytic processes using hydrolases, reductases, transaminases, oxidases etc., which are used for the preparation of therapeutic agents. A recent review included 25 recent biocatalysis case studies for pharmaceuticals manufacture. Innovative enzymes used for biocatalysis offered substantial economic benefits to the pharmaceutical industry.

Cocrystals, which are solids at ambient conditions, are comprised of two or more solid molecules that form a lattice structure distinctly different from those of the pure components. This is manifestly different from conventional solid state synthesis in that solid state synthetic methods typically mix two or more solids together in an amorphous mixture, all of which possess their own distinct lattice structures, and which can then potentially react with one another. Since cocrystals contain solids that have been crystallized together (i.e. “cocrystallized”) to form a new, unique lattice structure there are distinct intermolecular interactions (i.e. hydrogen bonding interactions) in the crystal lattice that bring functional groups in close proximity to each other - close enough to react with one another. Hence, the formation of cocrystals that contain two or more molecular entities that can be induced to undergo reaction is referred to as Cocrystal Controlled Solid State Synthesis, C3S3.

Perhaps the earliest example of a cocrystal is that discovered by Wöhler in 1844 where *p*benzoquinone forms a cocrystal with hydroquinone and subsequently can react to give quinhydrone . Solid state synthesis is now a well established area of chemistry while that of Cocrystal Controlled Solid State Synthesis, C3S3, has thus far been limited to photodimerizations , nucleophilic aromatic substitutions and the condensations described here.



1,4,5,8-naphthalenetetracarboxylic dianhydride, **1**, or phthalic anhydride, **2**, with 3-aminobenzoic acid, **3**

Cocrystals that comprise two or more molecules (cocrystal formers1) that are solids under ambient conditions represent a longknown class of compound. However, they remain relatively unexplored; a Cambridge Structural Database (CSD) survey reveals that they represent less than 0.5% of published crystal structures. Nevertheless, their potential impact upon pharmaceutical formulation and green chemistry is of topical and growing interest. In particular, that all components are solids under ambient conditions has important practical considerations, because synthesis of cocrystals can be achieved via solid-state techniques (mechanochemistry) and chemists can execute a degree of control over the composition of a cocrystal, by invoking molecular recognition, especially hydrogen bonding, during the selection of cocrystal formers. These features distinguish cocrystals from another broad and well-known group of multiple component compounds, solvates. Solvates are much more widely characterized than cocrystals, although this could change because most molecular compounds are solids under ambient conditions. Whereas solid-state organic synthesis represents a wellestablished area of research, cocrystal-controlled solid-state synthesis (C3S3) is presently limited to photodimerizations or photopolymerizations and nucleophilic substitution. In the case of the former, one cocrystal former typically serves to align or “template” the reactant, which is the other cocrystal former. In the case of the latter, both cocrystal formers are reactants, although there are examples in which the reactive moieties are in the same molecule and therefore generate polymeric structures. C3S3 offers broad potential in the context of green chemistry, and herein, we address the issue of whether or not C3S3 can effect the formation of imides, a class of compound that is generally prepared via condensation of acid anhydrides and primary amines (Scheme 1). Cocrystals are accessible via solvent-drop grinding, i.e., two or more solid cocrystal formers milled in the presence of a small amount of solvent. A selected group of anhydrides and primary amines were investigated to determine the following: if they form cocrystals via solvent-drop grinding under ambient conditions and if the ground mixtures so obtained can be converted to imides simply by applying heat. The majority of reactants studied were observed to form imides after heating, but it was not always possible to isolate a cocrystal. Indeed, our CSD survey reveals no previous examples of cocrystals between amines and anhydrides. However, two combinations of cocrystal formers were isolated as cocrystals that facilitate high-yield, low-waste formation of imides.

Green chemistry a Sustainable development

Sustainable development

Development that meets the needs of the present without compromising the ability of future generations to meet their own needs.

Green chemistry, which was established about two decades ago, has attracted much attention. It reflects the efforts of academia and industry to address the challenges related to sustainable development of the chemical industry, and continuous progress is being made, both in academia and industry. Briefly, green chemistry is the utilization of a set of principles to reduce or eliminate the use or generation of hazardous substances in the design, manufacture and applications of chemical products. Green chemistry is a multidisciplinary field and covers areas such as synthesis, solvents, catalysis, raw materials, products and efficient processes.

Efficient synthetic routes

Most current chemical production processes lack efficiency in using feedstocks and produce large amount of wastes. Increasing atom economy is crucial for reducing both the depletion of raw materials and the generation of waste. Ideally, all the atoms in reactants should be transformed into the desired products. However, the achievement of 100% atom economy in all industrial chemical processes is not realistic. Another way to eliminate waste is integration of different reactions and processes, in which the by-product in one reaction is the feedstock of another. Exploration of atom-economic synthetic protocols and routes to increase the synthetic efficiency and reduce or eliminate wastes is a long-term task.

Greener and functional solvents

Huge amounts of toxic, flammable and volatile organic solvents are used in chemical processes to prepare chemicals and materials. About 20 million tons of organic solvents are released to the atmosphere each year, leading to solvent waste and environmental pollution. The use of greener solvents such as water, supercritical fluids, ionic liquids, non-toxic liquid polymers and their various combinations in chemical processes has become a major focus of research in academia and industry. A green solvent should meet some basic requirements such as low toxicity, ease of availability and recycling, and high process efficiency. It is known that the efficiency of a process usually depends strongly on the properties of the solvents used. Because of their special properties and functions, green solvents can be used to optimize chemical processes, decrease solvent usage and processing steps, and develop new routes and technologies that meet the requirements of sustainability.

Greener Catalysis

Catalysis plays a key role in the chemical industry because most chemical processes need catalysts to accelerate reactions, enhance selectivity and lower energy requirements. Current catalysts are often based on expensive, toxic, harmful or noble metals. Green catalysts should have some common characteristics such as high activity, selectivity, and stability, and ease of separation and reuse; they should be based on environmentally benign and widely available raw materials such as abundant metals, organic compounds and enzymes. The exploration and development of new synthetic routes and chemical processes rely strongly on progress in catalysis. The design and use of green catalysts and catalytic systems to achieve the dual goals of environmental protection and economic benefits is an important task, and is essential for the sustainability of the chemical industry.

Use of Green and Renewable Feedstocks

Currently, our energy supply and the feedstocks for producing organic chemicals and materials are mainly based on fossil resources, which are not renewable and are diminishing. The use of renewable carbon resources, i.e. biomass and CO_2, in the chemical and energy industries is extremely important, and different routes and processes have been developed. However, we face thermodynamic, kinetic and technical challenges in the conversion of biomass and CO_2 into fuels and chemicals. Many current routes are technically feasible, but economically prohibitive, and only very small proportions of the resources are currently used. The development of efficient methods for converting biomass and CO_2 into useful chemicals and liquid fuels through energetically and economically viable industrial processes is of great importance, but is challenging. Moreover, the use of greener, cheaper, safer reactants and sustainable energy sources, such as oxygen, hydrogen peroxide and solar energy, in chemical processes is also an interesting area.

Green Engineering and Products

It should be emphasized that green chemistry covers engineering aspects and green products. Chemicals and materials are produced by industrial chemical processes, and therefore, clean, energy-efficient and mass-efficient processes and technologies are essential tools for achieving the goal of maximizing efficiency and minimizing wastes. Many current pharmaceuticals, fine chemicals, commodity chemicals and polymers are harmful. Products that are benign to human health and the environment need be designed and produced to replace hazardous products. Clearly, the exploration of synthetic routes, design of sustainable products and solvents, and exploration of new catalysts and chemical processes are closely related, and should be integrated.

In addition, economic benefits are the central driver for the development of green chemistry and technology

General Outlook

Green chemistry will be one of the most important fields in the future. Although this field has developed rapidly in the last 20 years, it is still at an early stage. Promoting green chemistry is a long-term task, and many challenging scientific and technological issues need to be resolved; these are related to chemistry, material science, engineering, environmental science, physics and biology. Scientists, engineers and industrialists should work together to promote the development of this field. There is no doubt that the development and implementation of green chemistry will contribute greatly to the sustainable development of our society

Green Chemistry

UNIT V

S.No	Question	a	b	c	d	Answer
1.	One among the fields of innovation for Green Chemistry and Green engineering is	Biocatalysis and biotransformations processes	Polyacrylates as scale inhibitors	PVC backing carpets	Friedel crafts reaction	Biocatalysis and biotransformations processes
2.	One among the fields of innovation for Green Chemistry and Green engineering is	New enzymes for organic synthesis	Polyacrylates as scale inhibitors	PVC backing carpets	Friedel crafts reaction	New enzymes for organic synthesis
3.	One among the fields of innovation for Green Chemistry and Green engineering is	Polyacrylates as scale inhibitors	PVC backing carpets	Friedel crafts reaction	Green chemistry and synthetic processes in the pharmaceutical industry	Green chemistry and synthetic processes in the pharmaceutical industry
4.	One among the fields of innovation for Green Chemistry and Green engineering is	Polyacrylates as scale inhibitors	PVC backing carpets	Friedel crafts reaction	Hydrogen production via catalytic splitting of water	Hydrogen production via catalytic splitting of water
5.	One among the fields of innovation for Green Chemistry and Green	Polyacrylates as scale inhibitors	PVC backing carpets	Friedel crafts reaction	Green and renewable energy sources	Green and renewable energy sources

	engineering is					
6.	One among the fields of innovation for Green Chemistry and Green engineering is	agricultural technologies benign to environment	Polyacrylates as scale inhibitors	PVC backing carpets	Friedel crafts reaction	agricultural technologies benign to environment
7.	It is the oxidation procedures that allows	petroleum based feed stocks to become chemical products,	Converts feed stocks in to petroleum based products	Reduction of feedstock materials	Diels Alder synthesis	petroleum based feed stocks to become chemical products
8.	A false statement with respect to biocatalytic conversions	Most of the reactions are performed in aqueous medium at very high temperature and pressure	The biocatalytic transformations normally involve only one step	Protection and deprotection of functional group in not necessary	The biocatalytic reactions are fast and the conversion are stereospecific	Most of the reactions are performed in aqueous medium at very high temperature and pressure
9.	A false statement with respect to biocatalytic conversions	Most of the reactions are performed in aqueous medium at ambient temperature and pressure	The biocatalytic transformations normally involve multiple steps	Protection and deprotection of functional group in not necessary	The biocatalytic reactions are fast and the conversion are stereospecific	The biocatalytic transformations normally involve multiple steps
10.	A false statement with respect to biocatalytic conversions	Most of the reactions are performed in aqueous medium at ambient temperature and pressure	The biocatalytic transformations normally involve only one step	Protection and deprotection of functional group necessary	The biocatalytic reactions are fast and the conversion are stereospecific	Protection and deprotection of functional group necessary
11.	A false statement with respect to biocatalytic	Most of the reactions are	The biocatalytic transformations	Protection and deprotection of	The biocatalytic reactions are	The biocatalytic reactions are

	conversions	performed in aqueous medium at ambient temperature and pressure	normally involve only one step	functional group in not necessary	slower and the conversion are not stereospecific	slower and the conversion are not stereospecific
12.	a practice of being able to make a large number of chemical compounds rapidly on a small scale through reaction matrices is called	Polymer chemistry	Combinatorial chemistry	Nano chemistry	Analytical chemistry	Combinatorial chemistry
13.	Combinatorial chemistry is	One step reaction which takes a long time for completion	Multi step reaction	a practice of being able to make a large number of chemical compounds rapidly on a small scale through reaction matrices	Combines reagents, catalyst, promotor in a single reaction	a practice of being able to make a large number of chemical compounds rapidly on a small scale through reaction matrices
14.	The practice is used on a large scale in the pharmaceutical sector.	Polymer chemistry	Nano chemistry	Analytical chemistry	Combinatorial chemistry	Combinatorial chemistry
15.	Reactions occur in solid phase	Solventless reactions	Homogenous reactions	Heterogenous reactions	Adsorption isotherms	Solventless reactions
16.	Which is not a sustainable process	Using industrial processes that uses hazardous chemicals.	Designing more efficient processes that minimize the production of waste materials	Using the most appropriate starting materials, reagents and catalysts.	New products designed should be biodegradable.	Using industrial processes that uses hazardous chemicals.
17.	Which is not a sustainable process	Using industrial processes that reduce or	Designing more efficient processes that maximise the	Using the most appropriate starting materials, reagents	New products designed should be biodegradable.	Designing more efficient processes that maximise the

		eliminate hazardous chemicals.	production of waste materials	and catalysts.		production of waste materials
18.	Which is not false with respect to sustainable process	Using industrial processes that reduce or eliminate hazardous chemicals.	Designing more efficient processes that minimize the production of waste materials	Using un appropriate starting materials, reagents and catalysts.	New products designed should be biodegradable.	Using un appropriate starting materials, reagents and catalysts.
19.	Which is not true regarding sustainable process	Using industrial processes that reduce or eliminate hazardous chemicals.	Designing more efficient processes that minimize the production of waste materials	Using the most appropriate starting materials, reagents and catalysts.	New products designed should be non-biodegradable.	New products designed should be non-biodegradable.
20.	Bionic Leaf’ is used for	Hydrogen generated from solar-driven water-splitting	photovoltaic and photoelectrochemical apparatus	Photovoltaic cells	photoelectrochemical apparatus	Hydrogen generated from solar-driven water-splitting
21.	Cocrystals are	solids at ambient conditions	Semi solids at ambient conditions	Liquids at ambient conditions	gases at ambient conditions	solids at ambient conditions
22.	comprised of two or more solid molecules that form a lattice structure distinctly different from those of the pure components	Co-crystals	Covalent solids	Ionic solids	Liquid crystals	Co-crystals
23.	An example for a cocrystal is	*p*-benzoquinone forms a cocrystal with hydroquinone	*p*benzoquinone forms a cocrystal with phenol	*aceto*quinone forms a cocrystal with hydroquinone	*aceto*quinone forms a cocrystal with phenol	*p*-benzoquinone forms a cocrystal with hydroquinone
24.	*p*-benzoquinone with	Co-crystals	Covalent solids	Ionic solids	Liquid crystals	Co-crystals

	hydroquinone is a					
25.	synthesis of cocrystals can be achieved via solid-state techniques is called	Mechano chemistry	Nanochemistry	Combinatorial chemistry	mechintronix	Mechano chemistry
26.	Which are considered as renewable starting materials ?	CO_2	methane gas	CO	CO_2 & methane gas	CO_2 & methane gas
27.	Known deposits of a material that can be extracted profitably are called	resources.	undiscovered reserves.	identified deposits.	reserves.	reserves.
28.	Which of the following is the most abundant fossil fuel?	oil	natural gas	coal	gasoline	coal
29.	Which of the following is not a renewable energy source?	biomass conversion	solar	hydroelectric	oil	oil
30.	What are the main constituents of natural gas?	CO	CO2	CH4 & C_2H_6	NO_2	CH4 & C_2H_6
31.	What is the name of the porous Teflon base of the reaction vessel?	Frit	Test tube	Flask	Filter	Frit
32.	What term is used to describe the release of molecules from the resin in combatorial chemistry?	Bond breaking	Synthesis	Cleavage	Decomposition	Cleavage
33.	What is the name of the process by which compounds related to a promising compound are made on a larger scale?	Computational chemistry	Combinational chemistry	Lead optimisation	Improvement	Lead optimisation

34.	Combinatorial and parallel synthesis can be useful at various stages of the drug design / development process. Which of the following is not such a stage?	Finding a lead compound	Optimising a lead compound	Structure determination of the lead compound	Structure-activity relationships of the lead compound	Structure determination of the lead compound
35.	What is meant by a linker or an anchor?	The bond which links a molecule to a solid support.	A reactive functional group on the solid support which allows a molecule to be attached to the solid support.	A molecular unit which is attached to the solid support and which contains a reactive functional group that allows attachment of a starting material.	The functional group on the starting material which is used to attach the molecule to the solid support.	A molecular unit which is attached to the solid support and which contains a reactive functional group that allows attachment of a starting material.
36.	What is meant by a scaffold?	The lead compound	The carbon skeleton of a compound	The core structure of a molecule that is common to a series of compounds	The pharmacophore	The core structure of a molecule that is common to a series of compounds
37.	According to EPA of USA, the following is not one of the six major pollutants?	Ozone	Carbon monoxide	Nitrogen oxides	Carbon di-oxide	Carbon di-oxide
38.	Which of the following is an organic gas?	Hydrocarbons	Aldehydes	Ketones	Ammonia	Ammonia
39.	Ozone of found in	Mesosphere	Ionosphere	Stratosphere	Exosphere	Stratosphere
40.	Ozone is formed in the upper atmosphere by a photochemical reaction with	Ultra violet solar radiation	Infra red radiation	Visible light	All of the above	Ultra violet solar radiation

41.	The principal source of volatile organics (Hydrocarbons) is	Transportation	Industrial processes	Stationary fuel combustion	Volcanoes	Industrial processes
42.	The function of automobile catalytic converter is to control emissions of	carbon dioxide and hydrogen	carbon monoxide and hydrogen	carbon monoxide and carbon dioxide	carbon monoxide and nitrogen dioxide	carbon monoxide and hydrogen
43.	The threshold concentration of sulphur dioxide in any industrial activity should not be permitted beyond	2ppm	3ppm	4ppm	5ppm	5ppm
44.	Which of the following is used as antiknock compound in gasoline?	tetramethyl lead	tetraethyl lead	trimethyl lead	triethyl lead	tetraethyl lead
45.	Which of the following is a fermentation product of molasses?	Methano	Formaldeyde	Ammonia	Acetone	Acetone
46.	The boiler flue gas is source of	HCl	NO	HF	Volatile organic compounds	NO
47.	Which of the following is true about carbon monoxide?	single largest source is from internal combustion engines	results from the actions of ultraviolet light on ozone	causes acid rain	leading cause of cancer in smokers	single largest source is from internal combustion engines
48.	Sulfur dioxide contributes to all of the following problems except	damage to buildings	acid rain.	death of vegetation	photochemical smog.	photochemical smog.
49.	Which of the following is not a major contributor to the greenhouse effect?	carbon dioxide	carbon monoxide	chlorofluorocarbons	methane gas	carbon monoxide
50.	Which of the following	phosphorylases	isomerases	hydrolases	dehydrogenases	dehydrogenases

	enzyme groups can catalyse oxidation reactions?					
51.	Enzymes differ from inorganic catalysts in that they are highly specific.Which property of an enzyme is responsible for this specificity?	The insoluble nature of enzymes.	The high molecular mass of enzymes.	The surface configuration of enzymes.	The absence of metallic ions in an enzyme.	The surface configuration of enzymes.
52.	Which of the following is an extracellular enzyme?	catalase	DNA polymerase	keratin	trypsin	trypsin
53.	Which one of the following conditions is least likely to denature an enzyme?	a high temperature	an extreme pH	heavy metal ions	a low temperature	a low temperature
54.	Which type of enzyme catalyses the conversion of a dipeptide into two separate amino acids?	decarboxylase	dehydrogenase	hydrolase	oxidoreductase	hydrolase
55.	An example for a renewable resource	Crude oil	petroleum	diesel	biomass	biomass
56.	Example for a biocatalyst	enzymes	Metallic salts	Raney Nickel	Coordination compounds	enzymes
57.	Using a biocatalyst in a reaction makes it	Environmentally friendly	unattractive	Economically unviable	Environmentally unviable	Environmentally friendly
58.	Using a biocatalyst in a reaction makes it	Environmentally un friendly	unattractive	Economically unviable	Environmentally viable	Environmentally viable
59.	d-glucose is used to prepare adipic acid is manufactured from	Corn starch	Animal protein	Raney Nickel	Animal fats	Corn starch
60.	Microwave radiation is also called as	Ultraviolet radiation	Infrared radiation	Electromagnetic radiation	Radiofrequency radiation	Electromagnetic radiation