16BESHOE06 GREEN CHEMISTRY

L	T	P	C
3	0	0	3

COURSE OBJECTIVES:

- To understand about the green chemistry
- To study the atom efficient process and synthesis elaborately.
- To gain knowledge on the green technology and renewable energy resources.
- To get the information on catalysis

LEARNING OUTCOME:

- Students will know the chemistry and application of green technology for energy sources. They will understand the role of green catalyst in industries.

UNIT I INTRODUCTION TO GREEN CHEMICAL PRINCIPLES (9)

Definition, tools, and twelve principles of green chemistry, solvent-less reactions and reactions in water, microwaves and fluorous solvents, green resolution of racemic mixtures, materials for a sustainable economy, chemistry of longer wear, agrochemicals: problems and green alternate solutions.

UNIT II ATOM EFFICIENT PROCESSES (9)

Atom efficient processes, evaluating chemical reagents according to their yield and atom efficiency, examples of efficient stoichiometric and catalytic processes, atom economy and homogeneous catalysis, halide-free synthesis and alternatives to Strecker synthesis.

UNIT III BIOTECHNOLOGY AND GREEN CHEMISTRY (9)

Bio technology and its applications in environmental protection-Bio informatics-Bio remediation, biological purification of contaminated air. Green chemistry for clean technology-Significance of green chemistry-Basic components of green chemistry, Industrial applications of green chemistry, green fuels-e-green propellants and bio catalysts.

UNIT IV RENEWABLE RESOURCES (9)

Use of renewable materials, evaluating feedstock and starting materials and their origins, toxicity, sustainability and the downstream implications of the choice of feedstock, commodity chemicals from glucose and biomass conversion.

UNIT V CATALYSIS IN GREEN CHEMISTRY (9)

Catalysis, energy requirements and usage, optimization of the reaction by minimizing the energy requirements, examples of efficient catalytic reactions including the use of heterogeneous catalysis, zeolites, oxidation using molecular oxygen.

Total Hours: 45

TEXT BOOKS:

1. Sanjay K. Sharma, Ackmez Mudhoo Green Chemistry for Environmental Sustainability CRC Press , London 2010
2. Ahluwalia V. K. and M.Kidwai New Trends in Green Chemistry 2nd edition Anamaya publishers., New Delhi. 2007

REFERENCES:

1. Dr. Sunita Ratan A Textbook of Engineering Chemistry S.K. Kataria and Sons., New Delhi.2012
2. Mukesh Doble. Ken Rollins, Anil Kumar Green Chemistry and Engineering, 1st edition Academic Press, Elesevier., New Delhi.2007
3. Desai K. R. Green Chemistry Himalaya Publishing House, Mumbai.2005
4. Matlack A. S. Introduction to Green Chemistry Marcel Dekker: New York 2001

WEBSITES:

1. http://www.organic-chemistry.org/topics/green-chemistry.shtm
2. http://www.essentialchemicalindustry.org/processes/green-chemistry.html
3. http://www.chm.bris.ac.uk/webprojects2004/vickery/green_solvents.htm
4. http://www.epa.gov/research/greenchemistry/
5. http://www.amazon.in/Green-Chemistry-Catalysis

KARPAGAM ACADEMY OF HIGHER EDUCATION

(*Established under section 3 of the UGC Act 1956*)

COIMBATORE – 641021

GREEN CHEMISTRY

16BESHOE16

LECTURE PLAN

TOTAL HOURS: 45

UNIT I - INTRODUCTION TO GREEN CHEMICAL PRINCIPLES

HOURS REQUIRED: 9

S.No	Topics	Hours
1.	Definition, tools, and twelve principles of green chemistry	1
2.	Solvent-less reactions and reactions in water	1
3.	Microwaves and fluorous solvents	1
4.	Green resolution of racemic mixtures	1
5.	Materials for a sustainable economy	1
6.	Chemistry of longer wear	1
7.	Agrochemicals	1
8.	Problems of agrochemicals	1
9.	Green alternate solutions	1

UNIT II - ATOM EFFICIENT PROCESSES

HOURS REQUIRED: 9

S.No	Topics	Hours
1.	Atom efficient processes	
2.	Evaluating chemical reagents according to their yield and atom efficiency	1
3.	Atom efficiency	1
4.	Examples of efficient stoichiometric Processes	1
5.	Catalytic processes	1
6.	Atom economy	1
7.	homogeneous catalysis	1
8.	halide-free synthesis	1
9.	Alternatives to Strecker synthesis	1

UNIT III - BIOTECHNOLOGY AND GREEN CHEMISTRY

HOURS REQUIRED: 9

S.No	Topics	Hours
1.	Bio technology and its applications in environmental protection	1
2.	Bio informatics-Bio remediation	1
3.	Biological purification of contaminated air	1
4.	Green chemistry for clean technology	1
5.	Significance of green chemistry	1
6.	Basic components of green chemistry	1
7.	Industrial applications of green chemistry	1
8.	Green fuels-e-green propellants	1
9.	Bio catalysts	1

UNIT IV - RENEWABLE RESOURCES

HOURS REQUIRED: 9

S.No	Topics	Hours
1.	Use of renewable materials	1
2.	Feedstock materials	1
3.	Evaluating feedstock materials and starting materials	1
4.	Origin of feedstock materials	1
5.	Toxicity	1
6.	Sustainability	1
7.	Downstream implications of the choice of feedstock	1
8.	commodity chemicals from glucose	1
9.	Biomass conversion	1

UNIT V - CATALYSIS IN GREEN CHEMISTRY

HOURS REQUIRED: 9

S.No	Topics	Hours
1.	Catalysis	1
2.	Energy requirements and usage	1
3.	Optimization of the reaction by minimizing the energy requirements	1
4.	Efficient catalytic reactions	1
5.	Heterogeneous catalysis	1
6.	Examples of efficient catalytic reactions	1
7.	Use of heterogeneous catalysis	1
8.	Zeolites	1
9.	Oxidation using molecular oxygen	1

TEXT BOOKS:

S. NO.	AUTHOR(S) NAME	TITLE OF THE BOOK	PUBLISHER	YEAR OF PUBLICATION
1.	Sanjay K. Sharma, Ackmez Mudhoo	Green Chemistry for Environmental Sustainability	CRC Press , London	2010
2.	Ahluwalia V. K. and M.Kidwai	New Trends in Green Chemistry 2nd edition	Anamaya publishers., New Delhi.	2007

REFERENCE BOOKS:

S. NO.	AUTHOR(S) NAME	TITLE OF THE BOOK	PUBLISHER	YEAR OF PUBLICATION
1.	Dr. Sunita Ratan	A Textbook of Engineering Chemistry	S.K. Kataria and Sons., New Delhi.	2012
2.	Mukesh Doble. Ken Rollins, Anil Kumar	Green Chemistry and Engineering, 1st edition	Academic Press, Elesevier., New Delhi.	2007

3.	Desai K. R.	Green Chemistry	Himalaya Publishing House, Mumbai.	2005
4.	Matlack A. S.	Introduction to Green Chemistry	Marcel Dekker: New York	2001

WEBSITES:

1. http://www.organic-chemistry.org/topics/green-chemistry.shtm
2. http://www.essentialchemicalindustry.org/processes/green-chemistry.html
3. http://www.chm.bris.ac.uk/webprojects2004/vickery/green_solvents.htm
4. http://www.epa.gov/research/greenchemistry/
5. http://www.amazon.in/Green-Chemistry-Catalysis

STAFF HoD

All matter, all things, the air around us, the water we must drink, and all living organisms are made of chemicals. For the past two centuries chemical science has been practiced on an ever-increasing scale and as a result it has enabled the production of a wide variety of goods that are valued by humans. With the persistent efforts of chemists and the chemical industry, the high standard of living has been enjoyed in modern industrialized societies. The quality of life has improved due to the discovery of many products, chemicals, pharmaceuticals, fertilizers, dyes, plastics, cosmetics, semi-conductors, electronic devices, and other materials.

But there can be no denying that in years past, and even at present, chemistry has been misused in many respects, such as the release of pollutants and toxic substances and the production of non biodegradable materials, resulting in harm to the environment and living things, including humans. It is now obvious that chemical science must be turned away from emphasis upon the exploitation of limited resources and the production of increasing amounts of products that ultimately end up as waste and toward the application of chemistry in ways that provide for human needs without damaging the Earth support system upon which all living things depend. Fortunately, the practice of chemical science and industry is moving steadily in the direction of environmental friendliness and resource sustainability. The practice of chemistry in a manner that maximizes its benefits while eliminating or at least greatly reducing its adverse impacts has come to be known as green chemistry.

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, bio chemistry, 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.

What is Green Chemistry?

Green chemistry is defined as environmentally benign chemical synthesis. It design the chemical processes and products that reduce or eliminate the use and/or the generation of hazardous substances.

The main purposes of green chemistry

1. Eco-friendly chemical technology:

Green chemistry aims to protect the environment and this is why it is also described as Environmentally Benign chemistry.

2. Replacement of organic solvent and to minimize the waste product:

Green chemistry aims to devise greener reaction conditions for the synthesis of chemicals so that waste product (specially toxic waste) formation can be minimized. It needs the replacement of organic solvent by water or complete of the use of solvent. It also needs to minimize the formation of by-products (specially the hazardous substances).

3. Use of renewable feedstocks:

Green chemistry aims to develop the greener synthesis of the required chemical products by using the renewable resources (e.g. biomass rather than petrochemical feedstocks). It reduces the consumption of nonrenewable resources (e.g. Crude oil).

4. To minimize the energy consumption:

Green chemistry aims to develop the greener conditions for the synthesis of chemical products so that energy consumption can be minimized. For many existing chemical technologies, drastic reaction conditions (e.g. high temperature, high pressure, etc.) which are energy requiring are applied. Greener synthesis aims to develop the mild or modest reaction conditions. Idealty, the reactions should be carried out at ambient temperature and pressure.

5. Use of more eco-friendly chemical products:

Green chemistry aims to design the new chemical products to replace the existing hazardous chemical products provided the new chemicals are having the same desirable properties of the existing ones (e.g. development of new pesticide which is only toxic to the target species and at the same time it biodegrades easily to harmless products).

6. Four R’s (4R’s) and integrated waste management (TWM):

These four R’s are: reduction (at source), recycling, reuse and recovery.

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:

(i) the design of processes to maximize the amount of raw material that ends up in the product;

(ii) the use of safe, environment-benign substances, including solvents, whenever possible;

(iii) the design of energy efficient processes;

(iv) 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.

Attempts are being made to quantify the *greenness* of a chemical process, to calculate chemical yield, the price of reaction components, safety in handling chemicals, hardware requirements, energy and ease of product workup and purification.

To Implement these Green Chemical Principles it requires investment, since the current, very inexpensive chemical processes must be redesigned.

However, in future, when certain raw materials cost and also the costs for energy increases, such an investment will pay back as the optimized processes become less expensive than the unoptimized ones. The development of greener procedures can therefore be seen as an investment for the future. It also helps to ensure that the production complies with future legal regulations.

1. Prevention of Waste

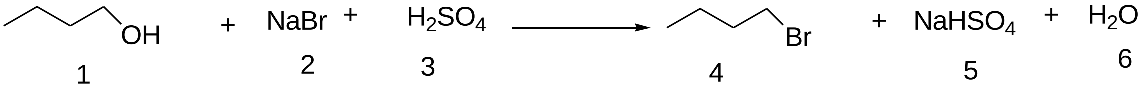
It is better to prevent waste than to treat or clean up waste after it has been created. The first principle aims to develop the zero waste technology (ZWT). Interms of ZWT, in a chemical synthesis, waste product should be zero or minimum. It also aims to use the waste product of one system as the raw material for other systems. As for example, bottom ash of thermal power station can be used as a raw material for cement and brick industry; effluent coming out from cleaning of machinery parts may be used as coolant water in thermal power station; municipal waste as a source of energy etc.

2. Maximize Atom Economy

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

The second principle of green chemistry can be simply stated as the “atom economy” of a reaction. Atom economy, asks the question “what atoms of the reactants are incorporated into the final desired product(s) and what atoms are wasted?”

Traditionally, the efficiency of a reaction has been measured by calculating the percent yield. Let us assume that the following substitution reaction gives 100% yield. While this is admirable, we can shed more light on the efficiency of a reaction by calculating the “percent atom economy” as follows:



% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100

= (137/275) X 100 = 50%

The percent atom economy is simply the formula weight of the desired product(s) (compound **4**, 137 g/mol) divided by the sum of the formula weights of all the reactants (275 g/mol), which gives 50% in this case. Simply put, even if our percent yield is 100%, only half the mass of the reactants atoms are incorporated in the desired product while the other half is wasted in unwanted by-products.

Principle #2 deals with the reactants. However, as those of us who have run a chemical reaction know, we usually use other materials such as solvents and separating agents during a synthesis. These materials usually make up the bulk of the material input, and thus we must also account for the waste that is produced from them.

3. Less Hazardous Chemical Synthesis

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

When you think about it, this is a two-part principle divided by the first two words, “wherever practicable.” Because it may not be practical or possible to avoid using substances that are toxic. Chemists use toxic substances all the time because reactive chemicals afford reactions that are kinetically and thermodynamically favorable. And unless—and until—replacement chemicals along with new synthetic protocols are developed, inherently toxic materials will continue to be used.

It’s not that adhering to this principle is particularly difficult to do; it’s more that chemists are disinterested in doing it. For the synthetic organic chemist, effecting a successful chemical transformation in a new way or with a new molecule or in a new order is what matters.

In fact, the chemistry or chemical transformation in a synthesis generally impacts the overall toxicity profile (and most other measures of sustainability and green) of a product or process the least, except in those cases where we deliberately are producing a molecule that is toxic or biologically active by design. That is certainly the case for many molecules that are synthesized as in the pharmaceutical or agriculture chemical business—the molecules are toxic and/or have other effects on living organisms by design.

The chemicals and materials used in effecting chemical transformations matter and chemists need to pay more attention to the choices they make about what goes into the flask. It’s easy to discount all the other “stuff” and focus all our energy on the synthetic pathway that delivers the desired product. But when we ignore all the other “stuff,” we pay a high price and it’s a price we need to stop paying. Occasionally, chemists do produce molecules that have toxic or other hazardous effects, and the next principle will have something to say about designing safer molecules.

4. Designing Safer Chemicals and Products

Chemical products should be designed to affect their desired function while minimizing their toxicity.

Minimizing toxicity, while simultaneously maintaining function and efficacy, may be one of the most challenging aspects of designing safer products and processes. Achieving this goal requires an understanding of not only chemistry but also of the principles of toxicology and environmental science. Highly reactive chemicals are often used by chemists to manufacture products because they are quite valuable at affecting molecular transformations. However, they are also more likely to react with unintended biological targets, human and ecological, resulting in unwanted adverse effects. Without understanding the fundamental structure hazard relationship, even the most skilled molecular magician enters the challenge lacking a complete toolkit.

Now is the ideal time to develop a comprehensive and cooperative effort between toxicologists and chemists, focused on training the next generation of scientists to design safer chemicals in a truly holistic and trans-disciplinary manner through innovative curricular advancements.

5. Safer Solvents, Auxiliaries and reaction conditions

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

It was a green chemistry conference and the very famous synthetic chemist had just received a question about why he had chosen a solvent that was a very poor choice. You have to be realistic, chemists know intuitively what's best, and solvents don't matter. It's the chemistry that counts.

Solvents and mass separation agents of all kinds matter a lot to the chemistry not to mention the chemical process and the overall "greenness" of the reaction. In many cases, reactions wouldn't proceed without solvents and/or mass separation agents. Solvents and separation agents provide for mass and energy transfer and without this, many reactions will not proceed.

It has also been shown that solvents account for 50 – 80 percent of the mass in a standard batch chemical operation, depending on whether you include water or you don't. Solvents and mass separation agents also drive most of the energy consumption in a process.

Solvents are alternately heated, distilled, cooled, pumped, mixed, distilled under vacuum, filtered, etc. And that's before they may or may not be recycled. If they're not recycled, they are often incinerated.

Solvents are also the major contributors to the overall toxicity profile. On average, they contribute the greatest concern for process safety issues because they are flammable and volatile, or under the right conditions, explosive. They also generally drive workers to have personal protective equipment of one kind or another.

The object is to choose solvents that make sense chemically, reduce the energy requirements, have the least toxicity, have the fewest life cycle environmental impacts and don't have major safety impacts.

6. **Increases Energy Efficiency**

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

In recent years synthetic organic chemists, give no consideration to temperature or pressure. The chemist just follows a protocol to get a reaction to go to completion and to separate the desired product at as high a yield as possible. Energy, from the chemist’s perspective, is irrelevant and for all intents and purposes, free. Just put the plug in the wall or the heating coil around the flask.

All the attention that energy gets from chemists is devoted to heating, cooling, separations, electrochemistry, pumping and reluctantly, to calculations related to thermodynamics (e.g., Gibbs Free Energy). The attention is not in minimizing or considering where energy comes from or if it matters what form is used, it's just a given that we need to heat or cool or shove electrons into the reaction to make or break bonds.

Energy is a key issue for the 21st century. A majority of the energy that is produced is based, on fossil fuels. And most of the energy that is delivered to the point of use is lost in conversion and transmission. What this means is that if you look at the life cycle of energy production, and you look at how much energy is actually available for useful work at the point of need, it is less than 1 or 2% of the energy that was originally available in the fossil fuel.

7. **Use of Renewable Feedstocks**

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

The concept of making all our future fuels, chemicals and materials from feedstocks that never deplete is an interesting concept which at first glance seems impracticable. Mankind currently removes fossil fuels, coal, oil and natural gas from the ground and extracts minerals for profit until they are exhausted. In particular, our fossil fuels for carbon-based chemicals and materials are being rapidly depleted in a predictable manner with the expected rise of global populations and expanding energy intensive economies on several continents. The impacts on human health and the environment are significant and present major challenges for our scientists and leaders in the next 50 years.

8. Reduce Chemical Derivatives

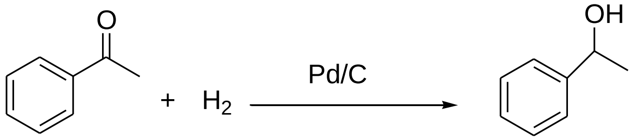
Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

One of the key principles of green chemistry is to reduce the use of derivatives and protecting groups in the synthesis of target molecules. One of the best ways of doing this is the use of enzymes. Enzymes are so specific that they can often react with one site of the molecule and leave the rest of the molecule alone and hence protecting groups are often not required.

9. Use Catalysis

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

A primary goal of green chemistry is the minimization or preferably the elimination of waste in the manufacture of chemicals and allied products: *"prevention is better than cure"*. This necessitates a paradigm shift in the concept of efficiency in organic synthesis, from one that is focused on chemical yield to one that assigns value to minimization of waste. What is the cause of waste? The key lies in the concept of atom economy: *"synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product"*. In the reaction scheme we compare, for example, the reduction of a ketone to the corresponding secondary alcohol using sodium borohydride or molecular hydrogen as the reductant. Reduction with the former has an atom economy of 81% while reduction with the latter are 100% atom economic, that is everything ends up in the product and, in principle, there is no waste.



Unfortunately, hydrogen does not react with ketones to any extent under normal conditions. For this we need a catalyst such as palladium-on-charcoal. A catalyst is defined as *"a substance that changes the velocity of a reaction without itself being changed in the process"*. It lowers the activation energy of the reaction but in so doing it is not consumed. This means that, in principle at least, it can be used in small amounts and be recycled indefinitely, that is it doesn't generate any waste. Moreover, molecular hydrogen is also the least expensive reductant and, for this reason, catalytic hydrogenations are widely applied in the petrochemical industry, where the use of other reductants is generally not economically viable. It is only in the last two decades, however, following the emergence of green chemistry, that catalysis has been widely applied in the pharmaceutical and fine chemical industries, with the goal of minimizing the enormous amounts of waste generated by the use of stoichiometric inorganic reagents. This involves the use of the full breadth of catalysis: heterogeneous, homogeneous, organocatalysts and, more recently, Nature's own exquisite catalysts: enzymes. The latter are particularly effective at catalyzing highly selective processes with complex substrates under mild conditions and, hence, are finding broad applications in the pharmaceutical and allied industries. Moreover, they are expected to play an important role in the transition from a chemical industry based on non-renewable fossil resources to a more sustainable bio-based economy utilizing renewable biomass as the raw material, yet another noble goal of green chemistry.

10. Design Chemicals and Products to Degrade after use.

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

Green chemistry practitioners aspire to optimize the commercial function of a chemical while minimizing its hazard and risk. Hazard, the capability to cause harm, is an inherent characteristic arising, like function, from a chemical’s stereochemistry (the content and arrangement of atoms).

A green chemistry objective is to design out molecular features responsible for hazardous characteristics and risk. Trade-offs, or alternative approaches, must be evaluated when the molecular features to be designed in for commercial function overlap with those to be designed out to reduce hazard and risk.

Biodegradation, hydrolysis, and photolysis can be designed into chemical products. In the same way that mechanistic toxicology knowledge is essential to identify and design out molecular features that are the basis for hazards, an understanding of the mechanisms of degradation and persistence are required to design in chemical features that promote degradation and eliminate features that promote persistence. Many persistent compounds are extensively chlorinated. Halogens such as chlorine are electron withdrawing, thereby inhibiting the enzyme systems of microbes because aerobic microbial degradation favors electron rich structures.

Prediction methods that can guide the design of molecular architecture expected to degrade include rules of thumb linking structural features to degradability or persistence, databases of existing knowledge, models that evaluate biodegradability or PBT attributes, and experimental testing. All of these tools can be adapted to individual chemical sectors and specific objectives.

Understanding the anticipated release and transport pathways for a chemical informs the selection of an effective design strategy. Degradation must occur within the relevant environmental compartment(s) and at a meaningful rate. Domestic wastewater typically passes through a vigorous bioreactor within wastewater treatment plants (WWTP). The consumer product industry has designed molecules for removal within these bioreactors. In the early 1960’s, industry transitioned from non-biodegradable branched surfactants, which caused extensive foaming and other health problems in surface waters receiving

WWTP effluent, to biodegradable linear alkyl benzene sulfonate based detergents – an approach to innovative design that continues today.

Tools currently exist to enable the implementation of principle 10, but advances in mechanistic understandings linking molecular features to hazards and degradability will enable more comprehensive application of green chemistry to control hazard and risk. Effective communication across disciplines is also essential to provide designers with knowledge they can factor into the complexities of product design. Because of regulatory and business constraints, many product design decisions must be made relatively early. Predictive decision-making tools must provide confidence about hazard and risk in a way that is aligned with the timing and magnitude of development decisions, and most importantly, while there is still flexibility to alter a molecular design or product formulation.

11. Real-time analysis for Pollution Prevention

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

Imagine driving down a busy highway in a car with all of the windows painted an opaque black!!! While that scenario many not seem realistic (or safe), what if you had a 360° camera and the sensors and technology being developed for self-driving cars? Now, the safety of your commute is more ensured.

This description, while applied to automobiles, is illustrative of the 11th principle of green chemistry. Just as we need real-time feedback for driving safety, real-time feedback is essential in proper functioning chemical processes. Most chemists are familiar with laboratory analysis from their undergraduate training. But analysis can also be performed in-line, on-line, or at-line in a chemical plant, a subdiscipline known as process analytical chemistry. Such analysis can detect changes in process temperature or pH prior to a reaction going out of control, poisoning of catalysts can be determined, and other deleterious events can be detected before a major incident occurs.

Process analysis is of such importance that the US Food and Drug Administration encourages such an approach for the manufacture, design, and control of pharmaceutical manufacturing. Since 1984, an industry-academic partnership, the Center for Process

Analytical Chemistry, has promoted research into emerging techniques for process analytical chemistry.

While the traditional roles of analytical chemistry also advance green chemistry goals, the effective application of process analytical chemistry directly contributes to the safe and efficient operation of chemical plants worldwide.

12. **Inherently Safer Chemistry for Accident Prevention**

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

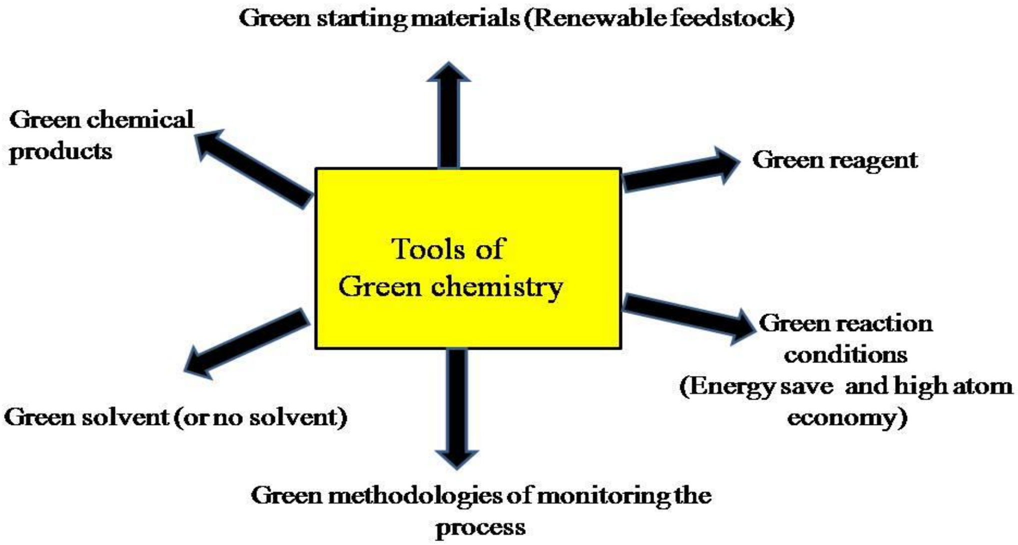
Safety can be defined as the control of recognized hazards to achieve an acceptable level of risk. Green Chemistry Principle # 12 is known as the "Safety Principle". It may be the most overlooked of the twelve principles, yet it is the logical outcome of many of the other principles. In fact it is practically impossible to achieve the goals of Principle 12 without the implementation of at least one of the others. Since the very essence of green chemistry is to "… reduce or eliminate the use or generation of hazardous substances" there is an intrinsic connection to laboratory safety. While there are a few exceptions, the majority of the Green Chemistry Principles will result in a scenario that is also safer.

Under the umbrella of the Environmental Protection Agency (EPA), Green Chemistry's primary focus is clearly to make the environment safer. Materials and processes that are safer for the environment also are likely to be safer for the general public. However, another population that benefits from green chemistry and is not often mentioned is workers. The manufacturing or laboratory worker is often the first in-line person to benefit from hazard reductions.

The health and safety of workers are under the purview of the Occupational Safety and Health Administration (OSHA). In a recent news release, OSHA unveiled a chemical management system designed to increase worker safety. The Hierarchy of Safety Controls as highlighted in OSHA's new Transitioning to Safer Chemicals Toolkit illustrates the difference between focusing on the control or hazard part of the safety definition. Traditional chemical safety models focus primarily on the control component of that definition. The graphic (adapted from OSHA) shows that the most effective means of increasing safety is eliminating the hazard component. Since the elimination of hazards is the basic tenet of Green Chemistry, this marriage of the ideas of Green

Chemistry from both OSHA and EPA should have a synergistic impact on hazard reduction. Combining the forces of these two agencies toward a common goal may lead to conversations and changes that result in safer conditions for workers, a safer environment for the general public, and a safer planet for us all.

Tools of Green Chemistry:



(i) Green starting materials (Renewable feedstock)

If it is technically and economically possible, then the renewable resources rather then the non renewable resources should be used as the raw material or feedstock.

(ii) Green reagent

If possible, the synthetic methodologies should avoid the use and generation of toxic and environmentally hazardous substances.

(iii)Green reaction conditions (Energy save and high atom economy)

In the synthesis of a chemical product, the energy consumption should be minimized to make the process more and more economic.

During the synthesis of a chemical product, the methodology should be designed in a way to maximize the incorporation of starting materials into the desired final product.

(iv)Green methodologies of monitoring the process

Analytical methodologies should be further developed to allow for real time in process monitoring and control prior to the generation of hazardous substances in the synthesis of chemical products.

(v) Green solvent (or no solvent)

If possible in a chemical synthesis, the use of auxillary substances like solvents, separating agents etc should be avoided. The use of ecofriendly reaction media are water, polyethylene glycol, room temperature ionic liquids, supercritical water (SCW), supercritical carbon dioxide (SC-CO_2) etc.

(vi) Green chemical products (degradable waste, degradable polymers, degradable pesticides)

At the end of function, the chemical products should degrade easily to harmless products i.e., after their function, they should not persist in the environment.

Solvents

All solvents are volatile organic compounds. They form street-level ozone and smog via free radical air oxidation processes. All solvent waste must be contained and treated. Organic solvents have good heat and mass transfer capacity and has low viscosities(good for kinetics). Also not all organic solvents are harmful. E.g. Isopropanol, ethylacetate, ethanol, 2-butanone, limonene (extracted from citrus fruit peel). Replacing organics may incur an increased energy input. Therefore industry has concentrated on eliminating the most toxic solvents first e.g. chlorocarbons, benzene, toluene, hexane, dioxane, pyridine and methanol.

Why arereactions 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 reactants.

Issues with organic solvents:

- ✓ Organic solvents are expensive.
- ✓ Organic solvents are highly regulated.
- ✓ Many organic solvents are volatile, flammable, toxic and carcinogenic.

The main alternatives to organic solvents are

1. Solvent free processes
2. Waste based chemistry
3. Use of super critical fluids (particularly water and CO_2)
4. Ionic liquids
5. Fluorous biphasic systems

There are several ways in which organic solvents may be replaced and a good argument can often be made for doing so on green chemistry grounds. However, it is important to remember that changing solvents may require additional energy (e.g. stronger heating), and organics may still be needed for work-up/ purification steps. The choice of green solvent depends upon the reaction, upon the catalyst(s) and upon the method of product separation.

The main disadvantages of solvent free synthesis are

1. Solvents are often still required during work up (e.g. extraction)
2. Poor heat transfer in the solid state (although this may be overcome using microwaves)
3. Fewer solvent-free examples exist for fine chemicals/pharmaceuticals

The water based chemistry - the ultimate green solvent. The advantages are non-toxic, cheap biorenewable, Non-flammable and high specific heat capacity.

The disadvantages are removal requires distillation (therefore energy intensive), waste streams may be difficult to treat, many reagents are water sensitive and generally a poor solvent for organics. Despite the disadvantages, water based organic synthesis is a very popular area of research.

Supercritical carbondioxide

The uses of supercritical carbondioxide are

1. Extraction of caffein from coffee (traditional method uses dichloromethane)
2. Extraction of fatty acid glycerides from crisps
3. Dry cleaning (traditional method uses C_2Cl_4)
4. Spray painting.

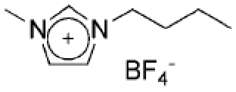
The advantages are

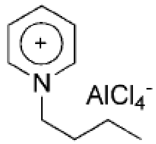
Non-toxic, readily removed (and recyclable), Non-flammable, low viscosity (fast diffusion), CO_2 is cheap. The disadvantages are high pressure equipment is expensive and potentially dangerous, Carbon dioxide is a relatively poor solvent, reacts with strong nucleophiles (e.g. amines)

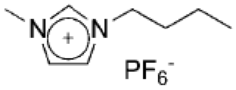
Ionic liquids

Liquids at room temperature (large non-coordinating ions pack poorly)

Examples of ionic liquids are







Advantages are

Readily prepared, very low vapour pressure, can act as catalysts, turnable viscosity (via anion), stgable at high temperature, highly solvating and recyclable.

The disadvantages are non-biodegradable, concerns over toxicity, synthesis always requires haloalkanes, product isolation often requires distillation or extraction into an organic solvent.

Fluorous biphasics

Fully fluorinated solvents (e.g. C_6F_{14}) are non-polar and immisible with organic solvents. Ideal if reactants are non-polar, but products are polar.

The disadvantages are that fluorinated solvents are expensive and concerns exist for their long-term environment impact.

Solvent less reactions

It is also known as dry media reaction or solid state reactions. Solvent less reactions is a chemical reaction system in the absence of a solvent. Solid state reactions follows 5th principle of green chemistry which avoid using toxic solvents in the chemical reactions. These reactions are easy to operate and cheaper alternatives and there is no worry of environmental pollution. Such reactions can be conducted in the following ways:

- Solid state reactions at room temperature.
- Solid state reactions on heating and solid state reactions using solid support.

The drive for the development of dry media reactions is

(i) This method is economical (Save money on solvent)

(ii) Not required to removal of solvent after the reaction completion ultimately purification step not required.

(iii)Reaction rate is high due to more availability of reactions

(iv)Environmentally friendly because solvent is not required.

Advantages:

- ✓ This method is more efficient with more selectivity compared to reactions carried out in solvent.
- ✓ Reactions are simple, to handle, reduces pollution compared to other methods.
- ✓ Lower Energy usage, Less expensive, cheaper to operate and are especially important in industry.
- ✓ There is no reaction medium to collect, purify and recyle.
- ✓ Reaction times can be dramatically shortened.

Disadvantages:

- ➢ Homogenous reactants must be mixed up in a system.
- ➢ Unsuitable for solvent involving reactions
- ➢ During the synthesis process like extraction, there is a need for the use of solvent.

Why using solvent less reactions?

Avoiding organic solvents during the reaction in organic synthesis

(i) Simplified work up.

(ii) Use of increase amount of reactants

(iii) Clean & efficient and economical technologies

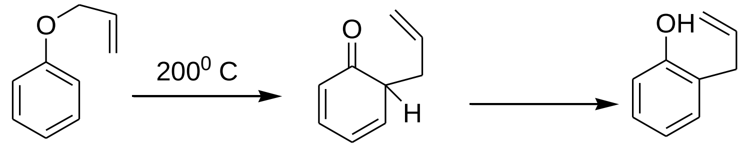
(iv) Largely increased safety

(v) Reduced costs

Solid phase organic synthesis without using any solvent

(i) Solid state reactions at room temperature:

(1) **Claisen rearrangement:**



Allylphenyl ether o-allylphenol

In this reactions where substituent moves from one atom to another atoms in the same molecules. Allylphenyl ether where substituent rearranges on heating 200°C to form o-allylphenol.

(2) **Grignard reaction:**

The reaction of benzophenone with powerded Grignard reagent gives more of the reduced product of the ketone than alcohol.

$$(C_6H_5)_2O + RMgX \xrightarrow{0.5h} (C_6H_5)_2CHOH + (C_6H_5)_2 RCOH$$

Benzophenone Adduct (A) Reduced product (B)

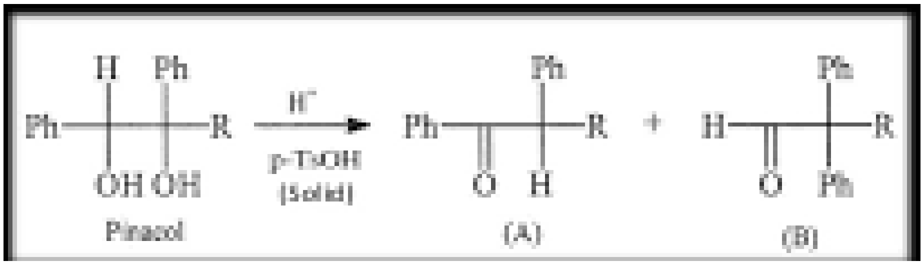
(3) Reformatsky reaction

Treatment of aromatic aldehydes with ethyl bromoacetate and Zn-NH4Cl in the solid gives the corresponding Reformatsky reaction product.

$$R\text{-}CHO + BrCH_2CO_2\ Et \xrightarrow[3h]{Zn\text{-}NH4Cl} RCH(OH)CH_2CO_2Et$$

(4) Pinacol-pinacolone rearrangement:

The process involves the irradiation of the diols with p-tosylate as solid in the presence of acid to give the rearrangement products.



(5) Backmann rearrangement:

Usually, Backmann rearrangement of oximes of ketones are converted into anilides by heating montmorillonite K 10 clay for 10 min.

(6) Synthesis of Azomethines

Aromatic amine reacts with aromatic aldehyde in the presence of solid catalyst to give azomethines.

$$ArNH_2 + ArCHO \longrightarrow ArN{=}CH\text{-}Ar^1$$

Aromatic amine aromatic aldehyde azomethines

Other examples of solid state reactions are deacetylation using natural alumina, oxidations of alocohol using clayfen, oxidation of alcohol using Activated MnO_2-Silica, solid state cannizzaro reactions, knoevenagel condensation, aldol condensation, micheal addition, aromatic condensation, wittig olefination reactions, nitration of styrene to Beta-nitrostyrene, synthesis of aspirin from salicyclic acid.

Reactions in Water

Water is the universal solvent in nature. It is comparatively a cheaper solvent. Water soluble substances can be used directly. This will be particularly useful in carbohydrate, protein and fermentation chemistry. In large industrial process, the products can be isolated by simple phase separation.

It is easier to control the reaction temperature.

Water can be readily recycled.

It is non toxic, non flammable and environmentally friendly solvent.

A number of solvents like CH_2Cl_2, $CHCl_3$, CCl_4, C_6H_6, $C_6H_5CH_3$ which are excellent solvent properties. Besides, these solvent responsible for environmental pollution particularly destroy ozone layer.

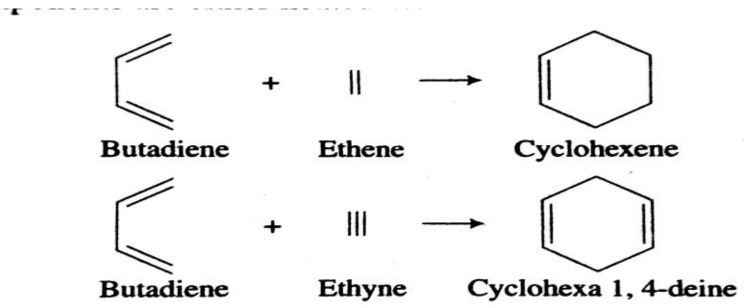
Why is water the best solvents?

- Environmental benefits
- Safety
- Synthetic efficiency
- Simple operation
- Potential for new synthetic methodologies
- Low cost.

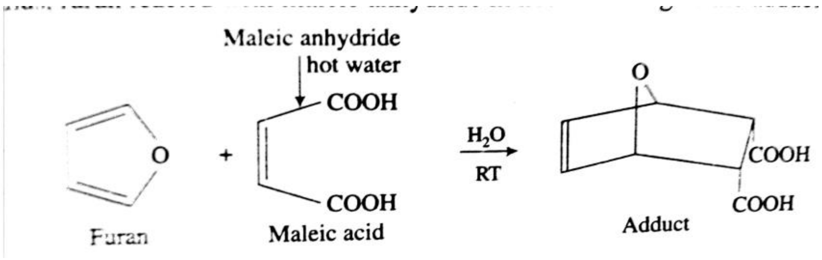
Following are some of the reactions which carried out in aqueous medium.

1. Diels-Alter reactions:

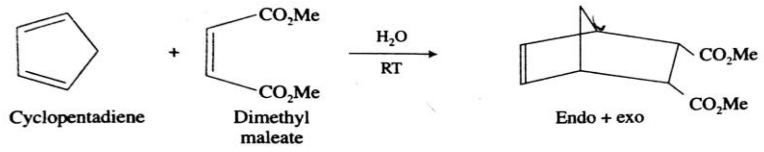
It is a (4+2) cycloaddition reaction between a conjugated diene (4π-electron system) and a compound having a double or triple bond called the dienophile (2π-electron system) to form an adduct. In this reaction, the two components are either heated alone or in an inert solvent.



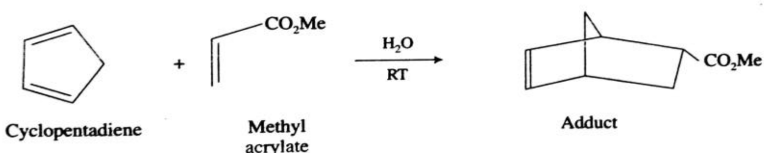
The Diels-Alter reaction in aqueous media was first carried out in the beginning of 19th century. In this reaction, furan reacted with maleic anhydride in hot water to give the adduct.



Water induced selectivity was also obersed in the reaction of cyclopentadiene with dimethyl maleate or methyl acrylate. In this cases, both the diene and dienophile are poorly soluble and are present as a separate phase, the influence of water on the selectivity is marked.

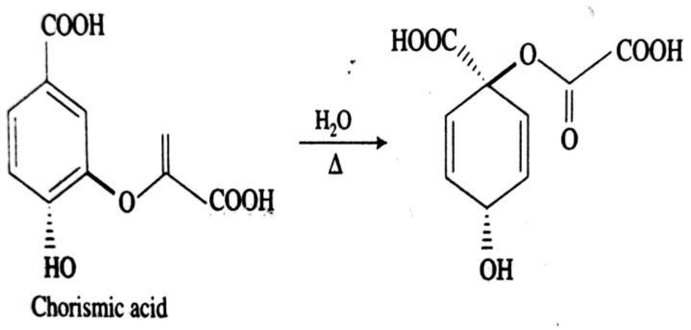


Scheme 2.5



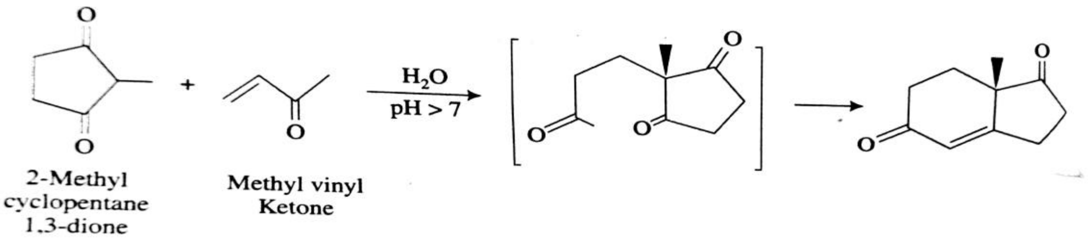
2.Claisen Rearrangement

Both aliphatic and aromatic claisen rearrangement involve a 3, 3-sigmatropic shift. In this reaction, the use of pure water in chorismic acid to give Claisen product.



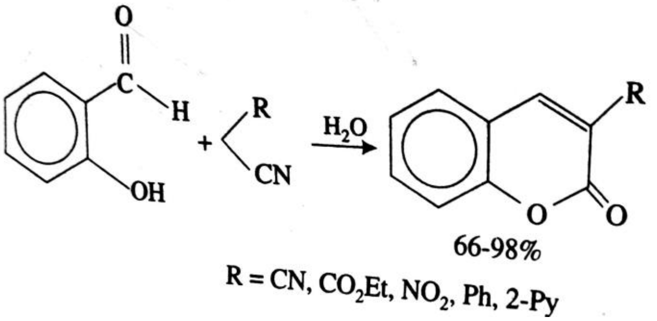
3. Michael Reaction

The first successful report of Michael reaction in aqueous medium was the reaction of 2-methylcyclopentane-1,3-dione with vinyl ketone in water to give adduct without the uses of a basic catalyst (pH>7). The adduct further cyclises to give a 5-6 fused ring system.



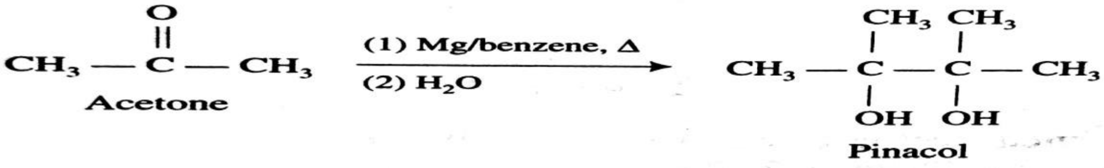
4.Knoevenagel Reaction:

It involves the condensation of aldehydes or ketones with acetonitriles gave the corresponding 3-substituted cocumarins.



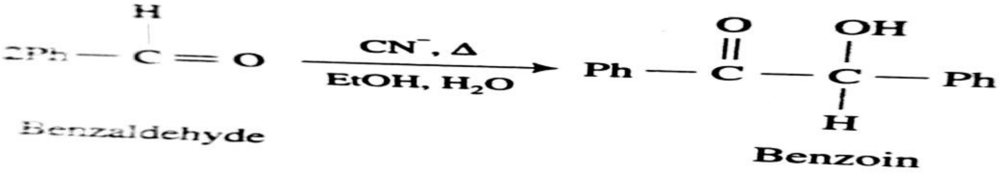
5.Pinacol coupling:

In this reaction, the use of water, Acetone on reaction with Mg/benzene give 1,2-diols (pinacols).



6. Benzoin condensation:

The reaction of aromatic aldehydes with inorganic salts (LiCl), usually in an aqueous solution give α-hydroxy ketones (benzoins). This reaction is known as benzoin condensation.



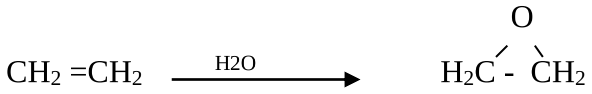
7. Oxidations

(i) Sulphides oxidized in the presence of water at room temperature for 2-3 hour to give sulphoxides.

R^1-S-R2 $\xrightarrow{\text{H2O / RT (2-3 h)}}$ R^1-SO-R2

Sulphides Sulphoxides

(ii) Alkene is oxidized in the presence of water to give epoxide (60-100% yield)



$CH_2 = CH_2 \xrightarrow{\text{H2O}} H_2C \overset{O}{-} CH_2$

Ethylene Epoxide

Other examples of reactions in water are aldol condensation, Claisen-Schmidt condensation, Heck reaction, Wurtz reaction, wittig-Horner reaction, reduction reactions etc.

<u>Microwave Assisted Organic synthesis</u>

Microwaves have wavelength between 1mm and 1m (Frequencies of 30 GHz to 300Hz). These are similar frequencies of radar and telecommunications devices. Now a days, countless synthesis initiated by microwaves with the help of microwave devices. Reactions have been carried out on a lab scale.

Disadvantages of usual organic reactions:

- Takes long time to complete the reactions.
- Requirement of prolonged heating or refluxing
- Unwanted side reactions
- Loss of energy.
- Loss of money.

Advantages in using this techniques:

- ✓ Reduction in the reaction time with comparable product yield.
- ✓ No requirement of prolonged heating or refluxing
- ✓ Unwanted side reactions can be suppressed
- ✓ Save energy
- ✓ Save money
- ✓ Some reactions may be done without using any solvent (solvent free microwave assisted reaction)
- ✓ Microwave radiation is selectively absorbed by the polar molecules.

When a substance possessing a dipole moment (water) is subject to electromagnetic radiation, it will attempt to align itself to the electromagnetic field by rotation. In liquids rotation causes friction between adjacent molecules which in turn causes temperature rise.

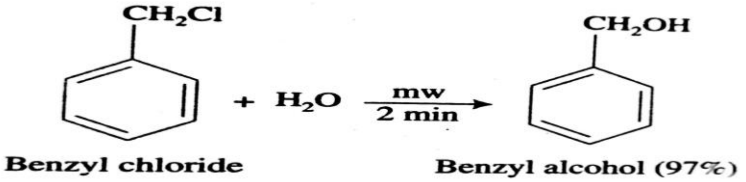
Organic synthesis using microwaves can be grouped three categories:

(i) Microwave assisted reaction in water
(ii) Microwave assisted reaction in organic solvents.
(iii)Microwave assisted reaction in Solid state

<u>(i) Microwave assisted reaction in water</u>

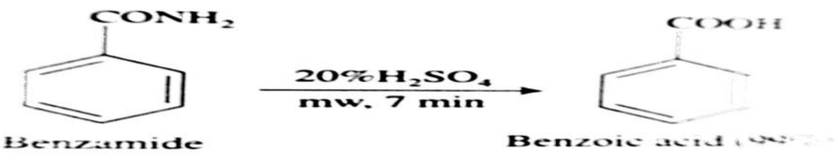
(a) Hydrolysis of Benzyl chloride:

Hydrolysis of benzyl chloride with water in microwave over gives 97% yield of benzyl alcohol in 2 min. The usual hydrolysis by usual heating takes about 35 min.



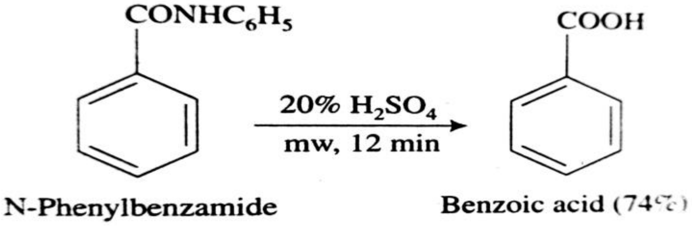
(b) Hydrolysis of Benzamide:

The usual hydrolysis of benzamide takes 1hr. However, under microwave, the hydrolysis is completed in 7 min giving 99% yield of benzoic acid.



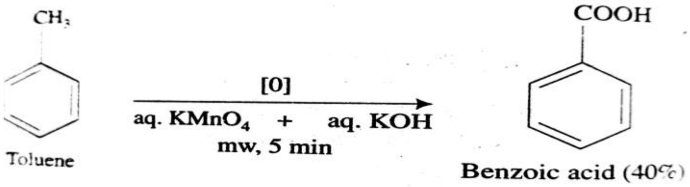
(c) Hydrolysis of N-phenyl Benzamide:

N-Phenyl benzamide on heating with 20% H_2SO_4 in an microwave oven for 12 min gives 74% yield of benzoic acid. The conventional heating procedure takes 18 hrs.



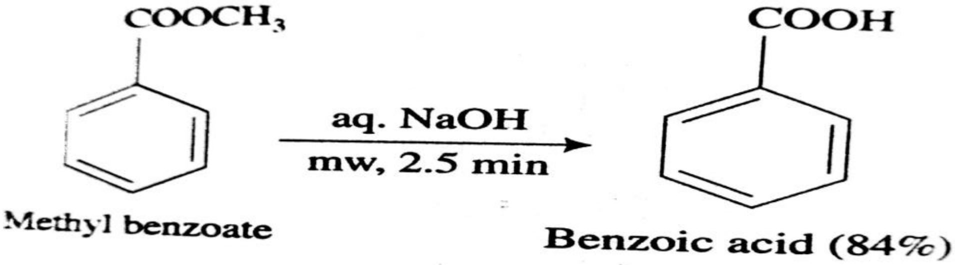
(d) Hydrolysis of Methyl Benzoate to Benzoic acid (saponification)

Saponification of methyl benzoate in aqueous sodium hydroxide under microwave irradiation (2.4 min) gives 84% yield of benzoic acid.



(e) Oxidation of Toluene:

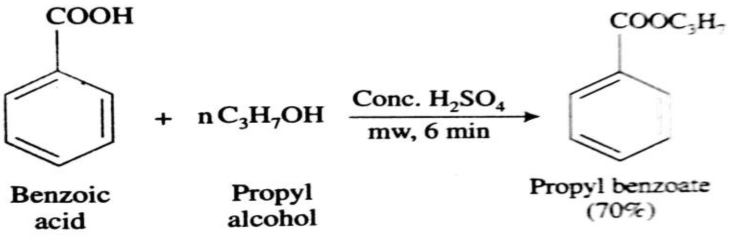
Oxidation of toluene with KMnO4 under normal condition of refluxing takes 10-12 hr compared to reaction in microwave conditions which takes only 5 min and the yield is 40%.



<u>(ii) Microwave assisted reaction in organic solvents:</u>

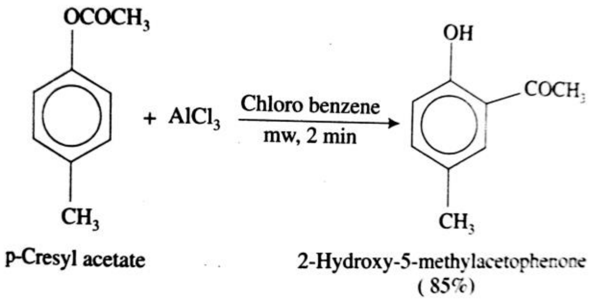
(a) Esterification: Reaction of carboxylic acid and alcohol:

A mixture of a carboxylic acid (e.g. benzoic acid) and an alcohol (e.g. n-propanol) on heating in a microwave oven for 6 min in presence of catalytic amount of sulphuric acid gives the corresponding ester (e.g.propylbenzoate)



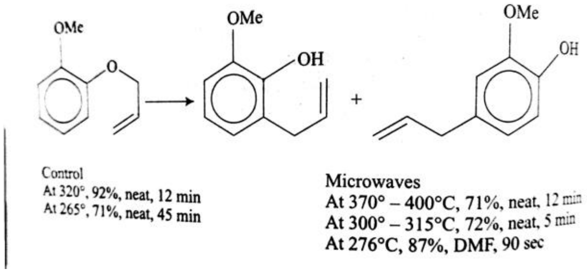
(b) Diels-Alder Reaction:

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 condition, the reaction requires a refluxing time of 90 min.

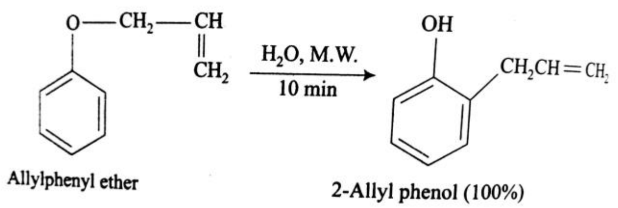


(c) Claisen Rearrangement

Claisen rearrangement of allyl ether in the absence of solvent under conventional thermolysis provides a good yield of product within a short period of time. The same rearrangement using microwaves in presence of N-methylformamide affords 87% of the product.

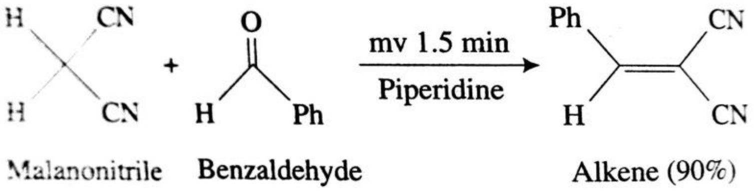


The ortho-claisen rearrangement of allyl phenyl ether has been achieved in aqueous media when 2-allylphenol is obtained exclusively after 10 min of irradiation.



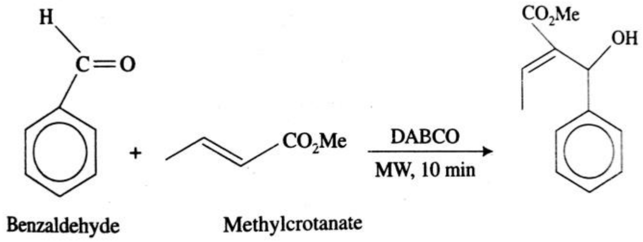
(d) Knoevenagel condensation:

It involving active methylene compounds and carbonyl groups for the synthesis of alkenes using microwave irradiation.



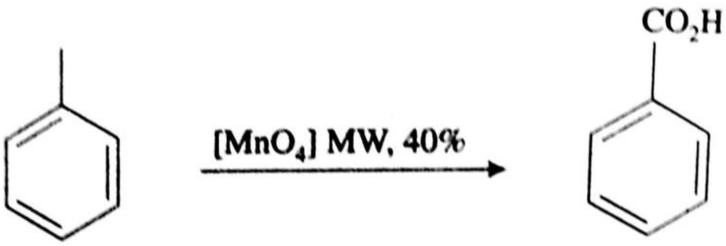
(e) Baylis-Hillman Reaction:

The reaction of benzaldehyde with methyl crotonate in presence of DABCO leads to the required product in good yield in 10 minutes.



(f) Oxidations

Oxidations of toluene with $KMnO_4$ has also achieved under microwave conditions. The reaction gives 40% yield after 5 minutes of microwave irradiation.



(iii) Microwave Assisted Reactions in Solid State:

(a) Grignard reaction:

The reaction of benzophenone with powerded Grignard reagent gives more of the reduced product of the ketone than alcohol.

$$(C_6H_5)_2O + RMgX \xrightarrow{\text{0.5h (solid)}} (C_6H_5)_2CHOH + (C_6H_5)_2 RCOH$$

Benzophenone Adduct (A) Reduced product (B)

(b) Reformatsky reaction

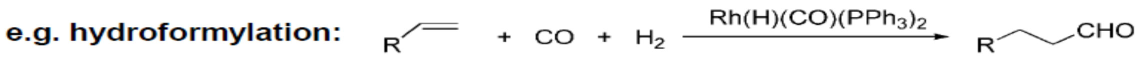
Treatment of aromatic aldehydes with ethyl bromoacetate and Zn-NH4Cl in the solid gives the corresponding Reformatsky reaction product.

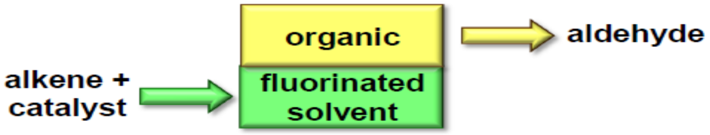
$$R\text{-}CHO + BrCH_2CO_2\ Et \xrightarrow[\text{Solid state (3h)}]{\text{Zn-NH4Cl}} RCH(OH)CH_2CO_2Et$$

Fluorous Solvents

Fully fluorinated solvents (e.g. C_6F_{14}) are non-polar and immiscible with organic solvents. Ideal if reactants are non-polar, but products are polar.

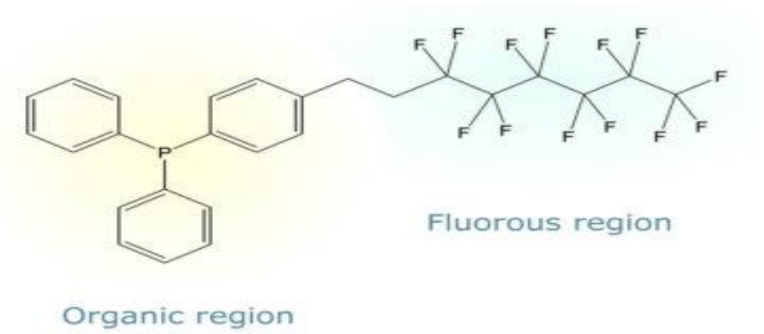
The disadvantages are that fluorinated solvents are expensive and concerns exist for their long-term environment impact.





Catalyst: $Rh(H)(CO)\{P(CH_2CH_2(CF_2)_5CF_3)_3\}_2$

Fluorous molecules comprise an organic domain and a highly fluorinated domain. Ideally, the organic domain controls reactivity and the fluorinated domain controls separation. The aim is to facilitate separation.



Characteristics of perflurous liquids

Most of the common perflurous liquids, especially perfluoroalkanes, perfluoroethers, and perfluoroamines exhibit unique characteristics.

The perfluoro liquids are inert against chemical treatment.

The boiling points of perfluorous liquids is dependent on their molar mass. The boiling points of fluorous alkanes are usually lower than the corresponding alkanes this is attributed to decreased Vander Waals interactions.

The density of perfluorous alkanes is higher than water and most other organic molecules.

Solubility of perfluorous liguids in organic solvents is temperature dependent.

At ambient temperature, most of the combinations of an organic and a fluorous solvent are biphasic and at higher temperature they become monophasic; lowering of the temperature will result in reformation of the biphasic system.

Following are commonly used and commercially available perfluorinated solvents

Perfluorohexane (C_6F_{14})

Perfluoroheptane (C_7F_{16})

Perfluoromethylcyclohexane (C_7F_{14})

Perfluorodecalin ($C_{10}F_{18}$)

Perfluorotributylamine ($C_{12}F_{27}N$)

Two basic approaches:

(i) Fluorous compounds with integral (permanent) fluorinated domains

(ii) Fluorous compounds with removable (temporary) fluorinated domains (tags)

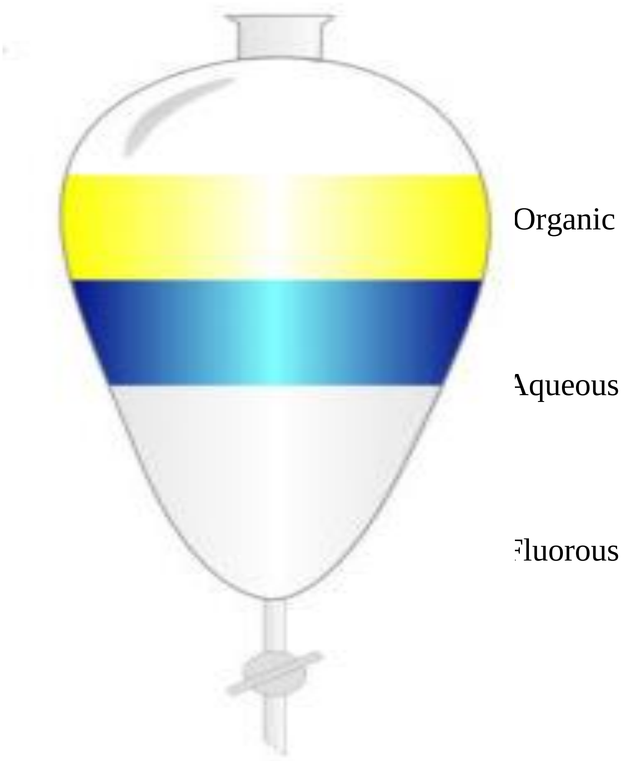
Heavy or Light fluorous compounds:

Generally, > 60% fluorine by weight is called a “heavy fluorous” compound. These materials have limited solubility in non-fluorous media, typically require perfluorinated solvents, and are expensive - all of which limits practical adoption.

“Light fluorous” compounds (< 40% by weight) are miscible in organic solvents and cost less. Since they typically will not form a separate fluorous liquid phase, light fluorous compounds are separated using a companion fluorous stationary phase.

Liquid-Liquid Extraction: Heavy Fluorous Techniques:

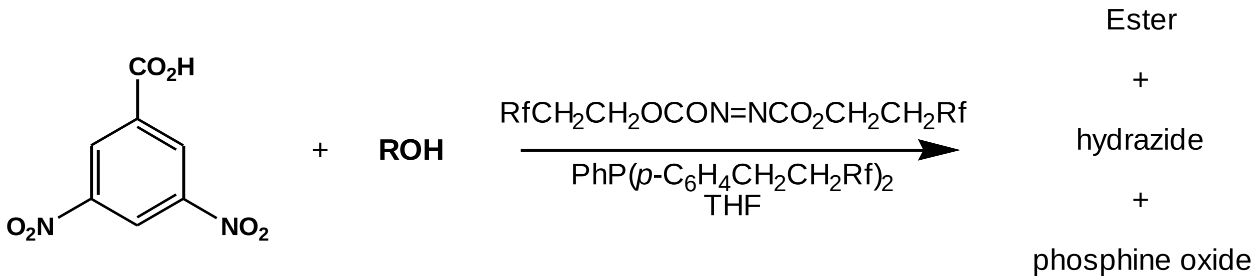
Whereas compounds bearing light fluorous tags are miscible in organic solvents, heavy fluorous compounds are soluble in perfluorinated solvents and form a distinct liquid phase. This can be exploited if a liquid-liquid separation is preferable, although reactivity is limited to the phase interface.

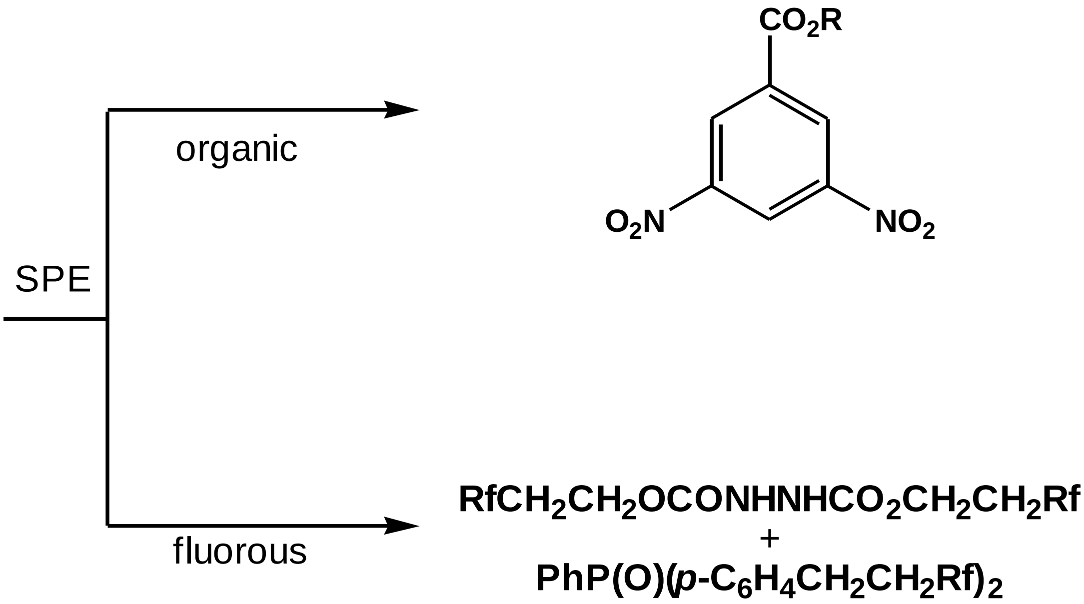


Light fluorous separation affinity techniques:

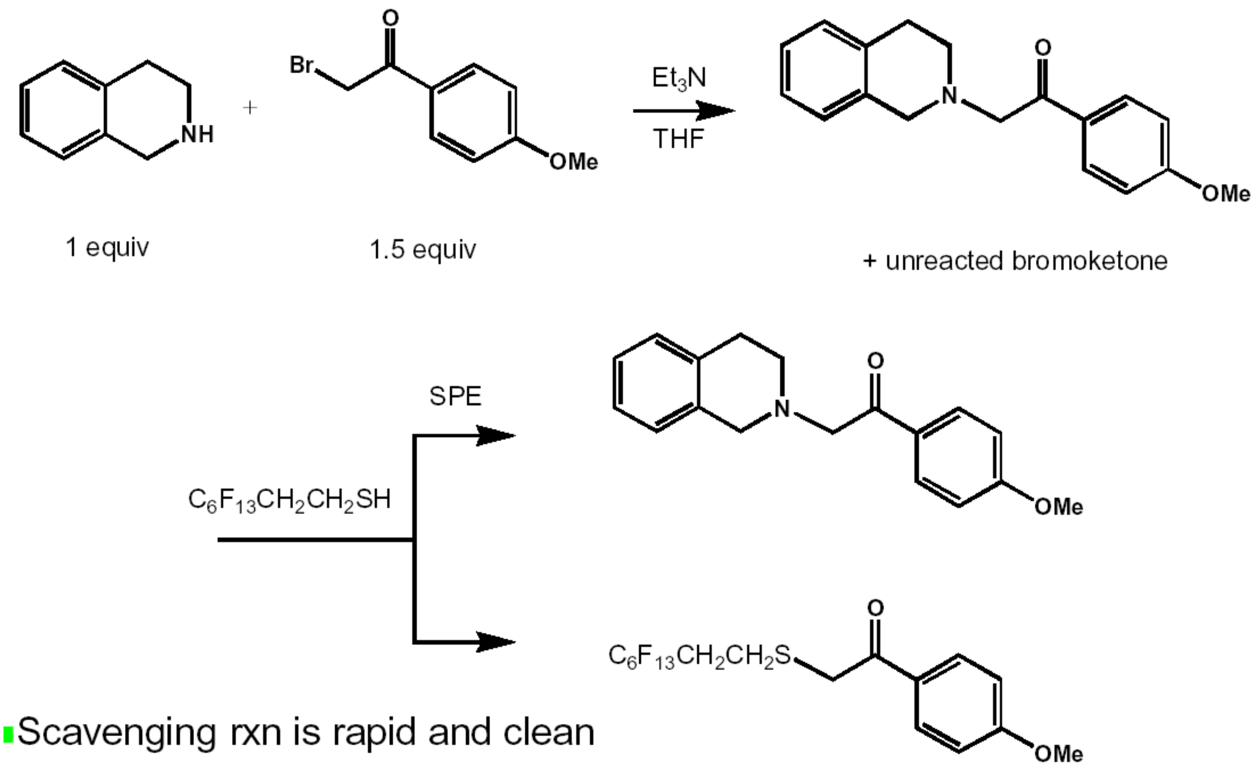
A fluorous sorbent is a chromatographic packing material modified with a highly fluorinated domain. Fluorous stationary phases exhibit high selectivity for retention of fluorous versus non-fluorous molecules. In addition, fluorous sorbents are able to resolve fluorous molecules of differing fluorine content (e.g. different size or number of fluorous tags).

Application in Organic synthesis:





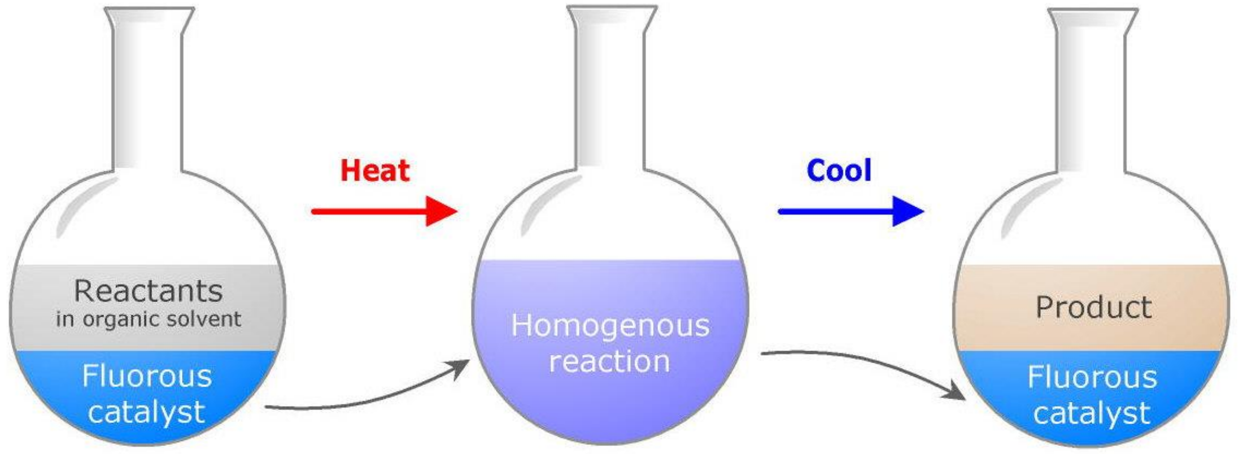
<u>Fluorous Scavenging:</u> A Solution Phase Fluorous Applications



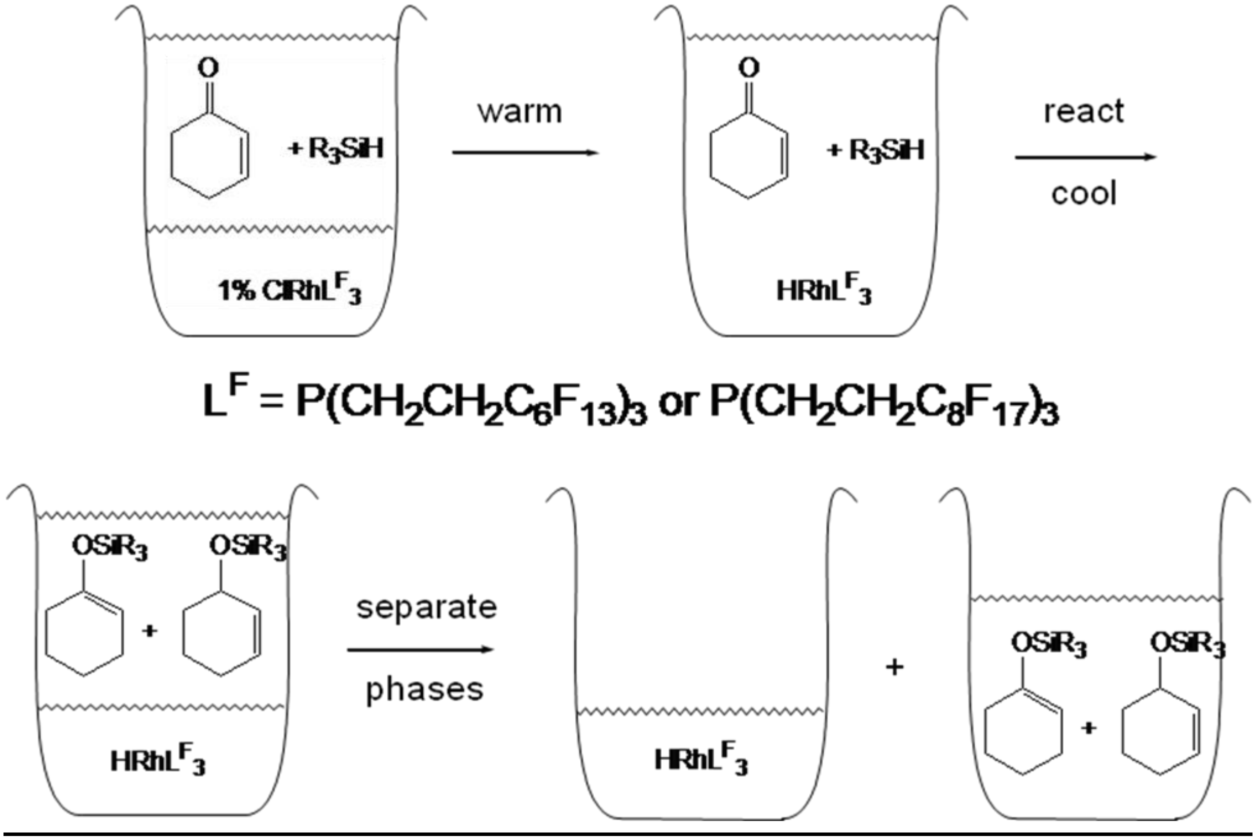
- Scavenging rxn is rapid and clean

Fluorous Biphasic catalyst

Fluorous-tagged ligands enable reliable L-L separation of catalyst – important for toxic and/or expensive catalysts. Variation shown here is *thermomorphic* fluorous biphasic catalysis. Solubility of the fluorous species in organic phase is promoted with heat, improving kinetics.



Fluorous Biphasic catalyst:



Materials for a Sustainable Economy

Most organic chemicals in use today are derived from nonrenewable petroleum and natural gas, with some still being made from coal. After use, the bulk of these ultimately end up as carbon dioxide, the main green house gas that is causing global warming. For sustainable future, there must be based on renewable resources from fields and forests. Before the advent of cheap petroleum and natural gas, many of them were. It is instructive to look back at these older methods to see if they might be economical today if the cost of global warming were included in the prices of the organic chemicals that we use. Further optimization of the processes with the knowledge that has accumulated since they were in use should increase yields and lower costs. Biocatalysts is an example. Formerly it was used more for the production of commodity chemicals than it is today. Some of these earlier fermentation methods have not been studied much lately. Because energy is often a large factor in producing chemicals, renewable sources will have to replace the fossil fuels used today. Biocatalysis with renewable raw materials has become more popular with the recent escalation of prices for oil and gas. The adoption of such sources of energy and raw materials will cut amount of acid rain substantially, for there is not much sulfur in either the raw materials or the fuels.

Some methods of converting oil and natural gas to commodity chemicals use as much as one third of the starting material for energy to fuel the process. They often involve high temperatures, with low conversions, and much recycling. Sometimes, it is necessary to quench a hot stream to obtain the desired product. After the product is separated, the stream must be reheated to the high temperature for the next cycle. Many of todays processes involve oxidation of the starting hydrocarbon to move oxygen into the molecule. Renewable raw materials have oxygen into the molecule. Renewable raw materials have oxygen in them, so that converting them to the desired products involves different methods, which may not require such extreme temperatures and so much energy. Removal of oxygen atoms may be involved. Although biogas (methane) derived from anaerobic fermentation of organic matter could be used with todays processes for natural gas, there would not be enough of it.

The 50 largest volume chemicals contain many derived from fossil carbon sources. The chemicals are ethylene, ammonia, propylene, methyl tert-butyl ether, ethylene dichloride, nitric acid, ammonium nitrate, benzene, urea, vinyl chloride, ethylbenzene, styrene, methanol, carbon dioxide, xylene, formaldehyde, terephthalic acid, ethylene oxide, toluene, p-xylene, cumene, ethylene glycol, acetic acid, phenol, propylene oxide, butadiene, carbon black, isobutylene, acrylonitrile, vinyl acetate, acetone, butyraldehyde, adipic acid, nitrobenzene and bisphenol A.

The use of natural polymers are cellulose, starch, Hemicellulose, chitin, Lignin, proteins, rubber etc. Today, the polymers used from renewable raw materials such as Furfural, polyurethanes, polyester, polyamides which are less expensive, eco-friendly, harmless, non-toxic products. These materials goes towards sustainable in future.

Chemistry of Longer Wear

The first step in achieving longer wear is to have reusable ones that can be used many times before they wear out or break and have to be recycled. If the process of wear or breakage is understood, it may be possible to intervene by altering the design or manner of use so that a longer service life is obtained.

Metals can rust or corrode. Rubber can harden and crack with age. Plastic may embrittle with age. Colors may fade in the sunlight. These are due to oxidation. Efforts to minimize these processes involve isolation of the object from the environment, by a coating or other means, or by the use of additives that prevent the oxidation. Concrete may deteriorate under the influence of deicing salts. Other objects wear out mechanically. A cutting edge becomes dull. The knees of the pants wear through from abrasion. Stockings snag and trip. Teeth come out of zippers. Plastics may scratch or stain. The rung on the chair may break. Glass and china objects may break if they are dropped or hit. Some plastics are brittle on impact. Biological factors may also be involved. The clothes moth likes to eat woolen garments. Water based paints, inks, cutting fluids, and such may serve as substrates for the growth of bacteria and fungi. Termites and carpenter ants may eat the wood in houses. Understanding the ecology of these organisms can sometimes provide means to prevent their entry. Otherwise, biocides are used.

There is often a weak link in an appliance or piece of equipment. A plain steel screw in a stainless steel pot will fail first. The screw is used because stainless steel is harder to machine. A plain steel knife keeps its cutting edge better than one made of stainless steel. A small spring may fatigue and break. A nut may be lost from a bold. Many nuts are locked on by putting a monomer on the threads, which then polymerizes when no more oxygen is present. This is an anaerobic adhesive. The important thing is for the equipment to be designed for ease of disassembly for easy replacement of the weak link. This will require more screws and fewer rivets, welds, and metal parts encased in plastic. It may require more standardization of sizes of screws or other parts. The second factor is that the spare part should be easy to obtain, preferably locally. Ideally, the weak link would be redesigned so that it is no longer weak. This may require chemists to devise new and better materials.

Some of the failures can be due to improper use of the object or lack of preventive maintenance. Running without coolant will damage some machinery (e.g., a car). Storing a steel bicycle or shovel outdoors will encourage rusting. Pain glass might crack in the oven, whereas pyrex glass would not. Glasses may etch in the dishwasher over time if the detergent is too alkaline. Making the china mug thicker than the delicate teacup reduces breakage. Putting wet objects directly on wooden furniture may ruin the finish. This can be avoided by using furniture with tops of melamine-formaldehyde resin laminates.

Some of the failures are due to the improper choice of materials or poor designs. The cutting edges on saws, planes, chisels, knives and such will stay sharp longer if they are made of a good tool steel. They should be easy to resharpen. A household strainer of stainless steel will last longer than one made of plain steel. Stainless steel knives, forks, and spoons will hold up better than those plated with silver, and there is no tarnish to be taken off.

Stabilizers for Polymers

Plastics fail for a variety of reasons. Cellulose nitrate film in museum collections is failing owing to the release of nitric acid. The degree of degradation is related to the amount of sulfate left in the sample when it was made. Old paper can be sterilized and coated by a plasma containing hexamethyldisiloxane to improve its life and tensile strength. A wide variety of stabilizers are used in plastics and rubbers. It is common for more than one to be used in a given polymer. The total amount added, for example, to polypropylene, is usually under 1%. Because stabilizers are used up in protecting the polymer, more may have to be added when used items are recycled by remolding.

Lubrication, wear and Related subjects

If two objects are rubbed together, they may wear by abrasion. The heat developed in the process may cause them to deteriorate by oxidation or loss of strength, or they may melt. In fact, this is one way to weld two pieces of plastics together. They are rotated against each other until the surfaces melt together and then removed from the apparatus to cool. A lubricant lowers the coefficient of friction, allowing one surface to slide over the other more easily without, or with less, abrasion. It can also, when passed through continuously, cool the surfaces and remove any particles that form.

Plastic gears of nylon or polytetrafluoroethylene are self-lubricating and need no added lubricant. They reduce the noise associated with machinery. They may be made with graphite or molebdenum disulfide in them as additional built in lubricants. These are layered substances where the layers tend to slide over one another easily. Carbon graphite normally has about 15% porosity. The pores can be filled with organic resins, Cu, Sb, bronze, or Ni-Cr to improve lubricity so that no liquid lubricant is needed.

High-oleic vegetable oils can be used in place of mineral oils. They can also be used as hydraulic fluids. They can be used as food-grade lubricants, are from renewable resources, and are biodegradable which helps if a spill occurs. Additives are also required for these oils. Ethanolysis of such oils would produce ethyl oleate for use as fuel with the same diesel engine that uses the oils for lubricant and in its hydraulic lines. Oligomeric esters of oleic acid, formed by self-addition of the carboxylic acid groups to the double bond in the presence of a sulfuric acid catalyst, can also be used as biodegradable lubricants. Some ionic liquids are lubricants.

Inhibition of Corrosion

Despite mans best efforts, many objects have their life times shortened by corrosion. One third of chemical plant failures in the US are due to corrosion.

A variety of reagents are used to inhibit corrosion. The shift from solvent based to water based paints, cleaning solutions, inks, cutting oils, and such will require increased use of such inhibitors. Corrosion can be inhibited in various ways. A reagent may complex with the metal surface and alter the redox potential of the metal or prevent adsorption of aggressive ions. The diffusion of oxygen to the surface may be inhibited or the oxygen in the surrounding medium may be scavenged.

Inorganic Inhibitors are molybdate, tungstate, cerium and magnesium compounds, calcium or magnesium carbonates, Hydrazine, sodium sulfite etc.

Organic inhibitors are benzotriazole, ethynylcyclohexanol, other heterocyclic compounds etc. Volatile corrosion inhibitors can be used with objects stored in closed containers such as tools during shipment. Dicyclohexylamine salt retards corrosion in containers.

Agrochemicals:

Chemical products used in agriculture are termed as agrochemicals. Agrochemicals include pesticides (insecticides, herbicides, fungicides and Rodenticides), synthetic fertilizers, Hormones, Growth agents and Animal manure.

Benefits of Agrochemicals:

- Improve plant nutrition
- Improve economic production
- Improve quantity and quality of food.
- Improve quality of life.

Demerits of Agrochemicals:

- ✓ Reduce soil fertility.
- ✓ Harmful to the environment
- ✓ Imbalance of nutrient
- ✓ Death of soil organisms.
- ✓ Prefer organic farming over synthetic agrochemicals.

Pesticides: A pesticide is any toxic substance used to kill animals or plants that causes economic damage to crop.

The common pests are insects, bacteria, fungi, rats, weeds.

Types of Pesticides

(a) Inorganic Pesticides:

Inorganic pesticides also called as inorganic chemicals which haven't contain carbon. It obtained from mineral ores.

Ex: Copper sulphate, sulphur , arsenic, lead, mercury etc.

(b) Organic Pesticides:

It contains carbon. It obtained from plant and materials.

Ex: organochlorine, organophosphorus, DDT (dichlorodiphenyltrichloroethane), BHC (Benzene hexa chloride), Alderin, Endrin, Malathion, Endosulfan, atrazine, Sulonylureas etc.

Herbicides:

- ➢ It destroy weeds and unwanted vegetation. It is crop protector.
- ➢ Some herbicides act on a particular class of plant growth regulators.

Ex: 2,4-dichlorophenoxyacetic acid. Triazine, Paraquat, Trifluralin, Glyphosate.

Insecticides:

- ➢ It kills the insects that are harmful to the plants.

Ex: Methopyrene, Pyriprozyfen, malathion, Endosulfan, BHC.

Methopyrene and Pyriprozyfen are insect growth regulators. This don't allow insect to grow properly but donot necessarily kill them.

Fungicides:

- ➢ It removes fungal species that destroy plants.

Ex: Benzimidazole, Imidazole, Triazole, Dicarboxymide.

Rodenticide:

- ✓ It kills rodents include not only rats and mice
- ✓ Ex: Metal phosphate, zinc phosphate, Al Phosphite, Ca Phosphite, Mg Phosphite.

Fertilizers:

Any organic or inorganic chemical supplements added to the soil to provide essential nutrients for supporting plant growth and development called fertilizers.

Fertilizers provides nutrients to soil.

(a) Micronutrients: Zn, Cu, Fe, B, Co etc
(b) Macronutrients: N,P,K, Ca, Mg, C, O etc.

Types of Fertilizers:

(i) Inorganic Fertilizers:

Advantage:

- ✓ Easily dissolved in soil
- ✓ Rate of uptake by plants is high
- ✓ High concentration of micro & macronutrients.

Disadvantage:

- ➢ They contaminate the water, soil and environment.

Ex: Nitrogen & potassium fertilizers.

(ii) Organic Fertilizers:

Advantage:

- ➢ Macro and micronutrients are released during the decay of organic matter.
- ➢ Very slow process
- ➢ Low concentration of plant nutrients
- ➢ Improve fertility of soil
- ➢ Organic nutrients increases the organisms.

Disadvantages:

- ✓ It may contain disease causing organisms.

<u>Hormones / Growth Agents:</u>

- ➢ Hormones are of Endogenous origin and are synthesized by plants

- ➢ These are growth regulators performing specific function in overall development of the plant.
- ➢ It is enhancing root growth, controlling plant height, improve fruit yield etc.

Problems with Pesticides

(i) Impact on the environment:

  (a) Air pollution

  - ✓ Pesticides can speared by volatilize and may be blown by winds into nearby areas.
  - ✓ Following factors affect to the spreading of pesticide in the air
    - Weather conditions at the time of application
    - Temperature.
    - Relative humidity
  - ✓ Ground spraying produces less spread than aerial spraying

  (b) Water pollution

  - ✓ There are four major routes through which pesticides reach the water
    - Contaminate water when they spraying. Ex: rice cultivation
    - It may percolate, or leach, through the soil.
    - It may be carried to the water as runoff.
  - ✓ After contaminate the water it makes lot of problems
    - Application of herbicides to bodies of water can cause fish kills.
    - Reduce the quantity of drinking water.
    - Reduce the amount of water available for cultivation.
    - Altering the physical characteristics of water bodies.
  - ✓ Insecticides are typically more toxic to aquatic life than herbicides and fungicides.
  - ✓ Ground water pollution due to pesticides is a worldwide problem.
  - ✓ Once ground water is polluted with toxic chemicals, it may take many years for the contamination to dissipate or be cleaned up.

  (c) Soil pollution.

  - ➢ The use of pesticides decreases the general biodiversity in the soil.

- Also affect to the soil micro-organisms & decrease the soil fertility.
- Effect on growth of the plants
- Residual effect of the pesticide in the soil.
- Enter to the food chain & bio magnification.
- Pesticides can kill bees and decline the pollinators.

(ii) Impact on Living organisms:

(a) Death of non target organism

Many insecticides not only kill target species but also kill the several non-target species, which are useful to us.

(b) Producing new pests

Some pest species usually survive even after the pesticide spray, which generates highly resistant generations. They are immune to all type of pesticides and are called superpests.

(c) Biomagnification

Many of the pesticides are non-biodegradable and keep on concentrating in the food chain. These process is called bio-magnification. These pesticides in a bio-magnified form is harmful to the human beings.

(d) Risk of cancer

Pesticides enhance the risks of cancer in two ways

- ✓ It directly acts as carcinogens
- ✓ It indirectly suppress the immune system.

(e) Effect on animals:

Pesticides can eliminate some animals essential food sources.

Residues can travel up the food chain.

Earthworms digest organic matter and increase nutrient content in the top layer of soil. Pesticides have harmful effects on growth and reproduction on earthworms.

Pesticides exposure can be linked to cancer, reproductive effects, neurotoxicity, kidney and liver damage, birth defects and developmental changes in a wide range of species.

(f) Neurological effect:

The risk of developing Parkinsons disease is 70% greater in these exposed to even low levels of pesticides.

People with Parkinsons were 61% more likely to report direct pesticide application.

(g) Reproductive effects:

Strong evidence links pesticide exposure to birth defects, fetal death and altered fetal growth.

It was also found that offspring that were at some point exposed to pesticides had a low birth weight and had developmental defects.

(h) Fertility effects:

A number of pesticides including dibromochlorophane and 2,4-D has been associated with impaired fertility in males.

(I) Ecological effects:

Loss of species diversity among the food chains and food webs.
Effect on pollinators
Effect on nutrient cycling in ecosystem.
Effect on soil erosion, structure and fertility.
Effects on water quality
Effect on human beings
Effect on birds
Contaminate the food.
Effect on fish and other aquatic organisms.

Problems in using Fertilizer:

(a) Micronutrient imbalance:

Most of the chemical fertilizers used in modern agriculture contain nitrogen, phosphorus and potassium (N,P,K) which are macronutrients. When excess of the fertilizers are used in the fields, it causes micronutrient imbalance.

Ex: Excessive use of the fertilizer in Punjab and Haryana has caused deficiency of the micronutrient zinc in the soil, which affect the productivity of the soil.

(b) Blue Baby syndrome (Nitrate Pollution)

When the nitrogenous fertilizers are applied in the fields, they leach deep into the Soil and contaminate the ground water. The nitrate concentration in the water gets increased. When the nitrate concentration exceeds 25 mg/lit, they cause serious health problem called ‘’Blue baby syndrome’’. This disease affects infants and leads even to death.

(c) Eutrophication:

A large proportion of N and P fertilizers used in crop fields is washed off by the runoff water and reaches the water bodies causing over nourishment of the lakes. This process is known as Eutrophication.

Due to eutrophication lakes get attacked by algal blooms. These algal species use up the nutrients rapidly and grow very fast. Since the life time of the algal species are less they die quickly and pollute the water, which inturn affect the aquatic life.

Alternative to Chemical Pesticides:

The serious limitations of chemical insecticides are

(i) accumulation of toxic chemicals in environment

(ii) development of resistance among the insects against the chemical insecticides.

This is why, the alternatives to chemical pesticides appear quite important These will destroy the insects without producing any burden of toxic chemicals in the environment. Different approaches are discussed below:

(1) Biological control of Pests

- ✓ Use of helpful insects (i.e., natural predators) to kill the harmful insects: some representative helpful insects are discussed here

(a) Ladybugs
(b) Green Lacewing
(c) Trichogramma
(d) Nematodes

- ✓ Bacterial insecticides:

(a) Bacillus popilliae
(b) Bacillus thursinglensis

- ✓ Viral insecticides: Just like the bacteria, some viruses may be used to kill the harmful insects. But this process is quite expensive.

(2) Third generation Pest Controller- Pheromones and Attractants

(3) Fourth generation Pest controller- Juvenile and Moulting Hormones and Antijuvenile Hormone.

(4) Chitin Inhibitors

(5) Integrated pest management (IPM)

It has multidirectional approach and recommends the minimum use of toxic and nondegradable chemical substances in pest control. The other important steps in IPM are

- ✓ Use of natural enemies or predators of the insects
- ✓ Use of beneficial microorganisms like bacteria and viruses to control the insects.
- ✓ Sterilisation of male insects by radiation or chemisterilant like aziridine group of components.
- ✓ Use of sex-pheromones and attractants- the insects may be wrongly diverted or the insects can be trapped.
- ✓ Use of hormones-juvenile hormones can keep the insects confined in the larva stage and prevent their maturation; moulting hormones can rapidly mature the larva without any other physical development; antijuvenile hormones can prevent the proper development of the insects from the larva stage to adult stage.
- ✓ Use of chitin inhibitors- that can inhibit the formation of chitin required to construct the shell in insects.
- ✓ Inducing genetic defects in the insects- this approach induces a genetic disorder in the insects.
- ✓ Development of resistance in the product- the insecticidal protein that protects the plants from the insects.
- ✓ Use of antifeeding compounds- such compounds can cause the death of insects by starvation.

  - ✓ Use of novel herbicides, fungicides and insecticides that disturb the environment to minimum level.

(6) Natural pesticides: Pyrethrum Flower, Neem leaves and oil, Tabacco leaves, Nuxvomica seed, Sabadilla seeds, Ryania root and stem, Derris root and rhizome.

Procedures to Minimize the Environmental problems caused by Fertilizers

The environmental hazards mainly arise from the N-based fertilizers. But the need of this fertilizer is of enormous importance to keep the wheel of green revolution running. The judicious use of fertilizers can minimize the problems. The different possible steps in this direction are discussed below:

- ✓ To avoid over-fertilisation
- ✓ To avoid crop-failure.
- ✓ To consider the residual fertilizer
- ✓ To consider crop rotation
- ✓ To consider the use of biofertiliser.

Atom Economy

The concept of Atom Economy was developed by Barry Trost of Stanford University (US), for which he received the Presidential Green Chemistry Challenge Award in 1998. It is a method of expressing how efficiently a particular reaction makes use of the reactant atoms.

Calculation of Atom Economy

$$\text{Atom economy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in reactants}} \text{ X } 100\ \%$$

This approach does not take yield into account, and does not allow for the fact that many real-world processes use deliberate excess of reactants. It does, however, help in comparing different pathways to a desired product.

How to calculate atom economy

Step 1: Write out balanced equation

Step 2: Calculate the total mass of all the products (remember to account for any numbers in front of the symbols

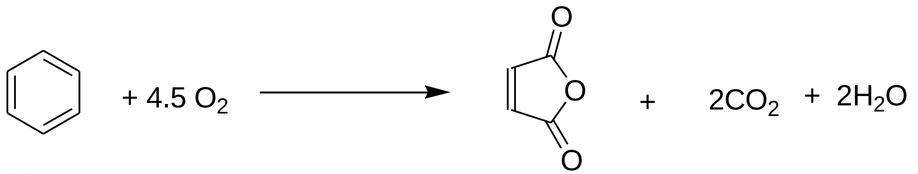
$$\underset{(28)}{N_2} + \underset{(6)}{3H_2} \longrightarrow \underset{(34)}{2NH_3}$$

Step 3: Workout which the products are wanted and calculate their mass.

Examples

Benzene can be oxidised to make **maleic anhydride**, an important intermediate chemical.

Maleic anhydride from benzene



benzene
(6X12) +
(6X1) = 78

Oxygen
4.5 X (2X6)
=144

Maleic anhydride
(4X2) + (3 X16) = 96

The Atom Economy of this reaction is 43%, calculated using the relative formula masses.

This means that 43% of the mass of the reactants ends up in the desired product.

$$\text{Atom economy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in reactants}} \times 100\,\% = \frac{96}{78+144} \times 100\% = 43\%$$

Calculating Yield:

This compares the expected (theoretical) mass of product with the actual mass of product, giving the percentage figure for the reaction. The expected mass is worked out from the balanced equation.

$$\text{Percentage Yield} = \frac{\text{Actual mass of the product}}{\text{Theoretical mass of the product}} \times 100\,\%$$

An example

A method used in the past to manufacture phenol from benzene link to phenol section used sulphuric acid and sodium hydroxide in several steps.

$$C_6H_6 + H_2SO_4 + 2NaOH \longrightarrow C_6H_5OH + Na_2SO_3 + 2H_2O$$

(12X6) +
(1X6)= 78

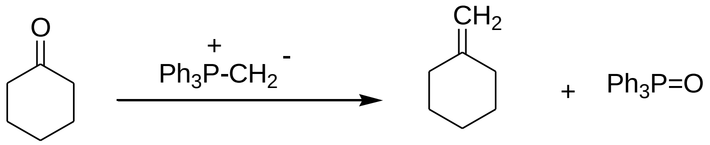
(12X6) +
(1X6) + 16 = 88

The equation indicates that 1 mole of benzene (78g) should yield 1 mole of phenol (88g).

Other reactions take place, however, and the actual mass of phenol will be in the region of 77g, giving a yield of about 88%.

$$\text{Percentage Yield} = \frac{\text{Actual mass of the product}}{\text{Theoretical mass of the product}} \times 100\,\% = \frac{78}{88} \times 100\% = 87.5\%$$

Wittig reaction



$$\text{Atom economy} = \frac{96}{98+276} = 25.7\%$$

Advantages of Atom economy calculations:

- Measure of the amount of starting materials that end up as useful products
- By minimizing the production of unwanted products, we save money.
- We also increase sustainability by wasting resources.
- Chemists try to find a use for these side products
- Money is not wasted.

Atom economy reactions

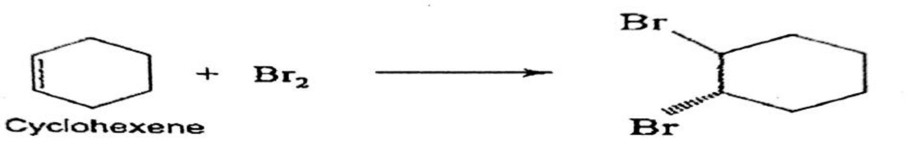
There are four types of atom economy reactions

(i) Addition reaction
(ii) Substitution reaction
(iii) Elimination reaction
(iv) Rearrangement reaction

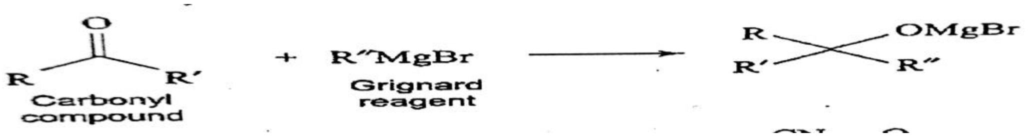
(i) Addition Reactions: (100% atom economy)

In these reactions, a reagent adds to a substrate, all reagents and the substrates are consumed during the reaction. No additional by products are generated and such reactions are very efficient and also 100% atom economical.

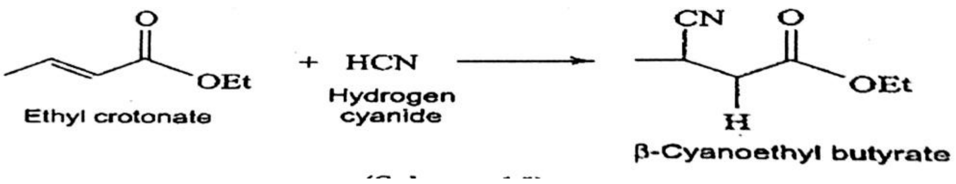
(a) Addition of bromine to an olefin



(b) Addition of Grignard reagent to a carbonyl compound



(c) Addition of hydrogen cyanide to an α,β-unsaturated carbonyl compounds



(d) Addition of water to olefins in presence of dilute sulphuric acid

$$CH_3CH=CH_2 + H_2O \xrightarrow{H2SO4} CH_3\text{-}CHOH\text{-}CH_3$$

Propylene propanol

(e) Addition of water to ethylene to give ethanol (100% atom economical)

$$CH_2=CH_2 + H_2O \longrightarrow C_2H_5OH$$

Ethylene Ethanol

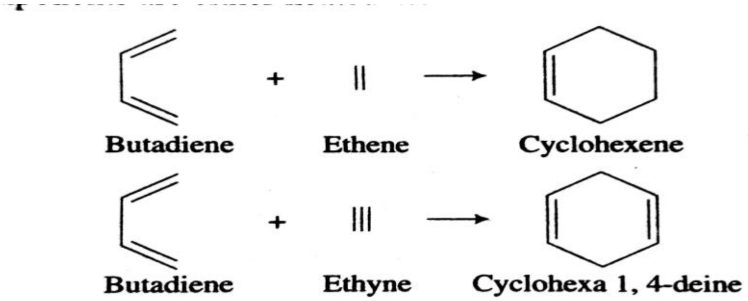
(f) Hydrogenation of propylene in presence of Ni as solid catalyst ((100% atom economical)

$$CH_3\text{-}CH=CH_2 + H_2 \xrightarrow{\text{Ni-catalyst}} CH_3\text{-}CH_2 – CH_3$$

1-propene propane

(g) **Diels-Alter reactions:** (100% atom economical)

It is a (4+2) cycloaddition reaction between a conjugated diene (4π-electron system) and a compound having a double or triple bond called the dienophile (2π-electron system) to form an adduct. In this reaction, the two components are either heated alone or in an inert solvent.



(h) Bromination of propene (100% atom economical)

$$H_3C\text{-}CH=CH_2 + Br_2 \xrightarrow{Cl_2} H_3C\text{-}CH(Br)\text{-}CH_2Br$$

propene 1,2-dibromopropane

Here, reactants (propene and bromine) are incorporated into the final product (1,2 dibromopropane). So this reaction is also 100% atom economical reaction.

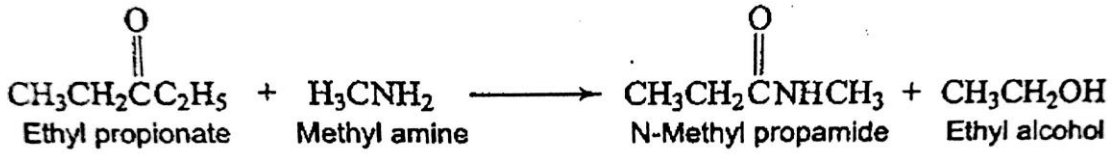
(i) Bromination of Butene (100% atom economical)

$$H_3C\text{-}CH_2\text{-}CH=CH_2 + Br_2 \longrightarrow H_3C\text{-}CH_2\text{-}CH(Br)\text{-}CH_2Br$$

1-butene 1,2-dibromobutane

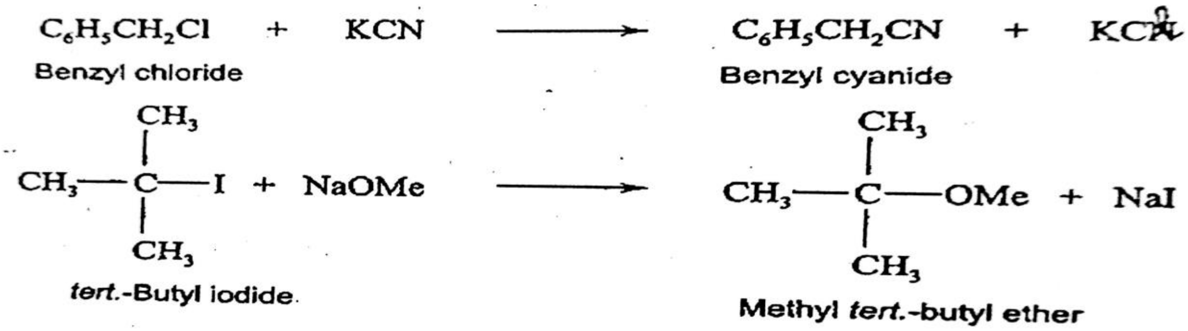
(ii) Substitution Reaction (less than 100% atom economy):
In these reactions, one atom (or group of atoms) is replaced by another atom (or group of atoms). The atom or group that is replaced is not utilized in the final product. So the substitution reactions are less atom economical than rearrangement or addition reactions.

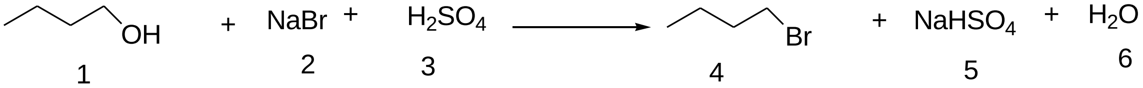
(a) The reaction of ethyl propionate with methyl amine.
In the above reaction, the leaving group (OC_2H_5) is not incorporated in the formed amide and also, one hydrogen atom of the amine is not utilized. The remaining atoms of the reactants are incorporated into the final product.



$$CH_3CH_2\overset{\overset{O}{\|}}{C}C_2H_5 + H_3CNH_2 \longrightarrow CH_3CH_2\overset{\overset{O}{\|}}{C}NHCH_3 + CH_3CH_2OH$$

Typical examples include the well known SN1 and SN2 reactions. In these reactions, nucleophilic reagents displace a leaving group in an aliphatic carbon atom, the product formed incorporates the nucleophile with removal of the leaving group.





% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100

= (137/275) X 100 = 50%

In some cases, the leaving group is the desired product. For example:
(b) Pottassium iodide demethylation of a carboxylic acid methyl ester to give free carboxylate salt and methyl iodide.

$$C_6H_5COOCH_3 + KI \longrightarrow C_6H_5COOK + CH_3I$$

Methyl benzoate Pot-benzoate Methyl iodide

(c) Alkayl halides undergo the nucleophilic substitution reaction. Thus alkyl halides are converted to alcohols by aqueous alkaline solution in water.

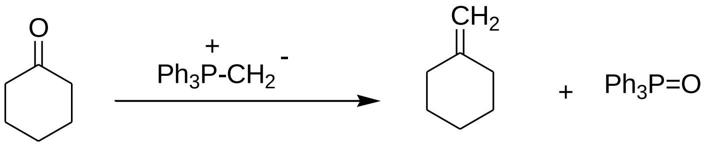
$$C_2H_5Br + NaOH \longrightarrow C_2H_5OH + NaBr$$

(d) Chlorination of methane

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

(e) Substitution of sodium methoxide

(f) Wittig reaction



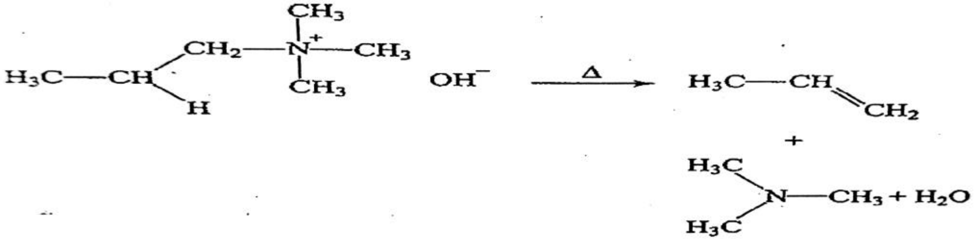
$$\text{Atom economy} = \frac{96}{98 + 276} = 25.7\%$$

(iii) Elimination Reaction: (less than 100% atom economy)

In an elimination reaction, two atoms or groups of atoms are lost from the reactant to form a π bond. The atom or group that is lost and is not utilized in the final product. So the elimination reactions are less atom economical than rearrangement or addition reactions.

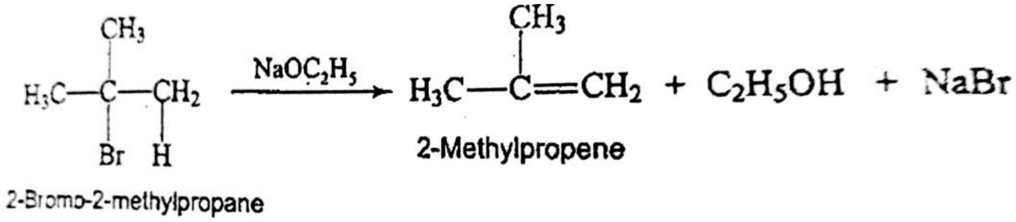
(a) Hoffmann elimination

The above elimination reaction is not very atom economical. The percentage atom economy is 35.3% and is the least atom economical of all the above reactions.



(b) Dehydrohalogenation of 2-bromo-2-methylpropane.

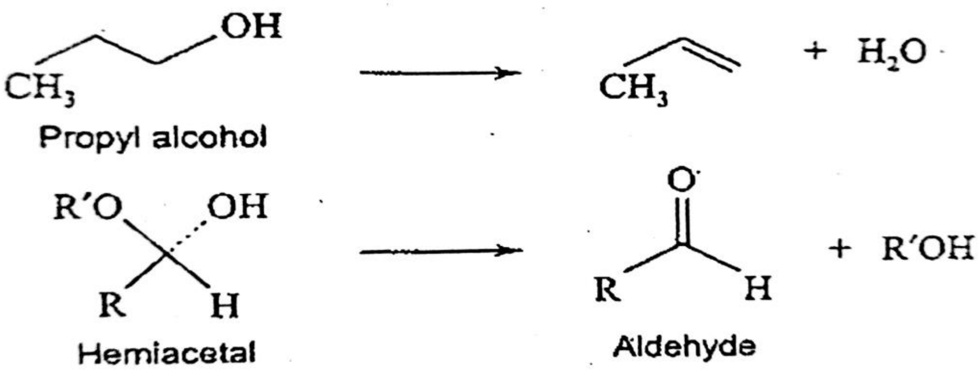
In an elimination reaction, dehydrohalogenation of 2-bromo-2-methylpropane with base to give 2-methylpropane.



The above dehydrohalogenation reaction is also not very atom economical. The percentage atom economy is 27% which is even less than the Hoffmann elimination reaction.

(c) Dehydration of an alcohol

This type of reaction include dehydration of an alcohol to give an olefin and loss of an alcohol from a hemiacetal to give an aldehyde.



$$CH_3CH_2OH \xrightarrow{\text{Conc.H2SO4}} CH_2{=}CH_2 + H_2O$$

(d) Dehydrogenation of alcohols

In an elimination reaction, dehydrogenation of alcohols to give aldehyde, ketone and Olefine.

$$CH_3CH_2OH \xrightarrow{\text{Cu (300°C) / H2CrO4}} CH_3CHO + H_2$$

$$CH_3\text{-}CH(CH_3)\text{-}OH \xrightarrow{\text{Cu (300°C) / H2CrO4}} CH_3\text{-} CO\text{-}CH_3 + H_2$$

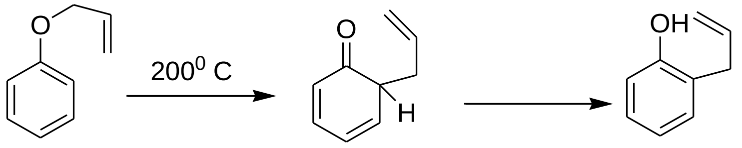
$$CH_3\text{-}C(CH_3)_2\text{-}OH \xrightarrow{\text{Cu (300°C)}} CH_3\text{-}C(CH_3){=}CH_2 + H_2O$$

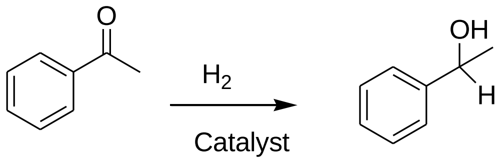
(e)Making ethanol from glucose:

$$C_6H_{12}O_6 \xrightarrow{\text{Fermenation of enzymes}} 2C_2H_5OH + 2CO_2$$

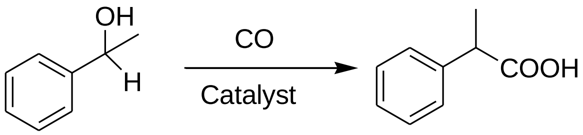
(iv) Rearrangement Reactions (100% atom economy)
These reactions involve rearrangement of atoms that make up a molecule. No additional by products are generated and such reactions are very efficient and also 100% atom economical.

(a)Claisen rearrangement:
Allyl phenyl ether on heating at 200°C gives o-allyl phenol.



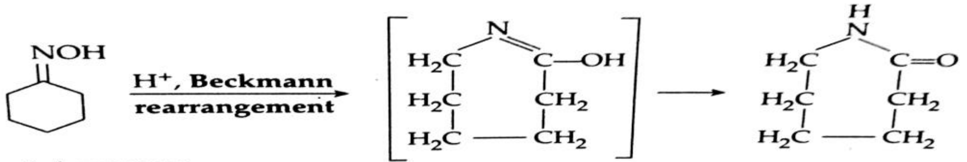


Hydrogenation



Carbonylation

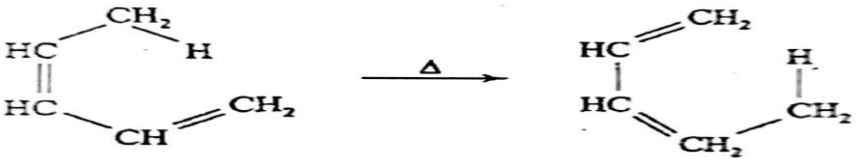
The above rearrangement reaction is 100% atom economical reaction, since all the reactants are incorporated into the product.
(b) Beckmann rearrangement:
Cyclohexanone oxide is converted into caprolactam in the presence of acid. The rearrangement reaction is 100% atom economical reaction.



Cyclohexanone oxime

Caprolactam

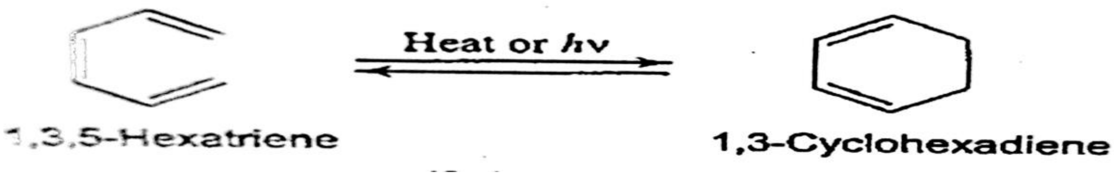
(c) Sigmatropic rearrangement:
These are concerted intramolecular rearrangements in which an atom or a group shift from one position to another.



1,3-Pentadiene

(d) Electrocyclic reactions:

These are reversible reactions in which a compound with two π electrons are used to form a sigma bond.



The above rearrangement reaction is 100% atom economical reaction, since all the reactants are incorporated into the product. There is no byproduct obtained in the above reactions.

Stoichiometric Reactions Versus Catalytic Reactions

In some reactions, the reactants (A and B) react to form a product (C), in which all the atoms contained within A and B are incorporated in the product (C). In such cases, stoichiometric reactions are equally environmentally benign from the point of material usuage as any other type of reactions. However, if one of the starting material (A or B) is a limiting reagent; in such cases, even if the yield is 100%, some unreacted starting material will be left over as waste. In other cases, if the reagents A and B do not give 100% yield of the product (C), both the excess of unreacted reagents will form part of waste. It is found that due to the reason mentioned above, catalysts, wherever available offter distinct advantages over typical stoichiometric reagents.

The catalyst facilitates the transformations without being consumed or without being incorporated into the final product. Catalyst are selective in their action, in that the degree of reaction that takes place is controlled, e.g., mono addition vs multiple addition; also the stereochemistry is controlled.

It should be understood that in stoichimetric processes, the product obtained is one mole for every mole of the reagent used. However, a catalyst will carry out thousands of transformations before being exhausted.

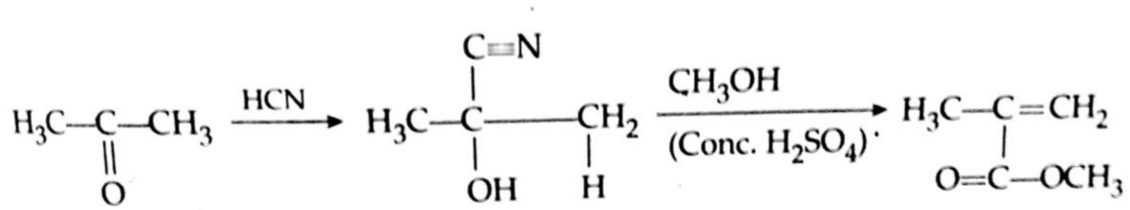
Selective catalytic reagents are superior to stoichiometric reagents in a chemical synthesis. This will save the energy and reduce the burden of by product. The use of catalysts is preferred because of the following advantages:

(i) 100% atom economy because the true catalysts are fully recovered without any change in their chemical and physical properties.
(ii) The catalysed reactions are faster i.e., energy save is possible.
(iii) Reaction yields are better.
(iv) Selective reaction products
(v) Maximum utilization of the starting material and minimum production of the waste material.

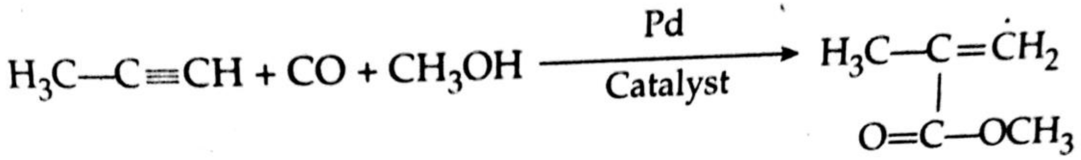
Some representive stoichiometric vs catalytic reactions (100% atom economy) are

(a) Greener synthesis of methyl methacrylate (MMA):

Methyl methacrylate is a monomer used for the manufacture a thermoplastic polymer, poly (Methyl methacrylate). It was earlier synthesized using stoichiometric amounts of hydrogen cyanide and sulphuric acid and had 47% atom economy.



(Atom economy = 47%)



(Atom economy = 100%) (MMA)

Subsequently, a green synthesis of methyl methacrylate was developed, which is 100% atom economical. The inefficient atom economy in the first method arises from the use of stoichiometric amount of HCN and H_2SO_4

(b) Green synthesis of acetophenone:

Classical oxidation of 1-phenylethanol consumes the stoichiometric amounts of CrO3 and H_2SO_4. Consequently its % atom economy is less. On the otherhand, catalytic oxidation by O_2 enjoys the higher atom economy.

$3PhCH(OH)CH_3 + 2CrO_3 + 3H_2SO_4 \rightarrow 3PhCOCH_3 + Cr_2(SO_4)_3 + 6H_2O$, **Atom economy = 42%**

(Stoichimetric oxidation)

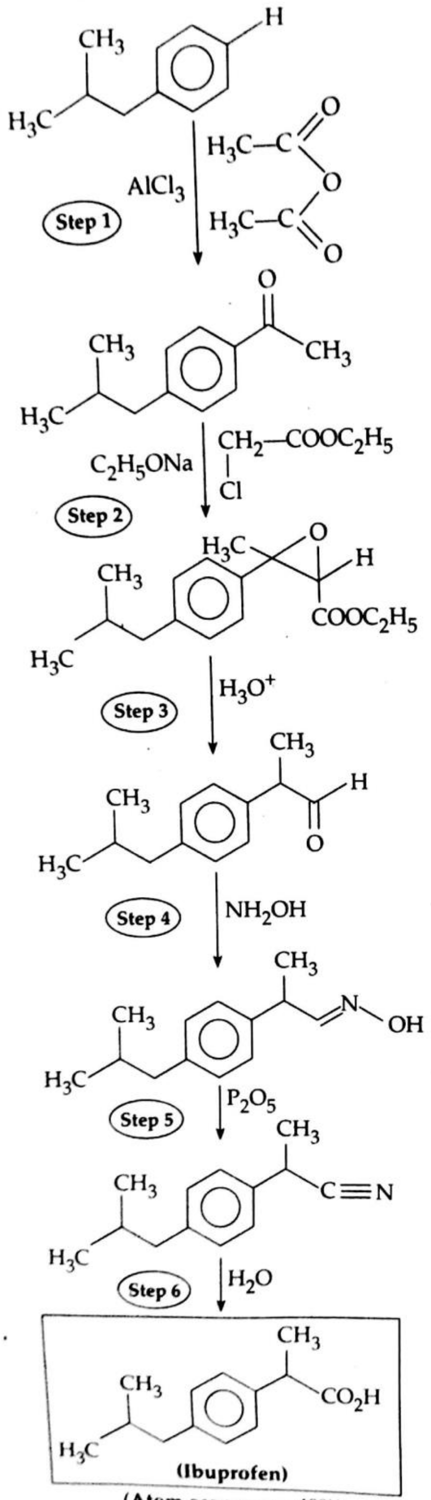
$PhCH(OH)CH_3 + \frac{1}{2}O_2 \rightarrow PhCOCH_3 + H_2O$, **Atom economy** = 87%

(**Catalytic oxidation**; only water is the by-product)

Synthesis of Ibuprofen:

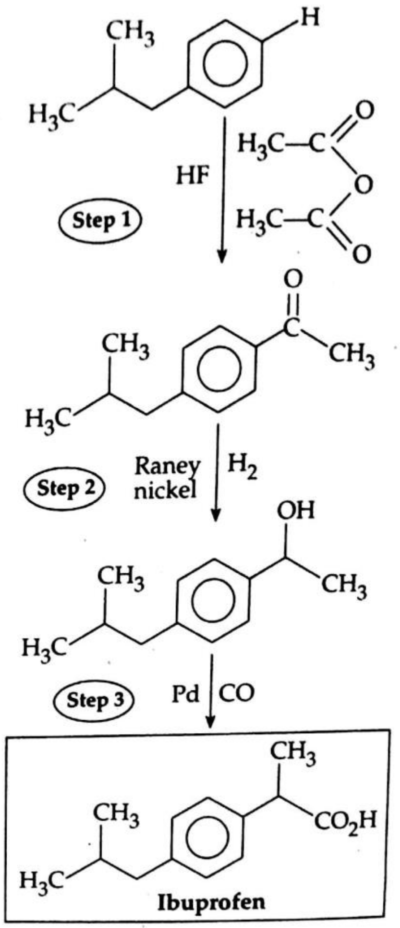
Ibuprofen is used in large quantities for making drugs used mostly an analgesics (pain killers). Its commercial synthesis was first introduced by Boots company of Nottingham, UK with atom economy only 40%. This methodology has been being used since 1960, but BHC (a joint venture of Boots company and Hoechst Celanese) has developed a new method with atom economy 77%. For this contribution, BHC won the PGCC award in 1997.

BOOTS – Synthesis



(Atom economy = 40%)

BHC – Synthesis

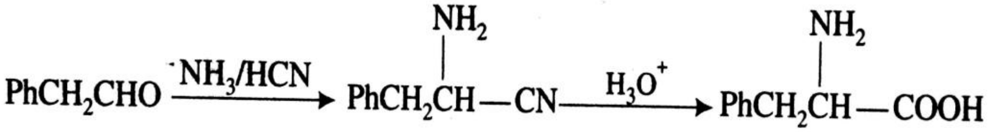


(Atom economy = 77%)

On an average, 30 million pounds of ibuprofen are synthesised annually and by the original Boots method it will produce more than 35 million ibuprofen of waste product which creates disposal problems. It has six step synthetic procedure. Subsequently BHC developed a greener synthesis of ibuprofen consisting of only three steps. It can dramatically reduce this waste product generation.

Strecker synthesis:

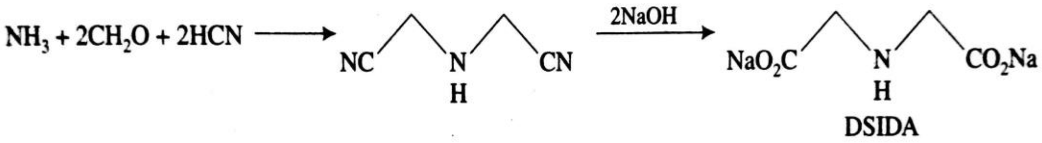
The reaction of an aldehyde with ammonia followed by reaction with HCN gives α-aminonitrile intermediates, which on hydrolysis gives α-amino acid. This reaction is known as Strecker synthesis.



$$PhCH_2CHO \xrightarrow{NH_3/HCN} PhCH_2\overset{NH_2}{\overset{|}{C}}H-CN \xrightarrow{H_3O^+} PhCH_2\overset{NH_2}{\overset{|}{C}}H-COOH$$

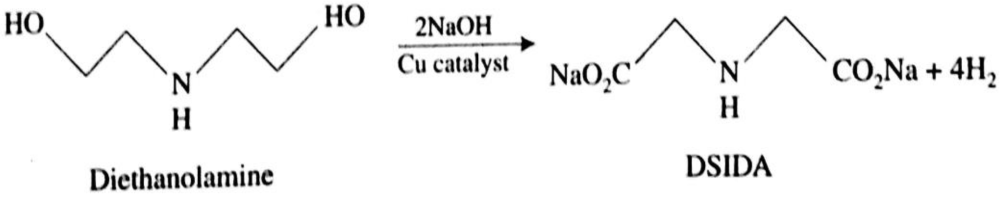
The α-aminonitrile can also be obtained by the treatment of aldehyde with HCN followed by reaction of the formed cyanohydrin with ammonia. This method is known as Erlenmeyer modification. A more convenient route is to treat the aldehyde in one step with ammonium chloride and sodium cyanide (this mixture is equivalent to ammonium cyanide, which in turn dissociates into ammonia and HCN). This procedure is referred as the Zelinsky-Stadnikoff modification. The final step is the hydrolysis of the intermediate α-aminonitrile under acidic or basic conditions.

Using Strecker synthesis, disodium iminodiacetate (DSIDA) an intermediate for the manufacture of Monsantos Roundup (herbicide) was synthesised. In the procedure hydrogen cyanide, a hazardous chemical is used and this requires special handling to minimise the risk to workers and the environment.



Strecker Synthesis of DSIDA

An alternative synthesis of DSIDA was developed by Monsanto; this is green synthesis, which avoids the uses of HCN and HCHO and is safter to operate.



Alternative Synthesis of DSIDA

Biotechnology in Environmental Protection;

Environmental biotechnology involves specific applications of biotechnology to the management of environment and related socio-economic and developmental issues, keeping in view the concept of sustainable development. Environmental biotechnology encompasses issues like

(i) Environmental monitoring
(ii) Restoration of environmental quality
(iii) Resource/residue/waste-recovery/utilization/treatment through application of r-DNA technology.
(iv) Substitution of non-renewable resources by renewable ones.
(v) Strain improvement for degradation of highly toxic pollutants with the production of chemicals.
(vi) Global changes
(vii) Biological diversity and
(viii) Risk management.

Industrial pollution management is thus amongst the many issues that environmental biotechnology addresses to. For a long time, the point of discussion in environmental pollution as an issue, has been symptoms rather than causes of pollution. This naturally influenced our thinking, and emphasis was given on measurement and removal (treatment technologies). The points useful in effective pollution management are:

(1) In-process treatment
(2) End-of-pipe treatment
(3) Remediation of polluted sites
(4) Modification of existing processes
(5) Introduction of new processes and products

Potential biological treatments are

(a) In-situ degradation of specific wastes, using specialized cultures or consortia.
(b) Inoculation of conventional waste treatment systems with adapted, specialized cultures.
(c) Decontamination and detoxification of spillages
(d) Heavy metal removal, recovery

(e) Bioscrubbing of odour and waste noxious gases (mercaptans, phenol, H2S, hydrocarbons etc.)
(f) Generation of biomass (SCP, mushrooms) from wastes.
(g) Biogassification and ethanol production from wastes.

Biotreatment technology is effective in the removal of many xenobiotic compounds from the aqueous, solid, gaseous wastes. Polynuclear aromatics, halogenated aliphatics, heterocyclic, polar non-halogenated nitrocompounds, hydrocarbons, cyanide, phenolics, sodium oxalate, urea, trichloroethylene etc., can be removed with the use of microorganisms or their enzymes in addition to the simple organic wastes that it can easily decompose.

Anaerobic biodegradation rather than the aerobic one is the major change in trend and this not only saves energy expenditures on treatment (otherwise aeration costs) but generates energy in the form of methane or ethanol. Wastes from food, agriculture, dairy, distillery industries are now better treated by anaerobic means than aerobic and effluent treatment is economically self-sufficient.

Bioremediation of land sites, groundwater polluted by spillage, drainage, leakage is also getting established as a successful remedial measure to remove hazardous chemicals like benzene, styrenes, xylene, vinyl chloride, pentachloro phenols, polyaromatic hydrocarbons (PAH’s), nitrates etc. Hazardous management is possible with biotechnology with one-fourth to one-fifth cost of the existing methods as is shown in various studies.

Biosorption processes using live or dead organisms to remove toxic heavy metals or recovery of rare (costly) metals from effluents of various industries is an interesting application of biotechnology.

SCP production (protein rich food) and mushroom cultivation is relatively old application of biotechnology. But now treating organic rich effluents from dairy, brewery, confectionary, fruit pulp processing and starch production units gives product formation from wastes. However, it is still mainly restricted to food, dairy and agricultural wastes.

There are now over a dozen of companies active in developing and marketing engineered microbes (packaged organisms) for effluent treatment.

Biological Purification of Air

The biological treatment of air pollution depends on aerobic microorganisms--mostly mesophilic bacteria--that feed on both organic and inorganic compounds in the waste gas. The microbes convert the pollutants into carbon dioxide, water, and salts.

Traditionally used for odor control (such as at livestock processing facilities), biofilters are now being used for ammonia control at composting facilities and for volatile organic carbon emissions control at wastewater treatment facilities, breweries, foundries, plastics, paper, and petrochemical industries. Biofilters also have been used to remove vapors from contaminated soil and groundwater.

There are two main types of biological treatment technologies:

1. **Biofilter**

   This is the simplest and least expensive biological treatment method. Its main component is a bed of compost, tree bark, peat, heather, or soil, about 1m deep, through which the contaminant gas is blown (see Figure 1). The material in the biofilter bed provides a diverse culture of microorganisms that degrade the gaseous pollutants passing through.

   Most biofilter units resemble towers, being designed as sealed vertical containers. The design allows for better process control and exhaust monitoring than do open chambers (see Figure 2). The inlet gas flow distribution and humidity must be carefully controlled; otherwise the bed will behave simply as an adsorption filter and eventually clog. Typically the inlet gas should be relatively dust-free, saturated with water vapor, and be at a temperature of 10-40 ºC. Such units last between one and seven years, depending on the contaminant loading.

2. **Bioscrubber**

   A bioscrubber couples traditional air pollution control and wastewater treatment technologies and consists of two units: a scrubber and a biological treatment basin. The soluble waste gases and oxygen are continuously absorbed into water in the scrubber. Biological oxidation occurs in the basin unit, which often is the activated sludge basin of a wastewater treatment plant. Bioscrubbers are used where the biological degradation products (such as the acids produced during H_2S and NH_3 removal) would harm a biofilter bed. In addition to hydrocarbons, bioscrubbers are being used to remove chlorinated organics.

   Bioscrubbers come in two forms:

<u>Activated-sludge scrubber</u>. Gaseous pollutants are absorbed by a solvent in a countercurrent packed column tower. The absorption solution generally is a water and sludge mixture (1-10 g sludge per liter of water). After absorption in the column, the solution proceeds to a sedimentation tank where biodegradation takes place. Clean solution from the sedimentation tank recycles back to the packed column.

Trickling-filter scrubbers. As with the activated-sludge scrubber, gaseous contaminants are transferred into the liquid phase with a countercurrent scrubber. Instead of being fed into an activated sludge pond, however, the pollutant-laden scrubber wastewater is spread over a trickling filter. The technology offers greater control than does the activated sludge scrubber. .

Bio-trickle filter

Bio-trickle filter consists of a sheet of a plastic or other microbial support medium hung in the contaminated air stream. The sheet is bathed continuously by a recirculating stream of water containing the nutrients and vitamins required by the microbes. Bio-oxidation rates per unit volume are high so bio-trickle filters can be as small as physico- chemical units.

Their disadvantages are that at high loading rates, biological reactions approach zero order kinetics and are incapable of responding to peak loads, accidental discharges and explosion incidents. Bio-trickle filters would seem to be susceptible to microbially produced bactericides and to invasion of less-desirable microbial populations.

Biological air pollution control is related to wastewater treatment and is only slowly being accepted on an industrial scale. Wastewater usually contains a. suitable mixture of nitrogen, phosphate and other chemicals as microbial growth factors. In contrast, industrial waste air might contain only a single carbon-, hydrogen molecule. Therefore, the bio-filter medium must supply the other growth factors including water so that the microorganisms may metabolize the "the empty calories" in the contaminated air.

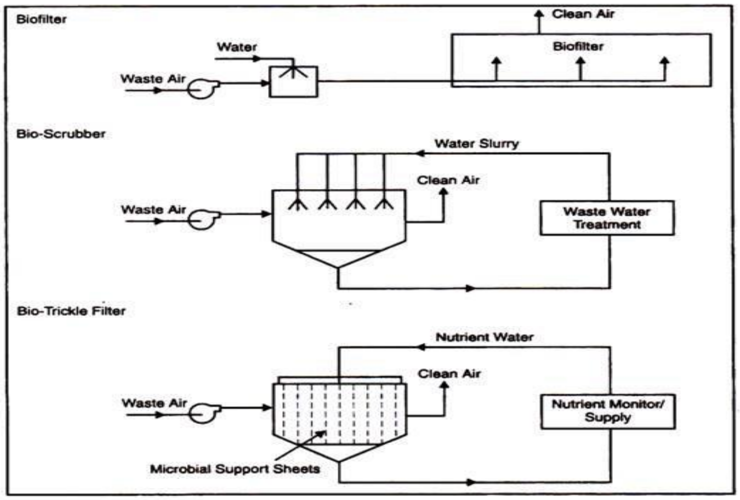


Fig. 9.5. Schematic drawing of a biofilter, bioscrubber, and bio-trickle filter.

Bioremediation:

The process of cleaning up the hazardous substances into non-toxic compounds is called the Bioremediation. This process is majorly used for any kind of technology clean up that uses the natural organisms.

Methods of Bioremediation:

On the basis of removal and transportation of wastes for treatment, there are two methods:

(i) In situ bioremediation
(ii) Ex situ bioremediation

(i) In situ bioremediation:

In situ bioremediation is the clean up approach which directly involves the contact between microorganisms and the dissolved and sorbed contaminants for biotransformation. Biotransformation in the surface environment is a very complex process.

Advantages:

- ✓ Minimal site disruption, simultaneous treatment of contaminated soil and ground water, minimal exposure of public and site personnel and low cost.
- ✓ It is carry out within that place.

Disadvantages:

- ➢ Time consuming method as compared to other remedial methods.
- ➢ Seasonal vatiation of microbial activity resulting from direct exposure to prevailing environmental factors, and lack of control of these factors.
- ➢ Problematic application of treatment additives (nutrients, surfactants and oxygen)

Types of In-situ bioremediation:

(a) Intrinsic Bioremediation
(b) Engineered in situ bioremediation

(a) Intrinsic Bioremediation:

Conversion of environmental pollutants into the harmless forms through the innate capabilities of naturally occurring microbial population is called intrinsic bioremediation. However, there is increasing interest on intrinsic bioremediation for control of all or some of the contamination at waste sites.

(b) Engineered in situ Bioremediation:

Intrinsic bioremediation is satisfactory at some places, but it is slow process due to poorly adapted microorganisms, limited ability of electron acceptor and nutrients, cold temperature and high concentration of contaminants. When site conditions are not suitable, bioremediation requires construction of engineered systems to supply materials that stimulate microorganisms. Engineered in situ bioremediation accelerates the desired biodegradation reactions by encouraging growth of more microorganisms via optimizing physic-chemical conditions. Oxygen and electron acceptors (e.g. NO_3^{1-} and SO_4^{2-} and nutrients (e.g. nitrogen and phosphorous) promote microbial growth in surface.

(ii) Ex situ Bioremediation:

Ex situ bioremediation involves removal of waste materials and their collection at a place to facilitate microbial degradation. Ex situ bioremediation technology includes most of disadvantages and limitations. It also suffers from costs associated with solid handling process e.g.excavation, screening, and fractionation, mixing, homogenizing and final disposal. On the basis of phases of contaminated materials under treatment ex situ bioremediation is classified into two

(a) Solid phase system (including land treatment and soil piles) i.e composting
(b) Slurry-phase systems (involving treatment of solid-liquid suspensions in bioreactors).

(a) Solid phase system:

Solid phase system includes organic wastes (e.g.leaves, animal manures and agricultural wastes), and problematic wastes (e.g.domestic and industrial wastes, sewage sludge and municipal solid wastes). The traditional clean up practice involves the informal processing of the organic materials and production of composts which may be used as soil amendment.

(i) Composting: Composting is a self heating, substrate-dense, managed microbial system and one solid phase biological treatment technology which is suitable to the treatment of large and amount of contaminated solid materials. Composting can be done in open system i.e., land treatment and in closed system.

(ii) Composting process

As composting is a solid-phase biological treatment, target compounds must be either solid or a liquid associated with a solid matrix. The hazardous compounds should be biologically transformed.

(b) Slurry phase Treatment: The contaminated solid materials (soil, degraded sediments, etc), microorganisms and water formulated into slurry are brought within a bioreactor i.e. fermenter. Thus slurry-phase treatment is a triphasic system involving three major components: water, suspended particulated matter and air. Here water serves as suspending medium where nutrients, trace elements, pH adjustment chemicals and desorbed contaminents are dissolved. Slurry base reactors are new design in bioremediation. The objectives of bioreactors designing are to (i) alleviate microbial growth limiting factors in soil environment such as substrate, nutrients and oxygen availability (ii) promote suitable environmental conditions for bacterial growth such as moisture, pH, temperature (iii) minimize mass transfer limitations and facilitate desorption of organic material from the soil matrix. Biologically there are three layers of slurry phase bioreactors: Aerated lagoons, low shear airlift reactor, and fludized bed soil reactor. The first two types are in use of full scale bioremediation, while the third one is in developmental stage.

Bioinformatics

Translation of billions of characters in DNA sequences that make the genome into biologically meaningful information has given birth to a new field of science called bioinformatics. The term bioinformatics has been derived by combining of biology and informatics.

Bioinformatics is a multidisciplinary science which aims to use the benefits of computer technologies in understanding the biology of life. Now, as a subject bioinformatics consists of three core areas:

(i) Molecular biology database
(ii) Sequence comparison and sequence analysis
(iii)The emerging technology of microarrays

In brief bioinformatics is the management and analysis of biological information stored in databases.

1. Database:

A database is a repository of sequences (DNA or aminoacids) which provide a centralized and homogenous view of its contents. The repository is created and modified through a database management system (DBMS). Every data item in the database is structured according to a scheme, defined as a set of pre-specified rules through the data definition language. The contents of database can be accessed through a graphical user interface (GUI) that allows browsing through the contents of the repository very much similar as one may browse through the books in library.

The databases are broadly classified into two categories: (a) Sequence database (that involves the sequences of both proteins and nucleic acids) (b) structural databases (that involves only protein databases). In addition, it is also classified into three categories:

(a) primary database
(b) Secondary database
(c) Composite database.

Information sources: There are several well developed data respositories that have facilitated the dissemination of genome and protein resources of humans and other organism. Some of the major biological databases are

1. NCBI’s genebank
2. Data collection EMBL Nucleotide Sequence Database
3. Data collection DNA data bank of Japan (DDBJ)
4. Data collection SWISS-PROT
5. NCBI’s dbSNP polymorphism
6. OMIM genomic disorder
7. GeneExpression
8. NCBI’s Microbial Genome Gateway
9. Mouse Genome Database (MGD)
10. Saccharomyces genome database (SGD)
11. Rice Genome Project (RGP)
12. Protein Database (PDB).

The most comprehensive resources are the NCBI, genome databse (GDB) and Mouse Genome Database (MGD). Each databse is informative and very useful.

Significance of Green chemistry:

- ✓ A novel approach that blends the application of chemistry with economic growth and environmental preservation.
- ✓ To develop strategy for sustainable chemical process industries.
- ✓ Achieve conservation of limited resources.

The main benefits of green chemistry are

(i) Human health

(a) Cleaner air: Less release of hazardous chemicals to air.

(b) Cleaner water: Reduce release of industrial wastes to water.

(c) Increased safety for workers in the chemical industry; less use of toxic materials; less personal protective equipment required; less potential for accidents (e.g.Fire or explosives)

(d) Safer consumer products of all types: (e.g drugs, pesticides, cleaning products)

(e) Safer food

(f) Less exposure to such toxic chemicals as endocrine disruptors.

(ii) Environment:

- ✓ Many chemicals end up in the environment by pesticides or manufacturing. Green chemicals either degrade to innocuous products or are recovered for further use.
- ✓ Plants and animals suffer less harm from toxic chemicals in the environment.
- ✓ Lower potential for global warming, ozone depletion and smog formation.
- ✓ Less chemical disruptions of ecosystems.
- ✓ Less use of landfills, especially hazardous waste land fills.

(iii) Economy and business:

- ➢ Higher yields for chemical reactions, consuming smaller amount of feedstock to obtain the same amount of product.
- ➢ Fewer synthetic steps, often allowing faster manufacturing of products, increasing plant capacity, saving energy and water.
- ➢ Reduced waste, eliminating costly remediation, hazardous waste disposal.
- ➢ Replacement of a purchased feedstock by a waste product.
- ➢ Reduced use of petroleum products.
- ➢ Reduced manufacturing plant size.

- Improved competitiveness of chemical manufacturers and their customers.

Components of Green chemistry:

1. Prevent waste
2. Maximize atom economy
3. Less hazardous chemical synthesis
4. Designing safer chemicals and Products
5. Designing safer solvents and reaction conditions
6. Increases Energy efficiency
7. Use of renewable feedstock
8. Avoid chemical derivatives (protecting groups)
9. Use catalysts
10. Design chemicals and products to degrade after use.
11. Analyze in real time to prevent pollution
12. Minimize potential for accidents.

Application of Biotechnology to control industrial pollution

Biotechnology is ecofriendly. It uses the enzyme catalysed processes. The main problem of the biotechnology based process is the slowness of the process. The better sides of biotechnology can be compared with the conventional chemical technology.

- ✓ Less energy is required for biotechnology based process.
- ✓ Less hazardous
- ✓ The process can occur normal temperature and pressure.
- ✓ The wastes produced in the biotechnology based processes are less harmful and sometimes the wastes are recyclable. The processes are less polluting.

1. Application of biotechnology in paper industry:

The effluent of paper industry carries a lot of biodegradable and hazardous chemicals. Application of biotechnology at different steps can reduce the pollution.

- ✓ Pulping
- ✓ Bleaching of pulp
- ✓ Deinking from waste paper for recycling
- ✓ Pitch removal from wood.
- ✓ Waste treatment.

2. Application of biotechnology in tanning industry:

Dehairing and degreasing:

It is done by using sulfides, alkalies, and surfactants. In terms of biotechnology, different enzymes like alkaline proteases, lipases and trypsins can perform the task. The use these digesting enzymes can cut down the use of chemicals and solvents required for degreasing.

Baiting: This process makes the leather soft through the partial degradation of protein. This can be done by pancreatic trypsins.

Waste water treatment: Fungi can be used to remove the toxic tannins present in tannery effluent. Fungi can also be used for leaching out chromium from tannery effluents.

3. Desulfurisation of coal and petroleum products

Coal burning produces a huge amount of SO_2 to cause air pollution. Coal burning produces the largest fraction of electricity required in several countries. Similarly, petroleum products produce also SO_2. This is why, desulfurization of such fossil fuels is essentially required to prevent air pollution. The flue gas desulfurization process is very much costly and many developing countries cannot bear this. In coal, sulfur remais as both organically bound and as inorganic sulfur. Most of the inorganic sulfur exists as iron-pyrites (FeS_2). The bacterial strain can remove the organic sulfur without damaging the coal. The iron bacteria can dissolved the inorganic sulfur i.e.pyrite. The bacteria like thiobacillus ferrooxidans, ferrobacillus ferrooxidans, etc. can oxidize pyrite as follows.

$$FeS_2 \longrightarrow Fe_2O_3 + H_2SO_4$$

It is believed that the bacterial oxidation of Fe^{2+} to Fe^{3+} releases electrons that can be used by the bacteria themselves for the reduction of CO_2 to generate the new cell material. Fe3+ thus produced can oxidize S2- ion nonbiologically as follows:

$$8Fe^{3+} + S^{2-} + 4H_2O \longrightarrow 8Fe^{2+} + SO_4^{2-} + 8H^+$$

Thus the Fe^{2+} produced is again enzymatically oxidized by the bacteria and Fe^{2+} acts as the source of electron for the bacteria. If may be noted that, in acidic condition aerial oxidation of S^{2+} to SO_4^{2-} is very slow but this process can be catalysed by some bacterial enzymes.

$$S^{2-} + 4H_2O \longrightarrow SO_4^{2-} + 8H^+ + 8e^-$$

(4) Use of biotechnology in drug industry:

To cut down the production cost of drugs, application of biotechnology is quite promising. This principle also cuts down the amount of production waste. The enzyme penicillin acylase is used to prepare the semisynthetic penicillin. Cephalosporins are better antibiotics than the penicillin but the production cost of cephalosporins is very high and the process of production is not ecofriendly. However, some enzymes have been identified to produce the required antibiotic intermediate, cephalosporic acid. It reduces the production waste by about 10 times. Several such examples are now being practicsed.

(5) Biotechnology in waste treatment:

If the effluent is rich in degradable organics as in the case of food processing industries, then the application of biotechnology can produce the fuels like ethanol, methane from the waste. In fact, now biomethanization reactions for such waste water have been developed. Biotreatment plants for the waste water containing a large number of pollutants (water miscible and water immiscible components, water soluble gases etc.) coming out from the industries like petrochemical industries have been set up in many places. Solid waste enriched with the degradable organics can be converted into biofertilizer by using the principle of vermiculture.

Green fuels:

The inflammable substances produced by the action of microbes, that can be set on fire, are called green fuels. Green fuels include ethanol, methane and hydrogen. They are produced from cheap raw materials or wastes. They do not release high proportion of carbon dioxide during combustion. This is the advantage of green fuels in monitoring air pollution due to carbon dioxide accumulation.

Ethanol:

Ethanol (ethyl alcohol) is a colourless, inflammable liquid. It is spirituous in odour. It is known as grain alcohol, spirit and gasohol. It is a good solvent for fats, resins, dyes, etc. It can be used as a fuel for lamps and stoves. In recent years, it is also used to run internal combustion engines.

In biotechnology based industries, ethanol is produced from wastes by the action of microbes. Any waste rich in carbohydrate is used as the substrate to produce ethanol.

Usually wastes are renewable resources being released in the environment by the activity of man. Therefore, there is no need to use living natural resources to make ethanol. As wastes are taken as raw materials, ethanol production opens a way to reuse wastes to clean up the environment

Ethanol is prepared from the following wastes and plant products

Sugarcane molasses
Cane juice
Sugar beets
Sugarbeet molasses
Cassava
Yams

Grain of
Maize
Corn
Sweet sorghum
Crop wastes

Ethanol Fermentation

The carbohydrates locked in the wastes are the source of glucose. A glucose molecule is metabolized into two molecules of pyruvic acid through glycolytic pathway. The pyruvic acid is converted into ethanol in the following route:

The pyruvic acid is decarboxylated to acetaldehyde in the presence of carboxylase and thiamine pyro-phosphate as co-factor. The acetaldehyde is then reduced to ethyl alcohol by the enzyme alcoholdehydrogenase and NADH2 as co-enzyme.

$$\underset{\text{Pyruvic acid}}{2CH_3COCOOH} \xrightarrow{\text{Catalase / TPP}} \underset{\text{acetaldehyde}}{2\,CH_3CHO} + 2CO_2$$

$$CH_3CHO + NADH_2 \xrightarrow{\text{Alcohol dehydrogenase}} \underset{\text{Ethanol}}{CH_3CH_2OH} + NAD$$

Ethanol fermentation takes place under anaerobic conditions. The metabolism of ethanol from glucose was first explained with reference to yeast by Guy-Lussac in 1815. Later many microbes are known to have this metabolic route to produce ethanol. Ethanol production involves the following steps:

(i) Formulation of medium
(ii) Designing of fermentation system
(iii)Culture of microbes in fermenters

(iv) Recovery of ethanol.

Applications of ethanol:

Ethanol is an active solvent of dyes, lubricants, adhesives, some pesticides, paints, explosives and resins. It is also used as an organic solvent for the extraction of some organic compounds from living things.

Ethanol is used in the manufacture of synthetic rubber.

It is used in the extraction of certain pharmaceutical products.

It is used in the manufacture of acetaldehyde

It is used in the manufacture of perfumes.

Biogas

Biogas or fuel gas consists of methane and carbon dioxide in the ratio of 2:1. It has 65% methane, 30% carbon dioxide, 1% of hydrogen sulphide and 4% of remaining compounds like oxygen, hydrogen, nitrogen and carbon monoxide. It is produced by fermentation effected by anaerobic bacteria is called methanogens.

The microbial conversion of biomass into methane was first discovered by Volta in 1776. Volta demonstrated the presence of methane in marsh gas. Hence the biogas is known as marsh gas. It is also named Klar-gas, refuse derived fuel (RDF), gobar gas and Will-of the wisp.

Characteristic features of Biogas:

1. Biogas is a colourless mixture of gases
2. It contains methane, carbondioxide, hydrogen sulphide, nitrogen, oxygen, hydrogen and carbon monoxide.
3. It is a odourless gas
4. It burns with a blue flame
5. It does not release smoke while burning
6. It does not release kitchen refuse while burning
7. It releases 22-28 MJm^{-3} energy during burning.
8. The energy contents of $28m^3$ of biogas is equal to 20.8 litres of petrol or 18.4 litres of diesel.

Biogas production involves the following important steps:

(i) Selection of feedstock

(ii) Selection of methanogens
(iii)Construction of biogas plant
(iv)Methane fermentation

Methane production from Hydrocarbons

Aromatic hydrocarbons are also used as substrates for the production of methane. Benzonate undergoes metabolic breakdown into acetate, formate and water. Acetate is metabolized into CO_4 and H_2O. The formate is metabolized into CO_2 and H_2. These CO_2 and H_2 are finally converted into methane and water. The overall reaction of methane formation is stated below:

$$4C_6H_5COOH + 8H_2O \longrightarrow 15CH_4 + 13CO_2$$

Uses of Biogas:

- The biogas produced in the gas plants is stored in gas cylinders for ready use.
- The gas is supplied to industries in order to reduce the requirement of electricity to run machines.
- The gas is distributed to houses as a fuel gas. It reduces the consumption of fuel wood. It is also used in emergency lights.
- The gas is also used to produce electricity.

Hydrogen gas

Photosynthesis is a characteristic feature of autotrophic organisms such as green plants, algae and some bacteria. They release hydrogen during the primary photochemical reaction. It is a light dependent process. It was first discovered by Gaffron and Rubin in 1942.

In photosynthetic microbes, hydrogen production is taking place in the electron transport chain. Ferridoxin accepts electrons from the electron transport system and gives them to the hydrogenase. The hydrogenase reduces H+ ions into H2. In some bacteria, ferridoxin is replaced by a few organic compounds. Eg. Glucose, pyruvate etc.

$$2H_2O + e\text{- (light energy)} \longrightarrow 2H_2 + O2$$

In the dark, carbohydrates act as electron donors. These electrons reduce H^+ ions into H_2. This reaction is catalysed by the enzyme hydrogenase.

$$RH_2 \xrightarrow{\text{hydrogenase}} R + H_2 \qquad (R = \text{ e- donor})$$

Importance of biological production of Hydrogen:

1. Hydrogen production takes place at a low physiological temperature between 10-40°C. It does not require high temperature (400-1000°C) as required for the production of hydrogen in chemical and physical methods.
2. During the production of hydrogen, the cells utilize the solar radiation. So the energy source is very cheap.
3. Agricultural wastes are used for the production of hydrogen.
4. During the hydrogen production, the biomass also multiplies more rapidly and yields single cell proteins.

Hydrogen production from Marine organisms

Sea contains ample of photosynthetic bacteria and algae; these organisms effectively produce hydrogen. The following steps are adopted to make a hydrogen-producing system using marine organisms:

1. The different species of organisms are collected from sea water, sediments, sea grasses, leaves of mangroves.
2. The collected organisms are cultured in sea water. Those strains producing hydrogen in large proportions are selected and cultured separately.
3. The conditions for the optimum growth of hydrogen producers are determined properly and the particular condition is given to the cultures.
4. A culture tanks of 1×8×8 meter size is used to culture the hydrogen producers. It is the average size of the hydrogen-producing system which fulfils the basic energy need of a single family, for its household works.

Advantages:

- The availability of sea water for culture is plenty.
- Sea water contains almost all nutrients for the growth of these organisms.
- Sea water acts as H+ donor in the hydrogen-producing system.
- The organisms grow permanently in the culture tank without any proper care, and produce hydrogen continuously.
- This is good system of using the natural energy for the production of hydrogen.
- The selection of right species is more easy and inexpensive.

- The biomass produced during the hydrogen production forms a good food for poultry, cattle and man.

Biocatalysts:

Biocatalysis has many attractive features in the context of green chemistry: mild reaction conditions (physiological pH and temperature), an environmentally compatible catalyst (an enzyme) and solvent (often water) combined with high activities and chemo- regio- and stereo-selectivities in multifunctional molecules.

` Enzymes are known as biocatalysts. These are proteins that act as biological catalysts, i.e. these alter the rates of biochemical reactions without undergoing any permanent change in themselves. These have a high degree of specificity besides high efficiency on rates of reactions. In nature, enzymes help million of chemical reactions to occur at extraordinary speeds and under moderate conditions. In the absence of enzymes most chemical reactions that maintain a living organism would occur only under very drastic conditions, e.g. at a temperature of the order of 100° or above which would 'kill' the fragile cell. At normal body temperatures, these reactions would often proceed at an extremely slow rate.

Furthermore, the use of enzymes generally circumvents the need for functional group activation and avoids protection and deprotection steps required in traditional organic syntheses. This affords processes which are shorter, generate less waste and are, therefore, both environmentally and economically more attractive than conventional routes.

An illustrative example of the benefits to be gained by replacing conventional chemistry by biocatalysis is provided by the manufacture of 6-aminopenicillanicacid (6-APA), a key raw material for semi-synthetic penicillin and cephalosporinantibiotics, by hydrolysis of penicillin G.

Up until the mid-1980s a chemical procedure was used for this hydrolysis (Fig.). It involved the use of environmentally unattractive reagents, a chlorinated hydrocarbon solvent (CH_2Cl_2) and a reaction temperature of -40^0C. Thus, 0.6 kg Me_3SiCl, 1.2 kg PCl_5, 1.6 kg$PhNMe_2$, 0.2 kg NH_3, 8.41 kg of n-BuOH and 8.41 kg of CH_2Cl_2 were required to produce 1 kg of 6-APA.

In contrast, enzymatic cleavage of penicillin G is performed in water at 37^0C and the only reagent used is NH_3 (0.9 kg per kg of 6-APA), to adjust the pH. The enzymatic process currently accounts for the majority of the several thousand tons of 6-APA produced annually on a world-wide basis.

zz

Traditionally, transition metals like palladium, platinum, and ruthenium are used to build catalysts for carbon-carbon bond-forming reactions. However, these metals are expensive and in low abundances in the Earth's crust. In some cases, the catalysts require large ligands to control the selectivity of a reaction, which can be considered wasteful according to the 12 principles. Therefore, researchers look to get the same functionality of these catalysts with a more available and sustainable metal: iron. Iron catalysts can carry out a wide range of cross coupling reactions.

Another independent area of research is nanoscience. Attaching catalysts to magnetic nanoparticles makes it easy for chemists to separate and recycle the catalyst after a reaction. Other types of catalysts can reduce safety risks Acid catalysts attached to silica, for example, reduce the aqueous waste generated by quenching and neutralizing a reaction.

Advantages and Limitations of Biocatalysis

Chemical reactions are usually carried out under rigorous conditions. They often involve highly reactive ingredients which may be toxic or carcinogenic, that are used in the organic solvents. High temperatures and pressures may be involved, especially in the production of commodity chemicals. Biocatalysis offers the possibility of making many of the products that we need in water at or near room temperature. It uses whole organisms, usually microorganisms, or the enzymes from them, to carry out the chemical transformations. It is an aspect of biotechnology. Chemoenzymatic syntheses, that is those sequences of reactions where both chemical and biological steps are involved, are becoming increasingly common.

Biocatalysis offers many advantages:

- Most of the reactions are performed in aqueous medium with no need for organic solvents.
- Often run at or near room temperature at atmospheric pressure.
- No toxic metal ions
- No carcinogens
- No noxious emissions, just carbon dioxide.
- No toxic wastes: wastes can be used as animal feed or composted.
- Often use organic wastes as starting materials
- Higher slectivities: it is often possible to react only one of two similar sites.
- Chiral compounds can be produced.
- No protecting groups are needed for reactions
- Less energy is needed.

There are limitations to biocatalysis that current research is endeavoring to overcome

- ✓ The reaction may be slow, especially if done in an organic medium.
- ✓ The run may have to be quite dilute.
- ✓ The enzyme may be expensive and difficult to recover for reuse.
- ✓ The enzyme may lose activity too quickly, especially if used at elevated temperatures.
- ✓ The recovery of the product from dilute solution may be complicated and expensive.
- ✓ The product may inhibit its further formation.
- ✓ It may be difficult to obtain a pure enzyme, free of contamination by other enzymes that might degrade the substrate or produce by products.

Biocatalytic process by Enzymes

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

1. Oxidoreductases:

   Oxidoreductases are enzymes which involve in biological oxidations and reductions. Oxidations means addition of oxygen or removal of hydrogen.

Reduction means addition of hydrogen or removal of oxygen. The important sub classes are :

(i) Dehydrogenases: Dehydrogenases are enzymes that catalyze the removal of hydrogen from one substrate and pass it on to second substrate.

$$AH_2 + B \xrightarrow{\text{dehyrogenase}} BH_2 + A$$

Eg.Alcohol dehydrogenase enzyme

(ii) Oxidases: Oxidases are enzymes which catalyze the removal of hydrogen from a substrate and pass it directly to oxygen.

$$AH_2 + O_2 \xrightarrow{\text{oxidase}} AH_2O$$

Eg. Cytochrome oxidase enzyme

(ii) Oxygenases: These are enzymes which catalyze the incorporation of oxygen directly into the substrate.

2. Transferases

These enzymes transfer a group from one substrate to another substrate. The reaction can be represented as follows:

$$AX + B \xrightarrow{\text{Transferase}} A + BX$$

Eg. Transaminase

3. Hydrolases: These are enzymes which catalyze hydrolysis. i.e., the direct addition of water molecule across a bond which is cleaved. Hydrolases are divided into three sub classes. They are proteases, esterases and carbohydrases.

4. Lyases: Lyases are the enzymes which catalyze either the removal of a group of atoms from their substrate leaving double bonds or add groups to double bonds without hydrolysis, oxidation or reduction

Eg. Aldolase, Enolase, Fumarase, Arginosuccinase

5. Isomerases or Mutases

Isomerases catalyze the interconversion of a compound to one of its isomers. These enzymes catalyze intramolecular rearrangements. The phosphohexose isomerase catalyzes the following interconversion:

$$\text{Glucose -6-phosphate} \xrightarrow{\text{phosphohexo isomerase}} \text{Fructose -6-phosphate}$$

6. Ligases or synthetases:

These enzymes catalyze synthesis reactions by joining two molecules coupled with the break down of a pyrophosphate bond of ATP → ADP. The common ligases are,

DNA ligase

RNA synthetase

Glutamine synthetase

Biochemical oxidations:

The oxidations accomplished by enzymes or microorganisms excel in regiospecificity, stereospecificity and enantioselectivity. Two important enzymatic oxidations have been very well known since early times. One is the conversion of alcohol into acetic acid by bacterium acetic in presence of air (the process is now known as quick vinegar process).

$$CH_3CH_2OH + O_2 \xrightarrow{\text{Bacterim acetic}} CH_3COOH + H_2O$$

The second one is the conversion of sucrose into ethyl alcohol by yeast (this process is used for the manufacture of ethyl alcohol).

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase- yeast}} 2C_6H_{12}O_6$$

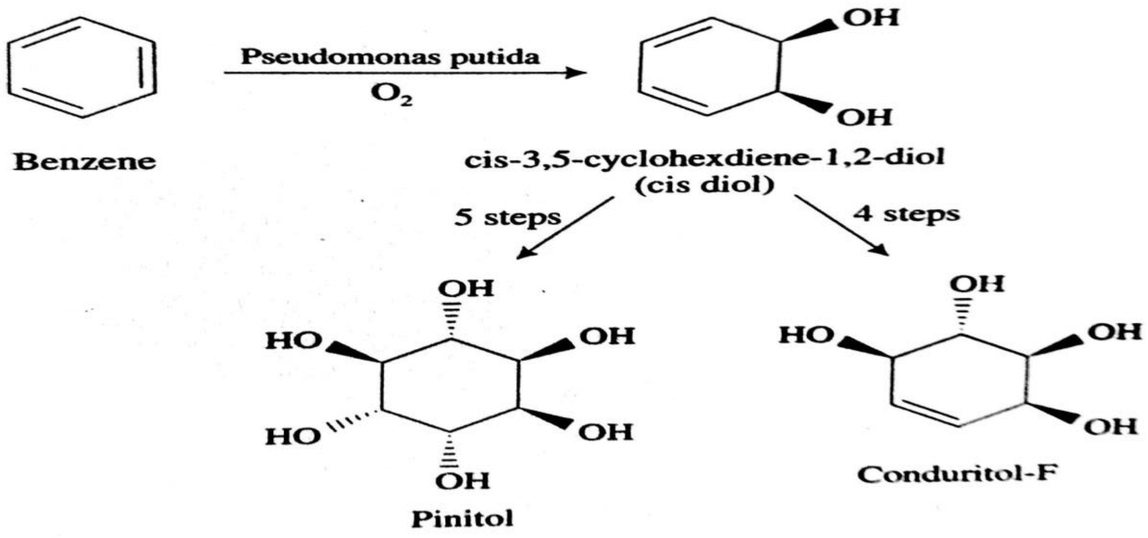
$$C_6H_{12}O_6 \xrightarrow{\text{Invertase- yeast}} 2C_2H_5OH + 2CO_2$$

In a similar way, lactose can be converted into lactic acid. This enzymatic oxidations are referred to as fermentation.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase- yeast}} 4CH_3CH(OH)COOH$$

Biochemical oxidations occur under mild conditions, usually around 70°C and in dilute solution. They are slow and often take days.

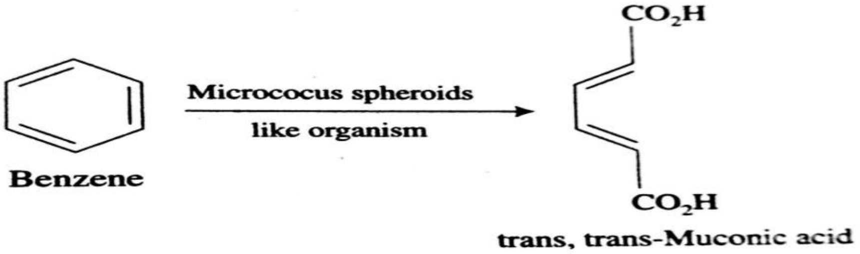
Benzene on oxidation with Pseudomonas putida in presence of oxygen gives the cis diol. This cis-diol obtained could be converted by four steps into 1,2, 3, 4-tetrahydroxy compound, conduritol-F and by five steps into the hexahydroxy compound, pinitol, an antidiabetic agent.

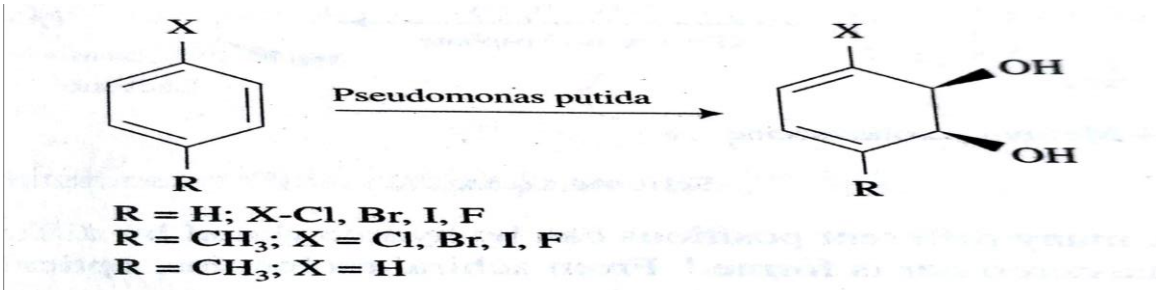


Scheme 14.6

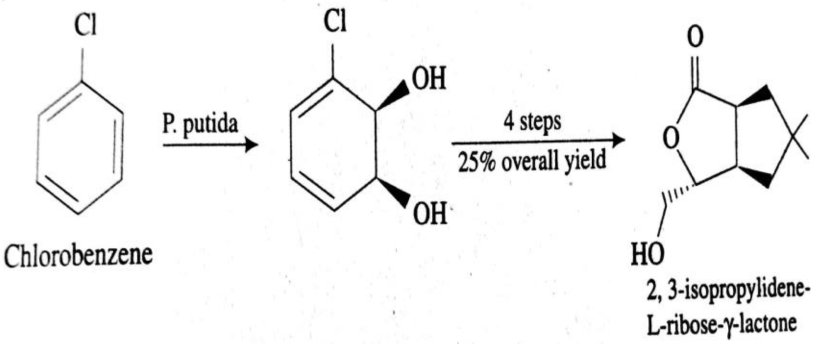
Micrococuus spheroids like organism converts benzene into trans, trans-muconic acid.

In a similar way, toluene, halogensubtituted benzenes, halogensubstituted toluene gave the corresponding cis diols.

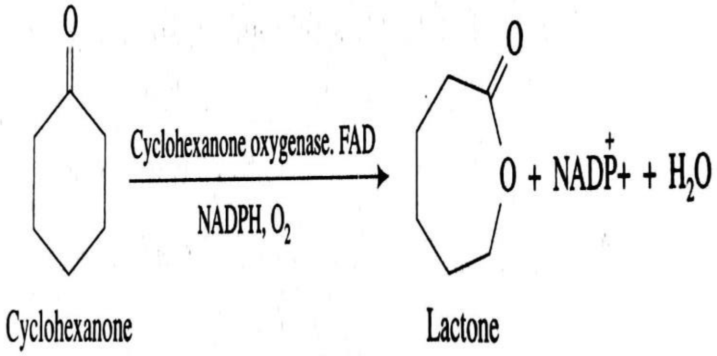




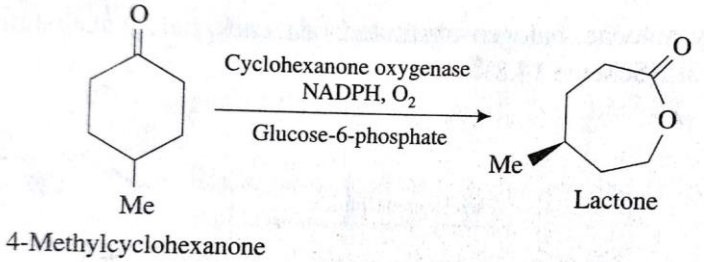
The cis-diol obtained from chlorobenzene is converted into 2, 3-isopropylidene – L-ribose-γ-lactone in four steps



A typical transformation in the enzymatic Baeyer-Villiger oxidation, which converts cyclohexanone into the lactone using a purified cyclohexanone oxygenase enzyme.

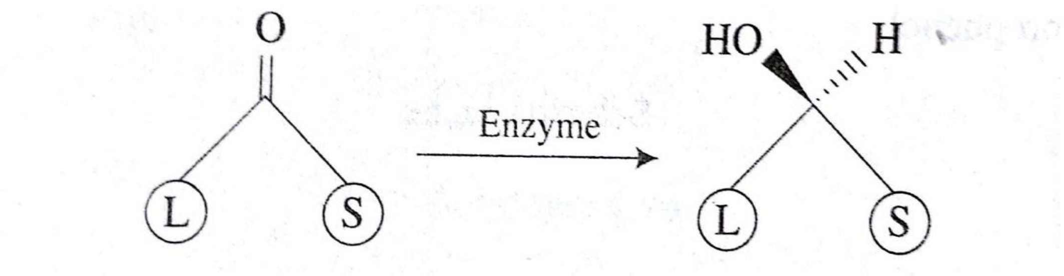


Similarly, 4-methylcyclohexanone can be converted into the corresponding lactone in 80% yield with >98% ee cyclohexanone oxygenase, obtained from acineto bacter.

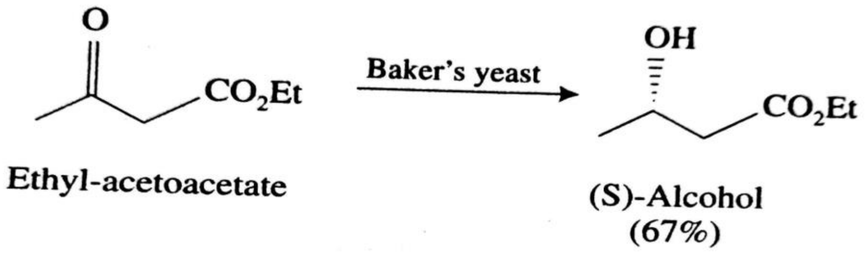


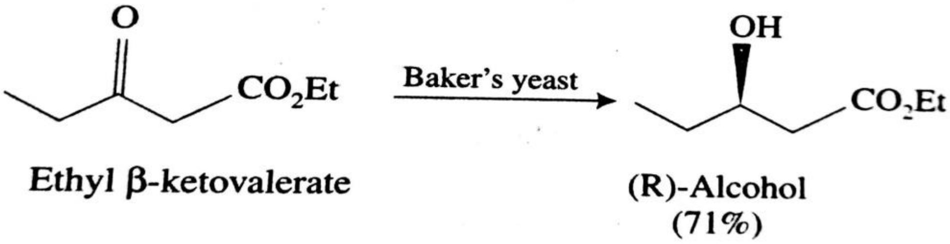
Biochemical Reductions:

Like enzymatic oxidations, the enzymatic reductions are straightforward and highly stereoselective. Prelog was the first to study the reduction of carbonyl compounds with a number of enzymatic systems. For example, reduction of ketones with curvularia fulcata gave predictable stereochemical induction based on the groups present (large and small) in the keto group. This is known as Prelog’s rule. According to this rule, if the steric difference between large (L) and small (S) groups attached to the carbonyl group is large enough, the enzymes deliver hydrogen from the less hindered face to give the corresponding alcohol.

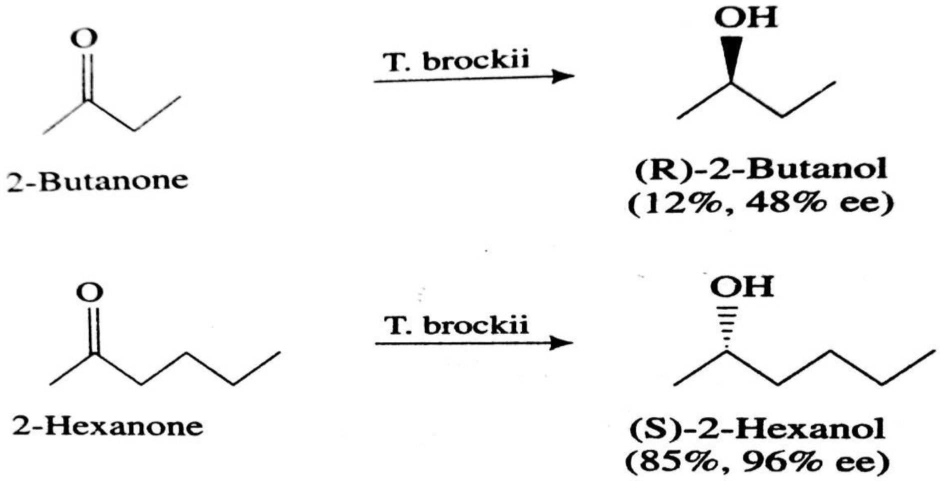


Baker’s yeast (Saccharomyces cerevisiae) is a very common ‘reagent’ and it selectively reduces β-ketoesters and β-diketones. Thus, reduction of ethylacetoacetate with Baker’s yeast gave the (S)-alcohol. On the other hand, reduction of ethyl β-ketovalerate gave the (R)-alcohol.

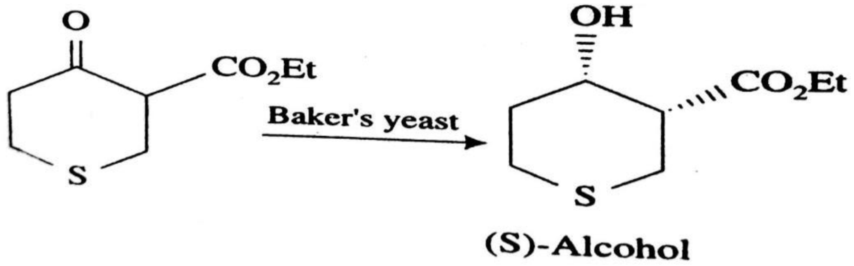




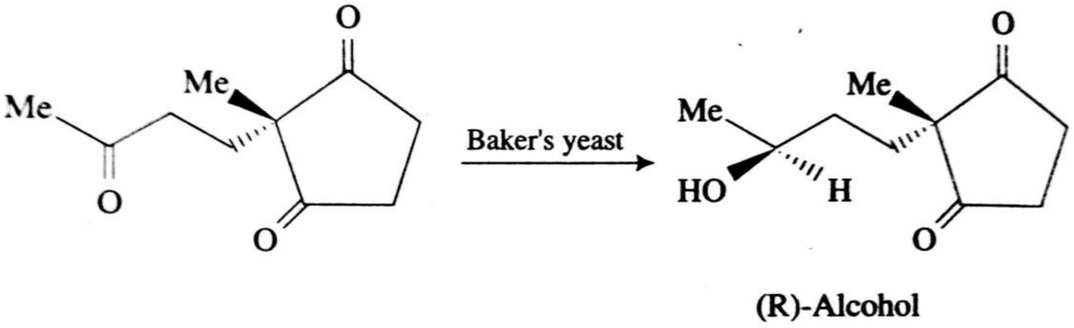
2-butanone is reduced by thermoanaerobium brockii which gave the (R)-alcohol (2-butanol) in 12% yield and 48% ee, but the large ketones are reduced to the (S)-alcohol (85% yield and 96% ee S).



Scheme 14.23



The reduction of the β-ketoester gave 71% yield of the alcohol which was used in the Hoffmanns synthesis of the cigarette beetle.



PROPELLANTS

Propellants are combustible compounds which on ignition undergo rapid combustion to release large quantities of hot gases. A propellant is a combination of an oxidizer and a fuel. Propellants are used to force an object to move forwards, from a firework-rocket, to a rocket to put people on the Moon. As propellants must be carried aboard, condense phase propellants (solid or liquid) are much preferable.

Working of a propellant. When a propellant is ignited, it burns is produce a large quantity of hot gases. These gases then come out through the nozzle of the rocket motor. The passage of gases through the nozzle of the rocket motor, provides the necessary thrust for the rocket to move forward according to the Newtons Third law of Motion (to every action, there is an equal and opposite reaction).

Liquid propellants may be grouped as:

Single base liquids, such as hydrazine ($N_2H_4(l)$) and derivatives (as mono-methyl-hydrazine MMH $N_2H_3CH_3(l)$) and unsymmetrical-dimethyl-hydrazine UDMH N_2H_2 (CH3)2(l))), or hydrogen peroxide (H_2O_2 more than 70 %wt concentrated), that are stable at ordinary temperatures, but decompose into hot gases when exposed to suitable catalysts or high temperatures (e.g. $2N_2H_4 = 2NH_3+N_2+H_2$).

• Double base liquids, stored apart. As oxidiser, liquid oxygen (LOX) or nitrogen tetroxide (NO_4) may be used. As fuels, liquid hydrogen or kerosene may be used.

Solid propellants (they do not allow intermittent operation) are categorised as

"single-base", "double base", and "multi-base" or "composite" powders or pastes: • Single-base powders, such as cordite, are mostly nitrocellulose (guncotton with some nitroglycerine). Black powder was used for solid-propellant rockets in the first third of the 20th c. They burn cool and cause little barrel wear in firearms. Double-base composite powders are now generally used as a propellant for solid-fuel rockets. • Double-base powders are mixtures of nitroglycerine and nitrocellulose such as ballistite, and burn hotter.

Composite powders are modern formulations that do not contain nitrocellulose or nitroglycerine, instead using more modern propellants that burn cool but are as powerful as double-base powder. Ammonium perchlorate composite propellant (APCP), one of the best solid rocket fuels, can be cast into shape (instead of pressed as a powder), making its setup more simple and reliable. Hypergolic propellant are substance pairs that ignite upon contact with each other without a spark, heat or other external aid, such as N_2H_4/N_2O_4, N_2H_4/NO_4, aniline and red fuming nitric acid (concentrated nitric acid in which nitrogen dioxide is dissolved), etc.

Green propellants are low toxicity, high energy liquid rocket propellants that will offer a high-performance, high-efficiency alternative to conventional chemical propellants for future spacecraft. Green propellants are attractive as possible substitutes for traditional hazardous propellants because of several factors.

Safer Propellant handling

Green propellants mitigate the cost and risk associated with the transport and storage, cleanup of accidental releases, and human exposure to traditional propellants. They have a lower toxicity and are less prone to ignition due to mishandling than traditional propellants.

Fuel efficiency

Some green propellants have a higher specific impulse (which is a measure of the amount of thrust that is produced per unit of propellant consumed) than conventional propellants. In addition, they have a lower freezing point than hydrazine, requiring less spacecraft power to maintain propellant temperature.

Commercialization and Lower Turnaround Times

Green propellants may offer a safer, faster and much less costly alternative for launch vehicles and spacecraft fuel loading operations making them a viable technology for commercial spaceports operating in the United States. The combined benefits of low toxicity and easy handling may shorten ground processing time from weeks to days, simplifying the launching of satellites and spacecraft.

NEED FOR GREEN PROPELLANT

To lessen air pollution through rocket launches, much research has been done to develop propellants that are environmental amicable (“green”) and contribute towards non-toxic propellants. These propellants are generally more facile and safer to use than the traditional ones, and are likely to bring down the costs associated with propellant convey and storage. In recent years low toxicity liquid rocket propellants have become captivating as possible substitutes for hydrazine and N_2O_4 in lower to medium thrust engines due to the cost reduction and minimized environmental impact and, more so, the benefits associated with the simplification of the long sought health and safety precautions. High-energy based green propellants (like ADN, HAN and HNF) are predicated on organic compounds and reimburse the high molecular weight of their decomposition products with proportionally higher operational temperatures, which still pose paramount challenges to the entelechy of durable catalytic reactors and radiative cooled thrust chambers. Hydrogen peroxide (H_2O_2) does not suffer from these shortcomings and is now being reviewed as a favourable green monopropellant and bipropellant (in conjunction with hydrocarbons) for low and medium thrust applications. Ammonium Nitrate (AN) Based propellants are always green but it is quite difficult to manufacture. As AN has many crystal phases, which transform into each other at different temperatures. This cause inhomogeneous effect in Solid Composite based on it, which ultimately leads to cracks in grain.

ADN BASED PROPELLANT

Solid Propallent– Solid propellants, in current era are widely used in booster in large boosters for launchers and, to minor extent, for in-space propulsion. Propellants for these applications are primarily based on the oxidizer ammonium perchlorate, NH_4ClO_4, and metal Al - powder embedded in a polymer binder matrix such as HTPB (Hydroxyl Terminated Polybutadiene) or PBAN (poly acrylonitrile-co-butadiene-co-acrylic acid). Although AP is an excellent oxidizer due to its relatively low hazardousness and the possibility to mould its airborne properties, it has negative impacts on the environment and on personal health. By replacing AP with ADN there will be no hydrochloric emission since ADN only contains hydrogen, oxygen and nitrogen as constituents. Calculations show that ADN-based solid propellant can achieve performance equal to or higher than that of the conventional AP-based propellants. It is not feasible to employ newly developed propellant to a large sized vehicle such as, launcher boosters. Thus smaller and less cost-sensitive applications seem to be a better choice. Hence, ADN-based propellants are expected to be employed for in-space propulsion applications, where liquid propulsion system is vastly used. Liquid rockets provide high performance and modifiable thrust, but they are costly and use toxic propellants for instance hydrazine, nitrogen tetroxide (NTO) and monomethyl hydrazine (MMH). Solid propellants possess benefits such as simplicity, storability and compactness. Furthermore, no propellant distribution system is required which enables immensely colossal amelioration in reliability and cost. One disadvantage is however their relatively low specific impulse. In spite of this, solid propellant rocket motors have been used to propel spacecraft in numerous missions since first used in the upper stage of the first U.S. Satellite Explorer I in 1958. In recent times solid propellant rocket motors are considered to be used for the ascend module in the Mars sample return mission. Substituting the AP-based propellant with ADN will provide higher performance and reduced environmental impact. Future work concerning solid ADN-based propellants will focus on improving the mechanical properties and to characterize the sensitivity.

Liquid Monopellant – One of the most promising alternatives to monopropellant hydrazine is blends predicated on an oxidizer salt dissolved in a fuel/dihydrogen monoxide coalescence. Hydroxyl ammonium nitrates (HAN) has been studied for this purport .Due to its high solubility, ADN can be utilized in the same way as HAN. The development of ADN-predicated monopropellants commenced at FOI in 1997 on a contract from the Swedish Space Corporation, SSC, and several different propellant formulations have been technologically advanced and substantiated. Future work concerning liquid ADN-based monopropellants will focus on ignition and thruster development.

Properties of a Good Propellant

- ✓ It should have high specific impulse and produce low molecular weight gases.
- ✓ It should have high density to minimize container space.
- ✓ It should have high stability during handling
- ✓ High flame temperature and large volume of gases should be produced.
- ✓ The flue gases produced should not be toxic or corrosive.

Applications

Probable application is the main driving force for the selection of a green propellant as exemplified by three examples following:

Boosters

Since the volume of propellant contained in launcher boosters is huge, propellant cost plays a vital role in selection. The explosion risk is also an important factor. As oxidizers or fuels having potential monopropellant behaviour are not very good contenders from safety point of view. All these constrictions are fulfilled by LOX-hydrocarbons combinations such as kerosene. Many US and Soviet launchers are using special kerosene amalgams to reduce adversities like coking and combustion instabilities. The green propellant that can be used in place of kerosene is *methane*. The biggest advantage of methane over kerosene is the possibility to use a fuel rich gas generator without soot formation and noble cooling efficiency of methane. Moreover, methane is injected in gaseous state lowering the risk of combustion instabilities. Besides the conventional LOX-kerosene and LOX-methane recipes, some light hydrocarbons and ethers offer striking properties such as greater Isp, higher density and regenerative cooling followed by gaseous injection.

Manned Capsule RCS And Landing Retrorockets

Till this date the reference propellants are MMH / N_2O_4. The substitution by non-toxic propellants would offer a significant improvement for the crew safety and for post recovery operations. Possible solution emerge viz. new monopropellants such as organic nitrate salts and mixtures or safe combinations like N_2O and organic liquids. Certainly, they offer lower Isp than MMH-N_2O_4. but they are much nontoxic. A critical point would be the ignition reliability which is unconditionally essential for the crew safety.

AIM (Automatic Interplanetary Missions)

Currently MMH-N_2O_4 or hydrogen are used extensively in AIMs. For manned missions LOX-LH_2 is perhaps the finest choice but may require considerable developments for the landing phase. For less severe Delta V requirements, N_2O / hydrocarbons or new monopropellants (AND or HAN) are preferable solutions.

Use of Renewable Sources:

If it is technically and economically possible, then the renewable resources (e.g.biomass) rather than the nonrenewable resources (e.g.crude oil) should be used as the raw material or feedstock.

7the principle of green chemistry encourages the use of starting material (i.e.raw material or feedstock) which should be renewable, if technically and economically practicable. In fact, continuous use (i.e.overexploitation) of the nonrenewable feedstock (e.g. petroleum product, fossil fuel) will deplete the resource and future generation will be deprived. Moreover, use of the these nonrenewable resources puts a burden on the environment.

On the other hand, use of sustainable or renewable resources e.g.agricultural or biological product ensures the sharing of resources by future generation. Moreover, this practice generally does not put much burden on the environment. The products and wastes are generally biodegradable.

Feedstocks

Feedstocks are the main ingredients that go into the production of chemical products.

Feedstocks may be acted upon by reagents, and often there is some overlap between the two categories of materials. There are three major components of the process by which raw materials from a source are obtained in a form that can be utilized in a chemical synthesis, then converted to a product.

The first of these is the source of the feedstock, an aspect that has a number of environmental and sustainability considerations. The source may consist of a depleting resource, such as petroleum, in which case the lifetime of the resource and the environmental implications of obtaining it must be considered. A preferable source consists of recycled materials, although not many recycled materials are suitable for chemical feed stocks. A third source that is very desirable consists of renewable resources, particularly from materials made by photosynthesis and biological processes.

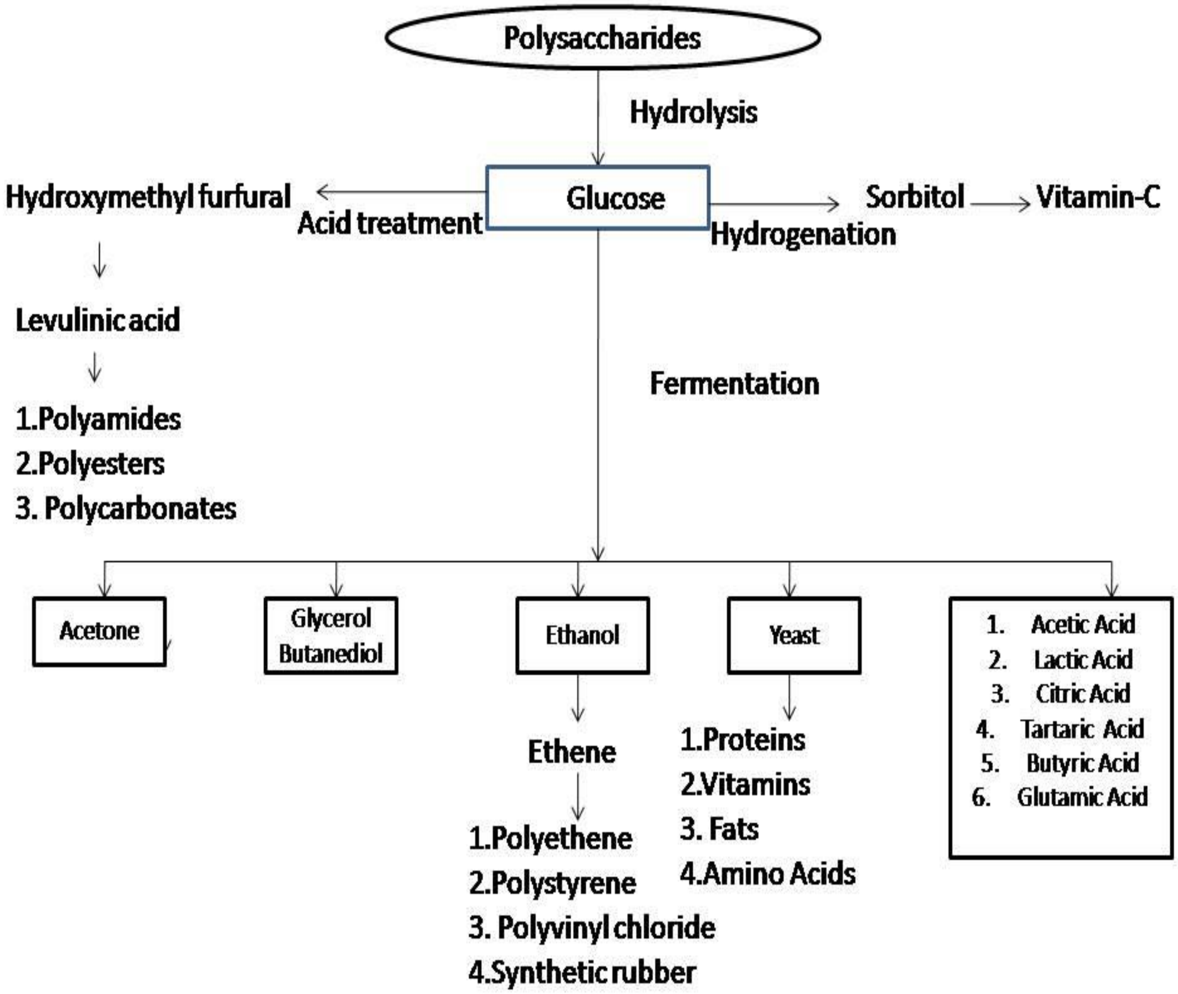
The second major aspect of converting feedstocks to final products is separation and isolation of the desired substance. An example of this step is the isolation of specific organic compounds from crude oil to provide a feedstock for organic chemical synthesis. It may be necessary to process raw materials from a source to convert it to the specific material used as a feedstock for a chemical process, in large part because of the relatively large amount of waste material that must be discarded in obtaining the needed feedstock.

Once a suitable chemical feedstock is obtained, it is subjected to chemical processes that give the final product.

Commodity chemicals from Glucose

Plants contain a mixture of carbohydrates such as monosaccarides, oligosaccharides and polysaccharides. The oligosaccharides and polysaccharides yield simple sugars like glucose during their hydrolysis. Three methods are generally employed to use glucose. They are acid treatment, hydrogenation and fermentation.

CONVERSION OF GLUCOSE

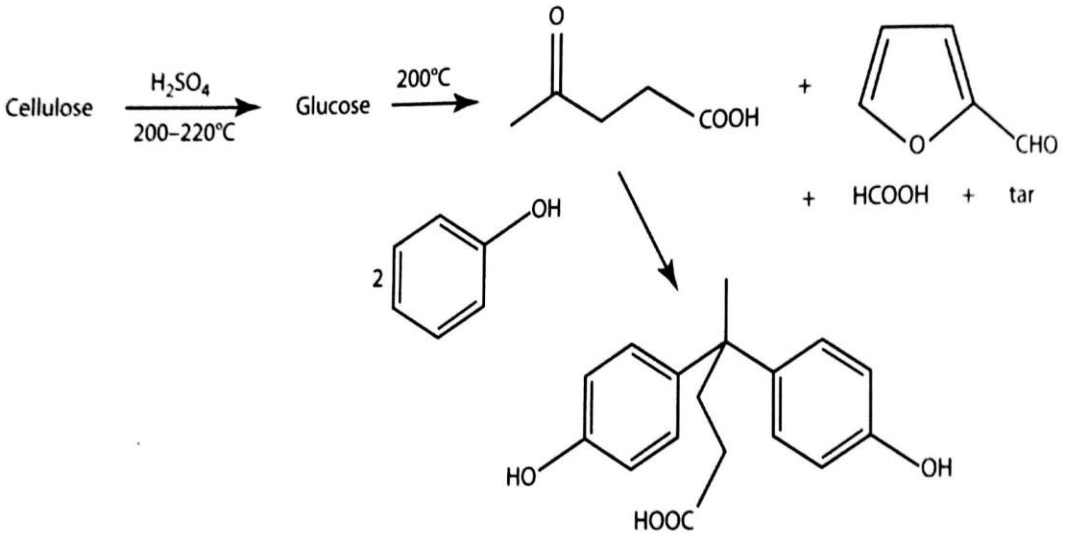


1. During acid treatment, glucose, produces hydroxymethylfurfural. It forms a starting material for plastics like polyamides, polyesters and polycarbons.
2. Glucose is hydrogenated into sorbital which is used as starting materials for the manufacture of ascorbic acid.
3. Glucose on fermentation yields a mixture of substances along with the biomass of microorganisms. The microbial biomass forms a source for the extraction of amino acids, fats, vitamins etc. The fermentation of glucose yields ethanol,

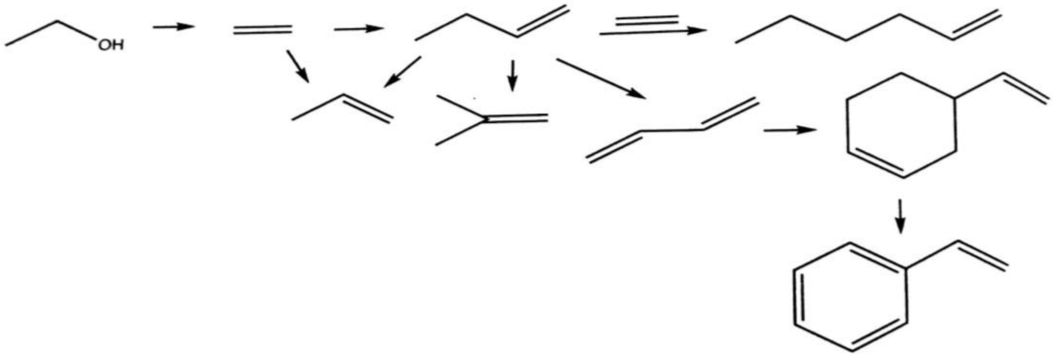
acetone, butanol, glycerol, acetic acid, lactic acid, citric acid, tartaric acid, butyric acid, glutamic acid etc.

4. Ethanol forms a raw material for the production of ethylene. Ethylene is used in the production of polyethylene, polystyrene, and polyvinyl chloride. They are used in the manufacture of plastics
5. Lactic acid produced during the fermentation is converted into acrylic acid and acrylate.

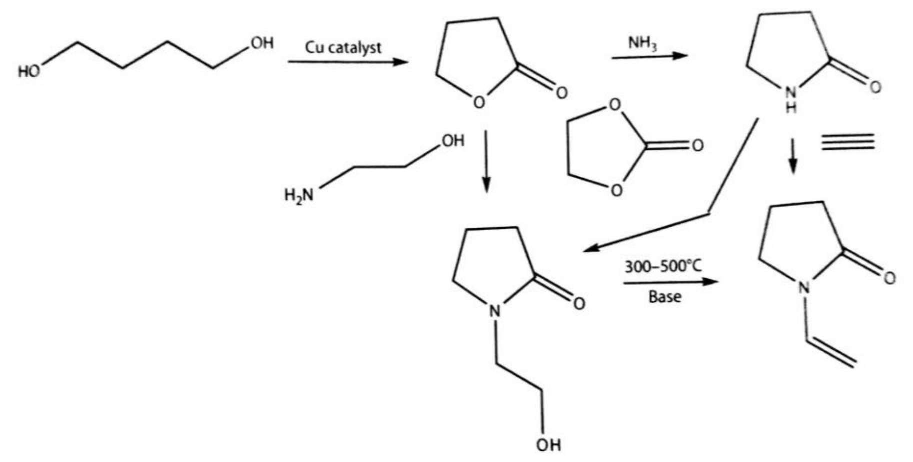
Hydrolysis of Glucose

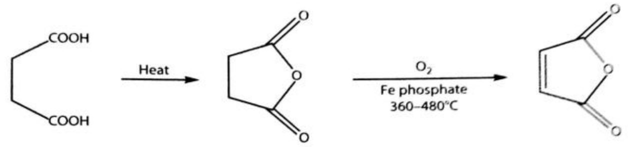


(ii) Preparation of olefins from sugar cane

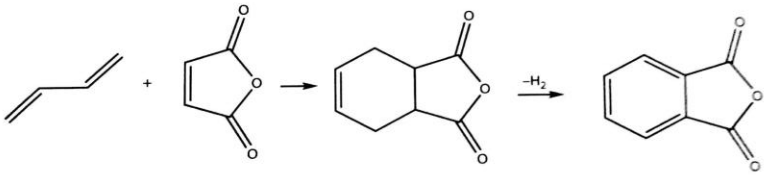


(iii) Preparation of alcohols and carboxylic acids from glucose





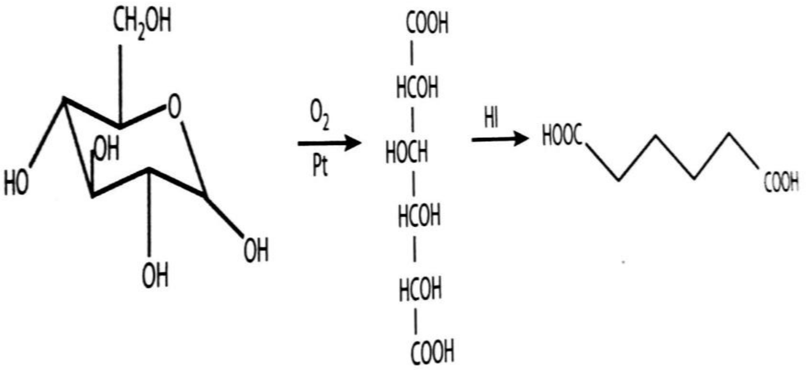
12.9 Schematic



Preparation of lauric acid

$CH_3(CH_2)_{10}CH{=}CH(CH_2)_4COOH \xrightarrow{O3} CH_3(CH_2)_{10}COOH + HOOC(CH_2)_4COOH$

Preparation of tartaric acid



Biomass

Biomass refers to solid carbonaceous material derived from plants and animals. These include residues of agriculture and forestry, animal waste and discarded material from food processing plants. Biomass being organic matter from terrestrial and marine vegetation, renews naturally in a short span of time, thus, classified as a renewable source of energy. It is a derivative of solar energy as plants grow by the process of photosynthesis by absorbing CO_2 from the atmosphere to form hexose (dextrose, glucose etc) expressed by the reaction.

$$6CO_2 + H_2O \xrightarrow{\text{Sunlight}} C_6H_{12}O_6 + 6O_2$$

Biomass does not add CO_2 to the atmosphere as it absorbs the same amount of carbon in growing the plants as it releases when consumed as fuel. It is a superior fuel as the energy produced from biomass is ‘carbon cycle neutral’

Biomass conversion Technologies

Biomass material from a variety of sources can be utilized optimally by adopting efficient and state of the art conversion technologies such as:

1. Densification of biomass
2. Combustion and incineration
3. Thermo-chemical conversion
4. Bio-chemical conversion

1. Densification:

Bulky biomass is reduced to a better volume to weight ratio by compressing in a die at a high temperature and pressure. It is shaped into briquettes or pellets to make a more compact source of energy, which is easier to transport and store than the natural biomass. Pellets and briquettes can be used as clean fuel in domestic chulhas, bakeries and hotels.

2. Combustion:

Direct combustion is the main process adopted for utilizing biomass energy. It is burnt to produce heat utilized for cooking, space heating, industrial processes and for electricity generation. This utilization method is very inefficient with heat transfer losses of 30-90% of the original energy contained in the biomass. The problem is addressed through the use of more efficient cook-stove for burning solid fuels.

Incineration:

Incineration is the process of burning completely the solid biomass to ashes by high temperature oxidation. The terms incineration and combustion are synonymous, but the process of combustion is applicable to all fuels, i.e. solid, liquid and gaseous. Incineration is a special process where the dry municipal solid waste (MSW) is incinerated to reduce the volume of solid refuse (90%) and to produce heat, steam and electricity.

Waste incineration plants are installed in large cities to dispose off urban refuse and generate energy. It constitutes a furnace with adequate supply of air to ensure complete combustion up to a capacity of 1000 tonnes/day.

3. Thermal-Chemical conversion:

Thermo-chemical conversion is a process to decompose biomass with various combinations of temperatures and pressures. It includes ‘pyrolysis and ‘gasification’

Pyrolysis

Biomass is heated in absence of oxygen or particularly combusted in a limited oxygen supply, to produce a hydrocarbon, rich in gas mixture (H_2, CO_2, CO, CH_4 and lower hydrocarbons), an oil like liquid and a carbon rich solid residue (charcoal).

The pyrolitic or bio-oil produced can easily be transported and refined into a series of products similar to refining crude oil. There is no waste product, the conversion efficiency is high (82%) depending upon the feedstock used, the process temperature in reactor and the fuel/ air ratio during combustion.

Gasification:

Gasification is conversion of a solid biomass, at a high temperature with controlled air, into a gaseous fuel. The output gas is known as producer gas, a mixture of H_2 (15-20%), CO (10-20%), CH_4 (1-5%), CO_2 (9-12%) and N_2 (45-55%). The gas is more versatile than the solid biomass, it can be burnt to produce process heat and steam, or used in internal combustion engines or gas turbines to generate electricity. The gasification process renders the use of biomass which is relatively clean and acceptable in environmental terms.

Liquefaction:

Liquefaction of biomass can be processed through ‘fast’ or ‘flash’ pyrolysis, called ‘ pyrolytic oil which is a dark brown liquid of low viscosity and a mixture of hydrocarbons. Pyrolysis liquid is a good substitute for heating oil.

Another liquefaction method is through methanol synthesis. Gasification of biomass produces synthetic gas containing a mixture of H_2 and CO. The gas is purified by adjusting the hydrogen and carbon monoxide composition. Finally, the purified gas is subjected to liquefaction process, converted to methanol over a zinc chromium catalyst. Methanol can be used as liquid fuel.

4. Biochemical conversion

There are two forms of biochemical conversions:

1. Anaerobic digestion
2. Ethanol fermentation.

1. Anaerobic Digestion:

This process converts the cattle dung, human wastes and other organic waste with high moisture content into biogas (gobar gas) through anaerobic fermentation in absence of air. Fermentation occurs in two stages by two different metabolic groups of bacteria. Initially the organic material is hydrolyzed into fatty acids, alcohol, sugars, H_2 and CO_2. Methane forming bacteria then converts the products of the first stage to CH_4 and CO_2, in the temperature range 30-55°C. Biogas produced can be used for heating, or for operating engine driven generators to produce electricity. Fermentation occurs in a sealed tank called ‘ digester’ where the sludge left behind is used as enriched fertilizer.

2. Ethanol Fermentation:

Ethanol can be produced by decomposition of biomass containing sugar like sugarcane, cassava sweet sorghum, beet, potato, corn, grape, etc. into sugar molecules such as glucose ($C_6H_{12}O_6$) and sucrose ($C_{12}H_{22}O_{11}$).

Ethanol fermentation involves biological conversion of sugar into ethanol and CO_2.

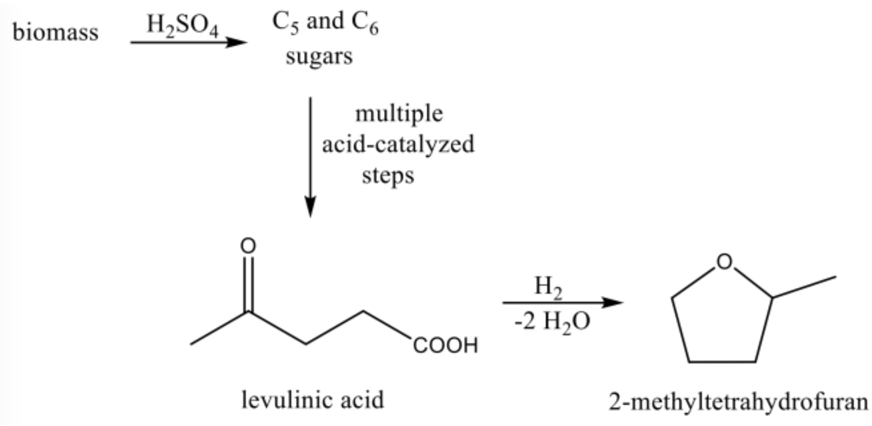
$$C_{12}H_{22}O_{11} + H_2O \longrightarrow 2C_6H_{12}O_6$$

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$

Ethanol has emerged as the major alcohol fuel and is blended with petrol.

Synthesis of Biomass Products:

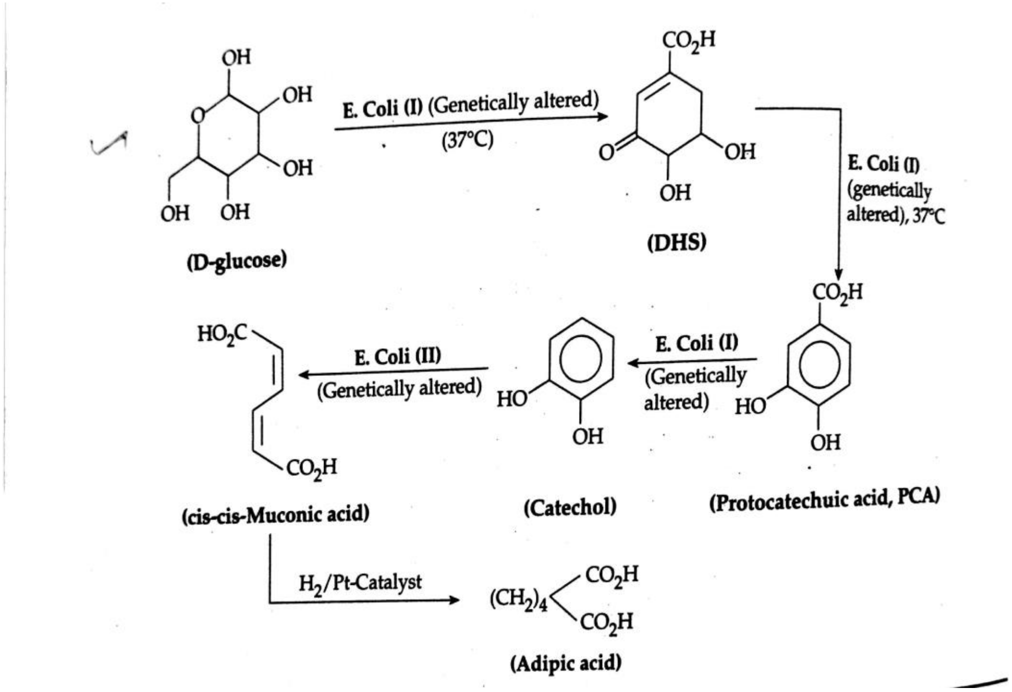
(a) Green synthesis of 2-methyltetrahydrofuran (THF)



It can be synthesized starting from biomass; after conversion to C_5 and C_6 sugars and subsequent acid-catalyzed steps, the intermediate levulinic acid can be hydrogenated to yield 2-methyl THF.

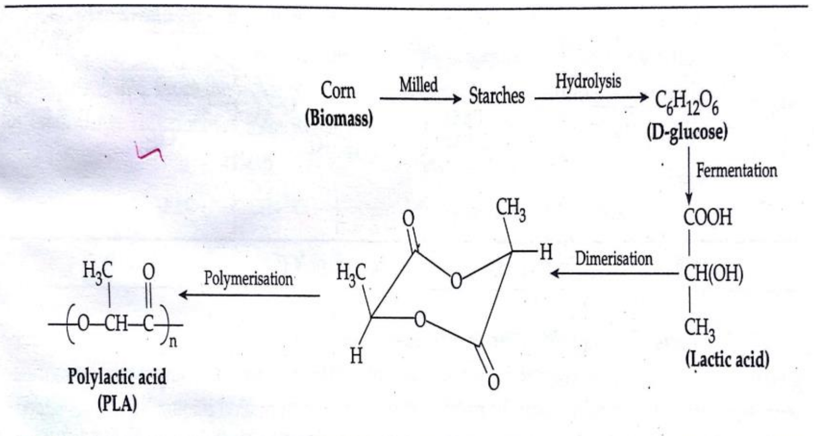
(b) Green synthesis of Catechol and Adipic acid

The synthesis of agro-based product as the feedstock and the biocatalyst is the genetically altered E.coli. The variety producting catechol is different from the species leading to adipic acid



(c) Synthesis of polyactic acid from renewable sources

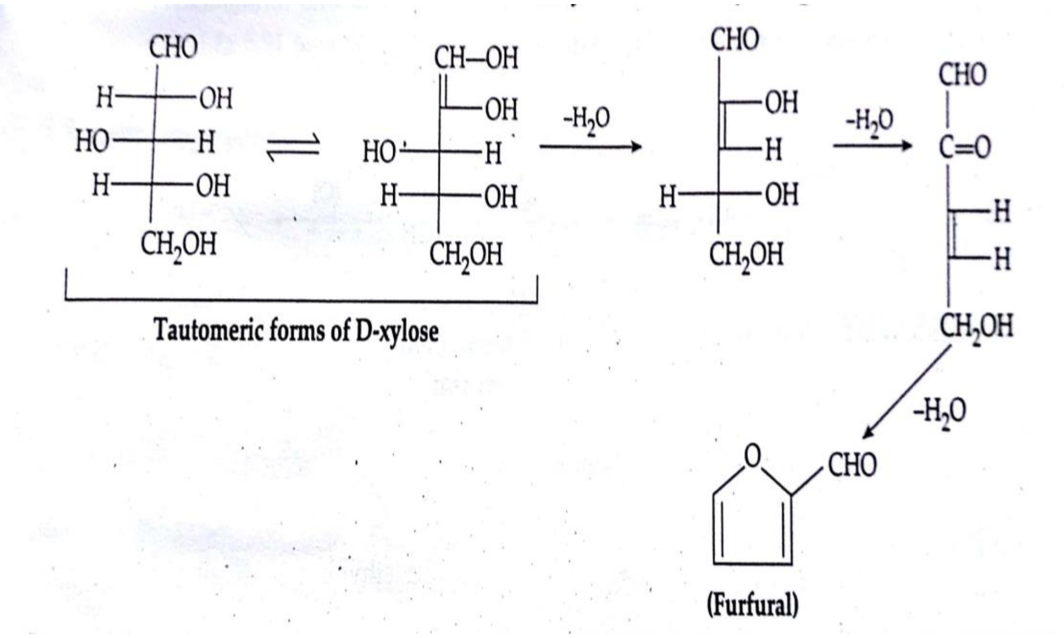
The polylactic acid (PLA) polymer can be obtained from the renewable sources like sugar beets and corn.



Scheme 19.5.4.1: *Synthesis of polylactic acid, a bio-degradable polymer from renewable sources.*

(d) Green synthesis of Furfural from Biomass

Furfural is an important chemical that finds uses in polymer industry (furfural-phenol plastics), in manufacture of pyromucic acid, in petroleum refinery etc. Green synthesis of furfural uses the biomass as the feedstock. Successive dehydration of D-xylose gives furfural.



Catalysis

Catalysts are known to facilitate chemical transformations. which are effected in much short time, consuming less energy and giving good yields. An advantages is that the catalysts are not consumed in the reaction and can often be recycled. Catalysis is generally divided into two types, homogeneous and heterogeneous. Heterogeneous catalysis is where the catalyst and the reactants are in the different physical phases, while homogeneous is where both are in the same phase.

Homogeneous Catalysis

The field of homogeneous catalysis can be characterized as a source of easily arranged, selective catalysts with high activity. The catalyst is in the same phase as the reactants and products. In general, homogeneous catalysts exhibit excellent catalytic activities with high selectivities in particular. But, it is difficult for the homogeneous catalyst to be separated from reaction media.

Heterogeneous Catalysis

Heterogeneous catalysts also offer many advantages, some of which are not displayed by their homogeneous counterparts, including recyclability, ease of separation from the reaction mixture and use in continuous flow processes. It is highly desirable to develop new systems that blend the many advantages of heterogeneous catalysis with the versatility of homogeneous catalysts.

Heterogeneous catalysts have several advantages compared to other catalytic processes

- they avoid formation of inorganic salts
- they are regenerable
- easy to handle, safe to store and has long life time
- easy and inexpensive of recovery and recycling
- the selectivity and activity of homogeneous catalysts under mild reaction conditions is unbeaten by their heterogeneous counter parts.

General Characteristics of catalytic reactions: (Or) Criteria of catalytic reactions:

The following are the general characteristics of most catalysts and catalytic reactions

(i) A catalyst remains unaltered in amount and chemical composition at the end of the reaction, however, it may undergo physical changes.

For example, granular MnO_2 used as the catalyst in the thermal decomposition of potassium chlorate which is recovered back as a fine powder at the end of the reaction.

(ii) A small amount of catalyst is generally sufficient to change the rate of reaction:

For example, 10-3 gm-ions/litre of Cu^{3+} is sufficient to change the rate of oxidation of sodium sulphate by oxygen in an aqueous solution.

(iii) A catalyst cannot initiate a reaction: It can only accelerate or retard the speed of a chemical reaction by decreasing or increasing the energy of activation.

(iv) A catalyst does not alter the equilibrium state of a reversible reaction: It simply alters the rate of both the forward and backward reactions so that the equilibrium condition is reached more quickly.

(v) Every catalyst has a specific action: For a particular reaction, there is a particular catalyst. Even the same reactants in presence of different catalysts give different products.

For example, hydrogen and carbon monoxide combine in presence of different catalyst to produce different products

$CO + 2H_2 \xrightarrow{\text{ZnO+ Cr2O3 at 250°C}} CH_3OH$

$CO + 3H_2 \xrightarrow{\text{Ni}} CH_4 + H_2O$

(vi) A catalyst can be poisoned by the presence of small amount of certain substances called as catalytic poisons.

Examples of catalytic poisons are carbon monoxide, arseneous oxide, hydrogen cyanide, hydrogen sulphide etc.

(vii) The activity of a catalyst is enhanced by the presence of substances called as promoters

Examples of catalytic promoters are molybdenum, bismuth, zinc oxide, chromium oxide etc.

Catalytic Reactions

Recently, attention is being focussed towards the development of catalytic systems with high performance from the point of environmentally greener processes, economical efficiency and minimum consumption of resources. The application of catalysis to reduce toxicity and renewable energy systems, and efficiency makes it a central focus area for green chemistry research. In Green Catalysis the urgently needed one is the design and use of environmentally benign catalysts. Green and sustainable catalyst should possess higher activity, higher selectivity, efficient recovery from reaction medium, durability or recyclability, cost effectiveness. In recent years the development of catalysts for processes to replace conventional ones has made a significant contribution to the reduction of environmental pollutants. Thus recently there is an increasing interest on the topic of green catalysis. It not only includes developing new catalysts which can offer stable, highly effective catalytic performances, but considers the application of environmentally friendly catalyst preparations.

Since a catalyst regenerates itself after a reaction, one molecule of catalyst can perform several transformations That allows scientists to get high yields from a reaction that uses only a relatively small amount of catalyst.

The waste generated in the manufacture of organic compounds consists primarily of inorganic salts. This is because of the use of stoichiometric inorganic reagents in organic synthesis. In particular, fine chemicals and pharmaceuticals manufacture follow ‘stoichiometric’ technologies.

Examples

1. Stoichiometric reductions with metals (Na, Mg, Zn, Fe) and metal hydride reagents ($LiAlH_4$, $NaBH_4$),
2. oxidations with permanganate, manganese dioxide and chromium(VI) reagents and
3. A wide variety of reactions, e.g. sulfonations, nitrations, halogenations, diazotizations and Friedel-Crafts acylations, employing stoichiometric amounts of mineral acids (H_2SO_4, HF, H_3PO_4) and Lewis acids ($AlCl_3$, $ZnCl_2$, BF_3).

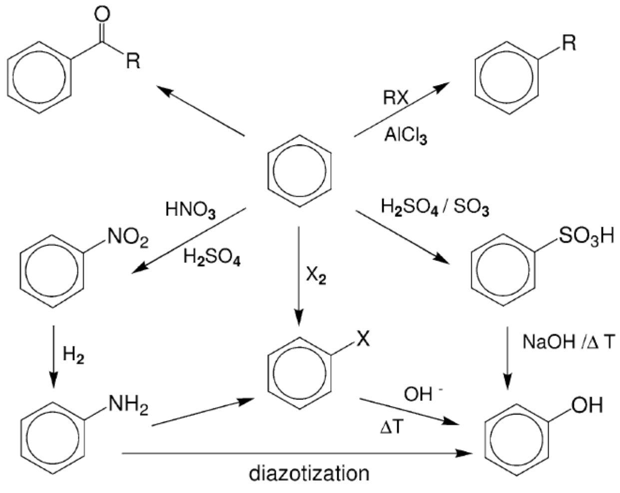
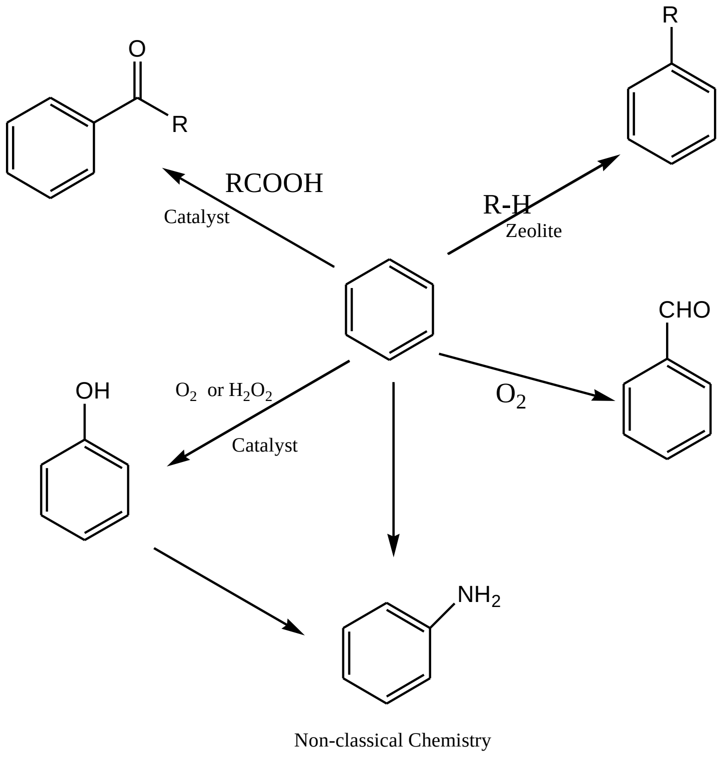


Fig. 1.4 Classical aromatic chemistry.

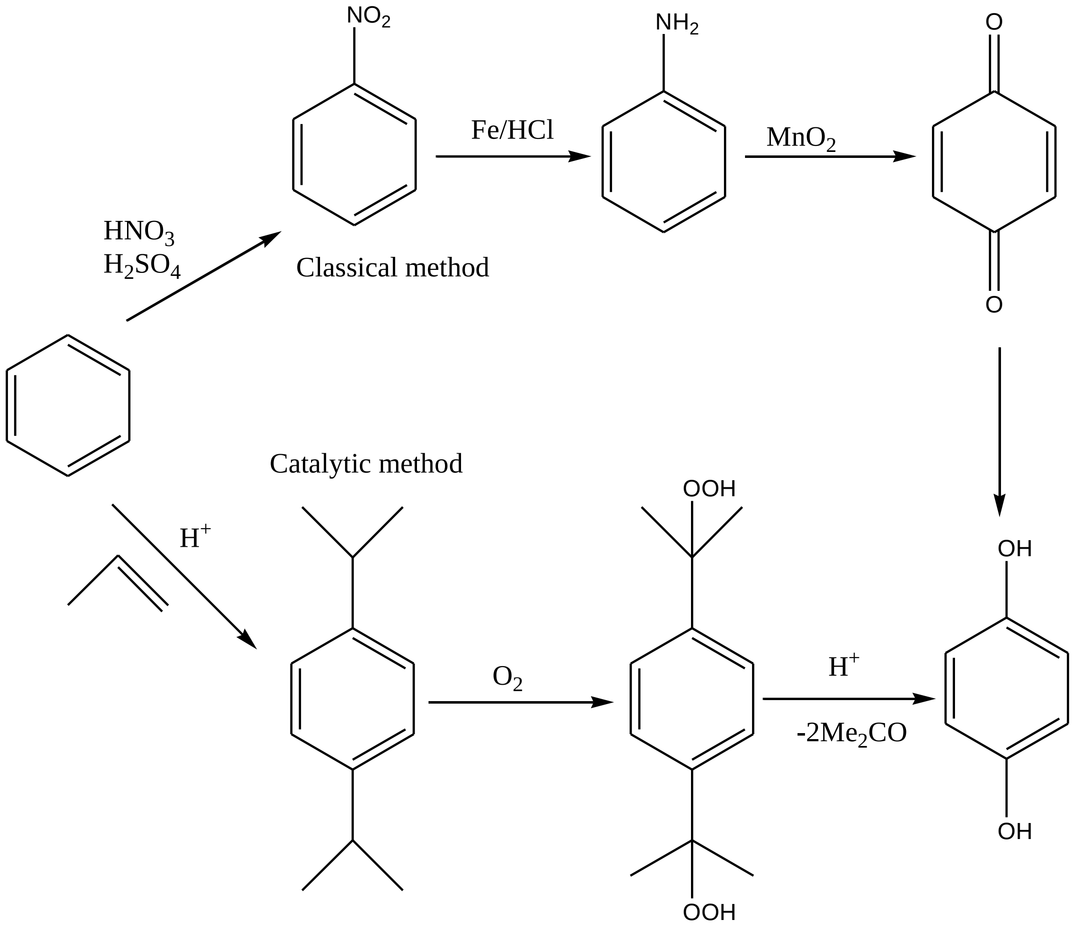
The solution is to substitute the classical stoichiometric methodologies with cleaner catalytic alternatives. Indeed, a major challenge in (fine) chemicals manufacture is to develop processes based on H_2, O_2, H_2O_2, CO, CO_2 and NH_3 as the direct source of H, O, C and N. Catalytic hydrogenation, oxidation and carbonylation are good examples of highly atom efficient, low-salt processes.

The generation of large amount of inorganic salts can similarly be largely circumvented by replacing stoichiometric mineral acids, such as H_2SO_4, and Lewis acids and stoichiometric bases, such as NaOH, KOH, with recyclable solid acids and bases, preferably in catalytic amounts.

For example, the technologies used for the production of many substituted aromatic compounds have not changed in more than a century and are, therefore, ripe for substitution by catalytic, low-salt alternatives.



An instructive example is provided by the manufacture of hydroquinone. Traditionally it was produced by oxidation of aniline with stoichiometric amounts of manganese dioxide to give benzoquinone, followed by reduction with iron and hydrochloric acid (Béchamp reduction). The aniline was derived from benzene via nitration and Béchamp reduction. The overall process generated more than 10 kg of inorganic salts ($MnSO_4$, $FeCl_2$, NaCl, Na_2SO_4) per kg of hydroquinone. This antiquated process has now been replaced by a more modern route involving autoxidation of p-diisopropylbenzene (produced by Friedel-Crafts alkylation of benzene), followed by acid-catalysed rearrangement of the bis-hydroperoxide, producing < 1 kg of inorganic salts per kg of hydroquinone. Alternatively, hydroquinone is produced (together with catechol) by titaniumsilicalite (TS-1)-catalysed hydroxylation of phenol with aqueous hydrogen peroxide.



Catalysis by Solid Acids and Bases

As noted above, a major source of waste in the (fine) chemicals industry is derived from the widespread use of liquid mineral acids (HF, H_2SO_4) and a varietyof Lewis acids. They cannot easily be recycled and generally end up, via ahydrolytic work-up, as waste streams containing large amounts of inorganicsalts. Their widespread replacement by recyclable solid acids would afford a dramaticreduction in waste. Solid acids, such as zeolites, acidic clays and relatedmaterials, have many advantages in this respect.

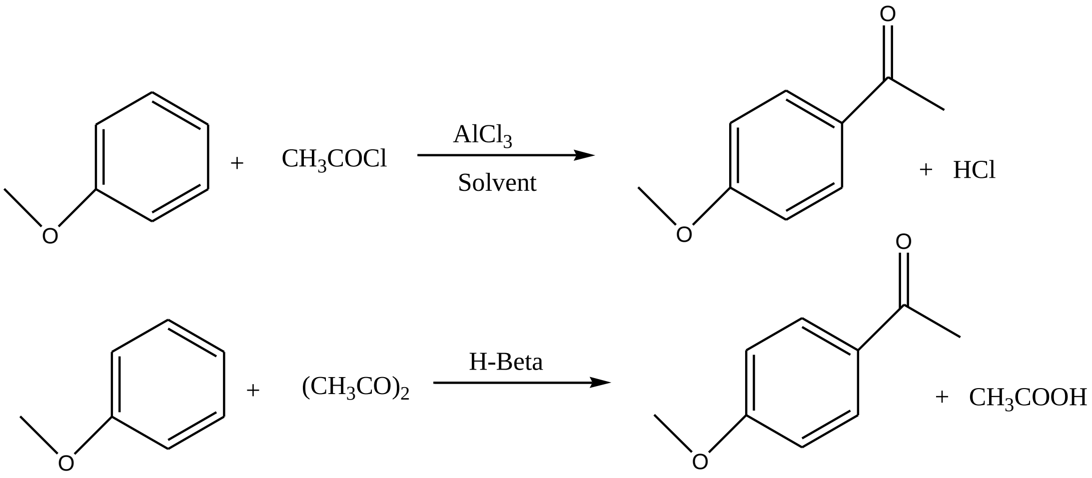
1. They are trulycatalytic and can easily be separated from liquid reaction mixtures, avoiding
the need for hydrolytic work-up, and recycled.

2. Moreover, solid acids are non-corrosiveand easier (safer) to handle than mineral acids such as H_2SO_4 or HF.

Solid acid catalysts are, used in a variety of process in organic synthesis. These include various electrophilic aromaticsubstitutions, e.g. nitrations, and Friedel-Crafts alkylations and acylations,and numerous rearrangement reactions such as the Beckmann and Fries rearrangements.

A prominent example is Friedel-Crafts acylation, a widely applied reaction in thefine chemicals industry. In contrast to the corresponding alkylations, which aretruly catalytic processes, Friedel-Crafts acylations generally require more thanone equivalent of, for example, $AlCl_3$ or BF_3. This is due to the strong complexationof the Lewis acid by the ketone product. Zeolite beta is employed as a catalyst, for the acetylation of anisole with acetic anhydride, to give *p*-methoxy acetophenone (Fig. 1.8). The original process used acetyl chloride in combination with 1.1 equivalents of $AlCl_3$ in a chlorinated hydrocarbon solvent, and generated 4.5 kg of aqueous effluent, containing $AlCl_3$, HCl, solvent residuesand acetic acid, per kg of product.

The catalytic alternative, in stark contrast, avoids the production of HCl in both the acylation and in the synthesis of acetyl chloride. It generates 0.035 kg of aqueous effluent, i.e. more than 100 times less, consisting of 99% water, 0.8% acetic acid and <0.2% other organics, and requires no solvent. Furthermore, a product of higher purity is obtained, in higher yield (>95% vs. 85–95%), the catalyst is recyclable and the number of unit operations is reduced fromtwelve to two. Hence, this process it is not only environmentally superior to the traditional process, it has more favorable economics.



Homogeneous	Heterogenous
$AlCl_3$> 1 equivalent	H-beta, catalytic &regenerable
Solvent	No solvent
Hydrolysis of products	No water necessary
4.5 Kg aqueous effluent per Kg	0.035 kg aqueous effluent per Kg
85-95% yield	➢ P5% yield

Catalytic Reduction

Catalytic hydrogenation perfectly embodies the concept of precision in organic synthesis. Molecular hydrogen is a clean and abundant raw material and catalytic hydrogenations are generally 100% atom efficient. They have a tremendously broad scope and exhibit high degrees of chemo-, regio- diastereo and enantioselectivity.

“Catalytic hydrogenation is one of the most useful and versatile tools available to the organic chemist. The scope of the reaction is very broad; most functional groups can be made to undergo reduction, frequently in high yield, to any of several products. Multifunctional molecules can often be reduced selectively at any of several functions. A high degree of stereochemical control is possible with considerable predictability, and products free of contaminating reagents are obtained easily. Scale up of laboratory experiments to industrial processes presents little difficulty.”

Most of the above comments apply to heterogeneous catalytic hydrogenations over supported Group VIII metals (Ni, Pd, Pt, etc.). Although catalytic hydrogenation is a mature technology that is widely applied in industrial organic synthesis, new applications continue to appear, sometimes in unexpected places.

For example, a time-honored reaction in organic synthesis is the Williamson synthesis of ethers, first described in 1852. Alow-salt, catalytic alternative to the Williamson synthesis, involving reductive alkylation of an aldehyde has been reported. This avoids the coproduction of NaCl, which may or may not be a problem, depending on the production volume. Furthermore, the aldehydes may, in some cases, be more readily available than the corresponding alkyl chloride.

Williamson Synthesis

$$R^1CH_2Cl + R^2ONa \longrightarrow R^1CH_2OR^2 + NaCl$$

Catalytic alternative

$$R^1CHO + R^2OH \longrightarrow R^1CH_2OR^2 + H_2O$$

Catalytic Oxidation

It is probably true to say that nowhere is there a greater need for green catalytic alternatives in fine chemicals manufacture than in oxidation reactions. In contrast to reductions, oxidations are still largely carried out with stoichiometric inorganic (or organic) oxidants such as chromium(VI) reagents, permanganate, manganese dioxide and periodate. There is clearly a definite need for catalytic alternatives employing clean primary oxidants such as oxygen or hydrogen peroxide. Catalytic oxidation with O_2 is widely used in the manufacture of bulk petrochemicals.

An elegant example is the BASF process for the synthesis of citral, a key intermediate for fragrances and vitamins A and E. The key step is a catalytic vapor phase oxidation over a supported silver catalyst, essentially the same as that used for the manufacture of formaldehyde from methanol.

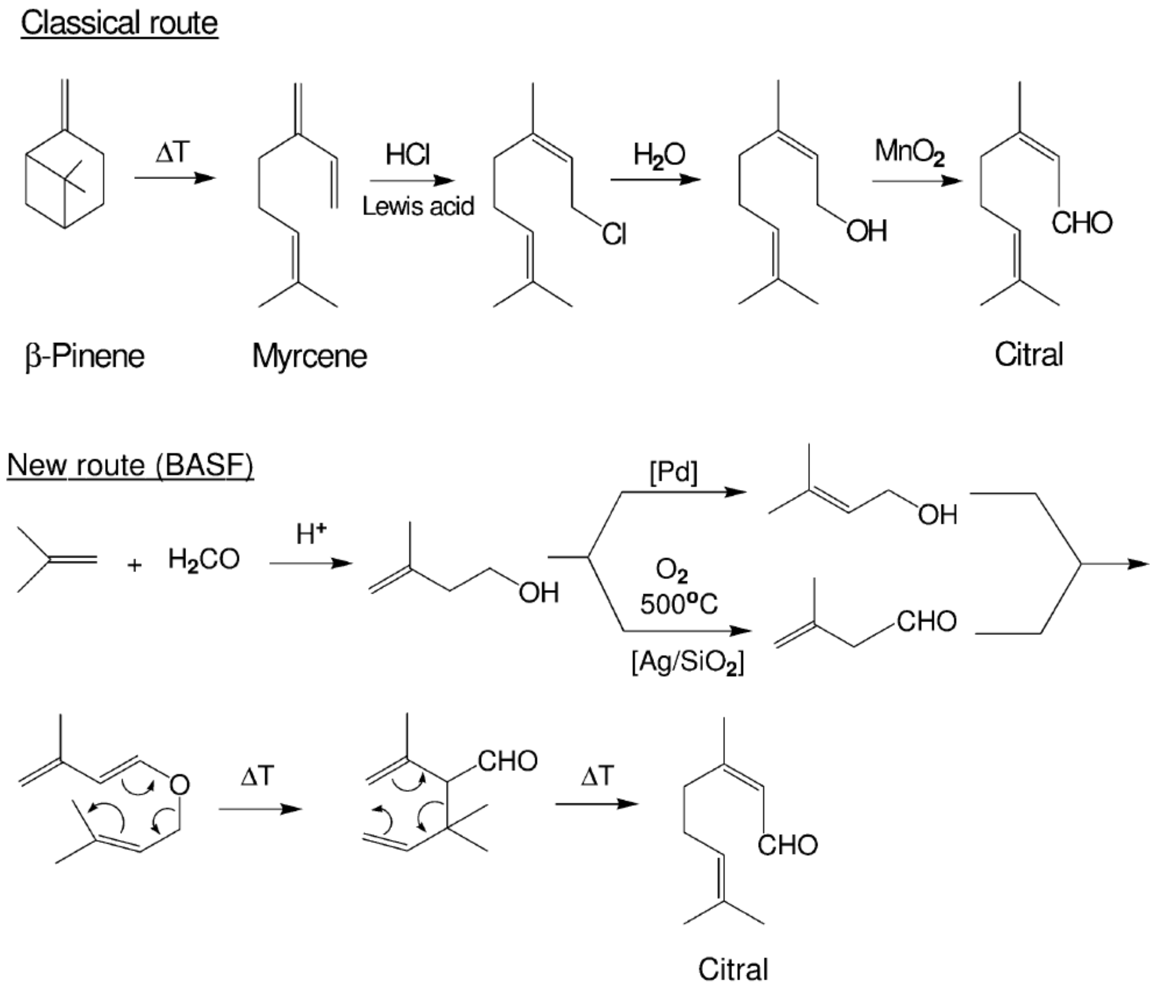
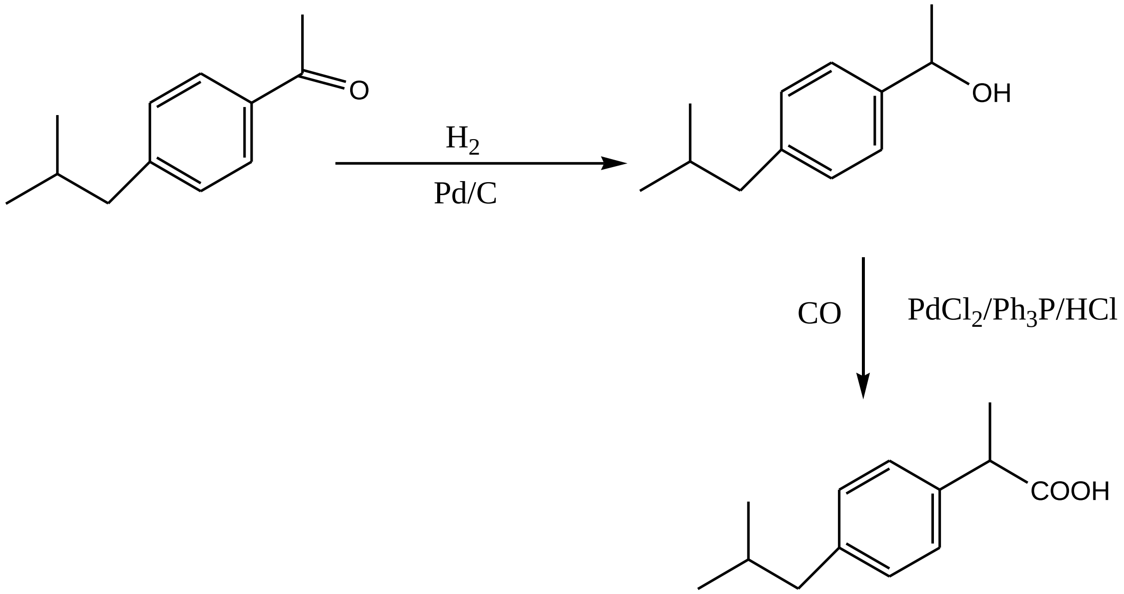


Fig. 1.19 Two routes to citral.

Catalytic C–C Bond Formation

Another key transformation in organic synthesis is C–C bond formation and an important catalytic methodology for generating C–C bonds is carbonylation. The reaction is used in the production of acetic acid by rhodium-catalysed carbonylation of methanol. Since such reactions are 100% atom efficient they are increasingly being applied to fine chemicals manufacture. An elegant example of this is the Hoechst-Celanese process for the manufacture of the analgesic, ibuprofen, with an annual production of several thousands tons. In this process ibuprofen is produced in two catalytic steps (hydrogenation and carbonylation) from *p*-isobutylactophenone with 100% atom efficiency. This process replaced a more classical route which involved more steps and a much higher E factor.



Ibuprofen

Zeolites

Zeolites are well known to chemical engineers for industrial separations and as catalysts; the average chemist in an organic chemical laboratory uses them only as molecular sieves for drying solvents. They offer the promise of more environmentally friendly catalysts that will improve selectivity and reduce waste.

Zeolites are inorganic aluminosilicate polymers. They contain AlO_4 and SiO_4 tetrahedra linked by shared oxygen atoms. No two alminum units are adjacent. For each aluminum, there must be an additional cation, usually from an alkali or alkaline earth metal, for electrical neutrality. There are about 50 neutral zeolites, with names such as chabazite, clinoptilolite, faujasite and mordenite. In addition, many are synthetic.

Zeolites can be made by the formation of a gel from sodium aluminate, sodium silicate, and sodium hydroxide in the presence of a template, usually a quaternary ammonium hydroxide, followed by digestion in which the material crystallizes.

$$NaAlO_2 + Na_2SiO_3 + NaOH + R_4N + OH^- \longrightarrow \text{Gel} \xrightarrow{100°C/6h} \text{Zeolite}$$

Types of Zeolites

(i) Natural Zeolites: The naturally available zeolite is green in color and is referred to as green sand. The common ones being Thomsonite (Na_2O, Al_2O_3, $3SiO_2.2H_2O$).

(ii) Synthetic Zeolites: Synthetic Zeolites are porous and posses a gel structure. They can be prepared by heating together solutions of sodium silicate, aluminium sulphate and sodium aluminate. Synthetic Zeolites possess higher exchange capacity compared to that of natural zeolites. The most common artificial zeolite is a white coloured substance prepared from feldspar, kaolin, clay and soda and is called permutit. Hence Zeolite process is sometimes referred to as permutit process.

Structure:

A zeolite crystal can be considered to be formed from the linking of several SiO_4 tetrahedra. In it, each oxygen of a tetrahedral is being shared with an adjacent one. The empirical formula is thus $(SiO_2)n$. However some of the Si^{4+} ions are replaced by Al^{3+} ions. In order to balance the charges, extra positive ion Na+ or K+ must be incorporated for every Al^{3+} introduced. Thus the linking of tetrahedral results in an open structure with cavities in which Na^+ or K^+ ions are loosely held.

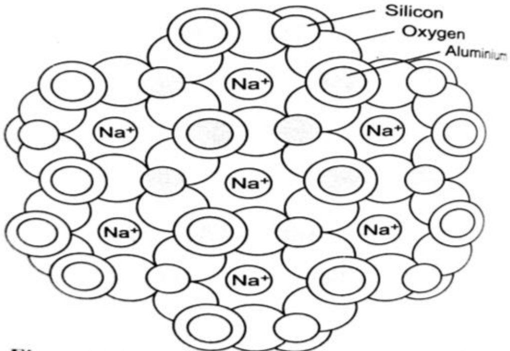


Fig. 1.10 *Structure of a naturally occuring zeolite; The sodium ions are loosely held in holes in the lattice.*

Principle of water sofening

Zeolite can be represented as Na_2Ze.

Where Z is the insoluble radical framework. When hard water is passed through a bed of active granular Na_2Ze, the Ca^{2+} and Mg^{2+} ions of the hard water are exchanged for Na+ ions of zeolite. The various reactions taking place may be indicated as follows:

$$Ca(HCO_3)_2 + Na_2Ze \longrightarrow CaZe + 2NaHCO_3$$

$$Mg(HCO_3)_2 + Na_2Ze \longrightarrow MgZe + 2NaHCO_3$$

$$CaSO_4 + Na_2Ze \longrightarrow CaZe + Na_2SO_4$$

$$MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$$

$$CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$$

$$MgCl_2 + Na_2Ze \longrightarrow MgZe + 2NaCl$$

It is seen from the above reactions that sodium zeolite is converted to calcium and magnesium zeolites. This exchange takes place because the extent of exchange increases with increasing valency of the exchanging ions i.e monovalent ions are exchanged for divalent ions.

Regeneration:

When the zeolite bed gets exhausted i.e nearly all its Na^+ are exchanged for Ca^{2+} and Mg^{2+} ions, it loses its sodium exchange capacity. The zeolite bed is regenerated by first backwashing it and then by passing a concentrated NaCl solution through it. Though other solutions like $NaNO_2$, Na_2SO_4, KCl etc can also be used, but brine solution (NaCl solution) is used because it is cheap and also because the products formed by regeneration reactions are $CaCl_2$ and $MgCl_2$ which are highly soluble and can be readily rinsed out from the zeolite bed.

The following reactions take place during regeneration process:

$$CaZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$

$$MgZe + 2NaCl \longrightarrow NaZe + MgCl2$$

Process: A zeolite softener consists of a steel tank packed with a thick layer of permutit or zeolite. The hard water is percolated at a specified rate through the bed of zeolite. Calcium and magnesium ions present in it are retained by the zeolite in the form of CaZe and MgZe respectively. The outgoing water becomes rich in sodium salts. The softened water is collected from the bottom.

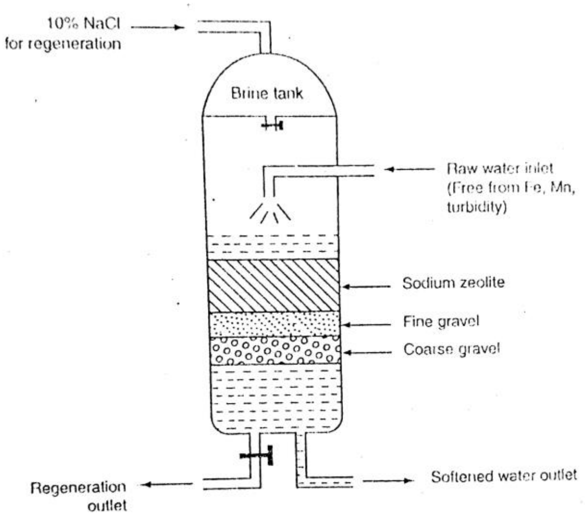


Fig. 4.10. Zeolite Softner

When a significant portion of the sodium in the zeolite has been replaced by calcium and magnesium, it is regenerated by first washing it with water by reversing the flow and then treating it with conc. NaCl solution. The soluble $CaCl_2$ and $MgCl_2$ so formed in regeneration process are washed with soft water and washings are led to sink. The zeolite bed is ready for use again for softening purpose.

Advantages of Zeolite Process:

(i) Water having very low hardness of about 10ppm

(ii) The plant is compact and occupies less space.

(iii) No sludge is formed and hence there is no problem of sludge disposal.

(iv) The running, maintenance and operation cost is quite less.

(v) The plant can be installed in the water supply line itself, avoiding double pumping.

(vi) It requires less skill for maintenance as well as operation.

<u>Disadvanges:</u>

(i) This process is not suitable for treating highly turbid waters because the turbidity will clog the pores of zeolite bed and thus make zeolite less efficient. Therefore the turbidity must be removed before the water is fed into zeolite.

(ii) The treated water contains more dissolved salt than treated by lime soda process.

(iii) Water containing excess of acidity and alkalinity may destroy the zeolite bed. It is preferable to have the pH of the water passing through the zeolite softener around 7.

Oxidation using Molecular oxygen (O_2)

The ordinary oxygen is known as ground state oxygen (triplet oxygen) having two electrons with parallel spins. It behaves like a diradical and is paramagnetic.

$$[\uparrow.O : O.\uparrow]$$

Though ordinary oxygen is not used as such. A classical example is the auto oxidation of benzaldehyde to benzoic acid and the well known photosynthesis, in which it is used along with carbondioxide in presence of sun light and chlorophyll. However, oxygen is used for various oxidations in presence of sun light and chlorophyll. However, oxygen is used for various oxidations in presence of certain catalysts. This procedure is called catalytic oxidation and its useful for the industrial preparations of a number of important products. Some of these are given below;

(i) Manufacture of formaldehyde by the controlled oxidation of methane

$$CH_4 + O_2 \xrightarrow{\text{controlled oxidation/ MoO, 400°C, 200atm}} HCHO + H_2O$$

(ii) Manufacture of methyl alcohol by oxidation of methane

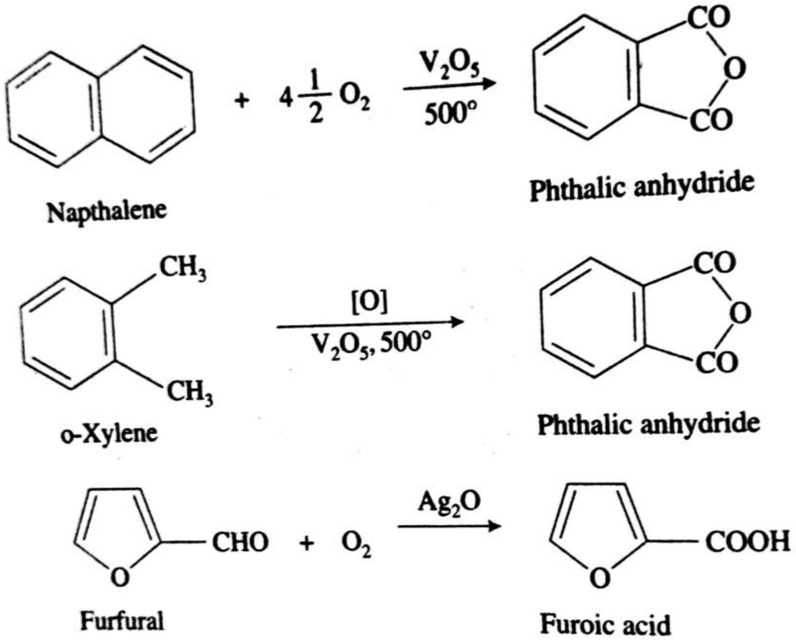
$$CH_4 + 1/2O_2 \xrightarrow{\text{Cu catalyst / 260°C, 100atm}} CH_3OH$$

(iii)Manufacture of acetaldehyde by oxidation of ethylene.

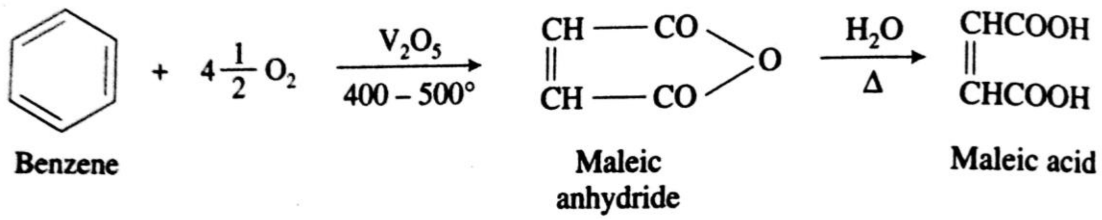
$$H_2C{=}\,CH_2 + {}^{1}/_{2}O_2 \xrightarrow{\text{PdCl2 / H2O / CuCl2}} CH_3CHO$$

(iv)Oxidation of toluene, naphthalene, o-xylene and furfural to important products

$$C_6H_5CH_3 + O_2 \xrightarrow{\text{MnO2/Mo2O3/ZrO2, 500°C}} C_6H_5CHO$$



(v) Manufacture of maleic acid by oxidation of benzene followed by hydrolysis



(vi)Manufacture of chlorine (Deacon process)

$$4HCl + O2 \xrightleftharpoons{CuCl2,\ 440^\circ C} 2Cl_2 \Uparrow + 2H_2O + \text{heat}$$

(vii) Manufacture of nitric acid (Birkeland-Eyde process)

$$N_2 + O_2 \xrightarrow{\text{Spark}} NO \xrightarrow{O2} NO_2 \xrightarrow{H2O} HNO_3$$

$$4NH_3 + 5O_2 \xrightarrow{\text{Pt-Rh catalyst, } 850^\circ\text{, 5atm}} 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$2NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$$

(viii) Manufacture of sulphuric acid (contact process)

$$S + O_2 \longrightarrow SO_2 \xrightarrow{[O],\text{ Pt catalyst}} SO_3 \xrightarrow{H2O} H_2SO_3$$

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
DEPARTMENT OF SCIENCE AND HUMANITIES

GREEN CHEMISTRY

UNIT I -INTRODUCTION TO GREEN CHEMICAL PRINCIPLES

	Questions	opt 1	opt 2	opt 3	opt 4	**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	Buisness 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**
6	What is the U.S. Presidental green chemistry challenge award?	An award related to recycling	An award for industry only	The only chemistry award given by the president	Challenge companies to become fuel efficient	**The only chemistry award given by the president**
7	The first listed of the 12 principles of green chemistry is?	Prevent waste	Catalysis	Atom economy	Benign solvents	**Prevent waste**
8	This word is synonymous with green chemistry and also means harmless, or gentle and not life threatening?	Sustainable	Benign	User friendly	Greenness	**Benign**

9	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**
10	When discussing sustainability and green chemistry often used moral arguments and	Environment	Technology	Politics	Ethics	**Ethics**
11	Which of the following three terms is used in the 'Sustainability triangle'?	Micro-economics	Planet	Social responsibility	economics	**Social responsibility**
12	The following legislation gave birth to today's green chemistry initiatives?	Clean water act of 1972	Montreal protocol of 1989	Pollution prevention act of 1990	Superfund act of 1980	**pollution prevention of act 1990**
13	In 1998, this state signed green chemistry legislation promising to remove politics from the evaluation of disputed chemicals?	Oregon	California	Newyork	Florida	**California**
14	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**
15	The first listed of the 12 Principles of Green Chemistry is?	Prevent waste	Catalysis	Atom economy	Benign solvents	**Prevent waste**
16	Percentage of nitrogen (N) in urea ($CH4N2O$) is	50%	46.60%	40%	20%	**46.60%**
17	Fertilizer which doesn't affect texture of soil is	urea	ammonium sulphate	ammonium phosphate	super phosphate	**urea**
18	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**
19	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**
20	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	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**
21	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**

22	Green chemistry synthesis could also involve which of the following?	High temperature	Dichloromethane	Fossil fuels	Microwave	**Microwave**
23	The term used to measure a product or person’s environmental impact is?	Handprint	CO2 print	Footprint	Hazardous print	**Footprint**
24	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**
25	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**
26	Who proposed green chemistry principles	Paul daldon	john Warner	William bent	Anastas	**john Warner**
27	Among them which is green solvent	benzene	dichloro methane	super critical water	duetrated water	**super critical water**
28	Green chemistry synthesis could also involve which of the following?	High temperature	Dichloromethane	Fossil fuels	Microwave	**Microwave**
29	When discussing sustainability and green chemistry often used moral arguments and	Environment	Technology	Politics	Ethics	**Ethics**
30	The following is often referred to as the universal solvent and is a preferred green solvent?	Water	Methanol	Ethyl acetate	Benzene	**Water**
31	Microwave radiation is selectively absorbed by the	Non polar molecules	Polar Molecules	Asymmetric molecules	Crystalline substances	**Polar Molecules**
32	The safer reagent for methylation is	Methyl iodide	Dimethyl sulfate	Dimethyl carbonate	Methyl bromide	**Dimethyl carbonate**
33	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**

34	Which of the following is the greenest solvent?	Formaldehyde	benzene	Ethanol	water	**Water**
35	which one is an excellent 'green' solvent as well as a greenhouse gas?	Methanol	CFCs	Carbon monoxide	Carbon dioxide	**Carbon dioxide**
36	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**
37	Microwave reaction are faster than thermal reaction	TRUE	FALSE	not change condition	variation of pressure	**TRUE**
38	Which of the following science is applying microwave radiation to chemical reactions	Microwave chemistry	environmental chemistry	green chemistry	synthetic chemistry	**Microwave chemistry**
39	Which is not a tool of green chemistry	Auxillary substances	renewable feed stock	High atom economy	Energy save	**Energy save**
40	The solvent selected for a particular reaction should not have any environmental pollution and health hazard is?	Selection of appropriate solvent	Selection of starting materials	Use of renewable feedstocks	Use of protecting group	**selection of appropriate solvent**
41	Compounds which are added in soil to provide essential elements to plants are called	fertilizers	carbonates	salts	metals	**fertilizers**
42	Insectisides generally attack	respiratory system	nervous system	muscular system	Circulatory system	**respiratory system**
43	Which one is green manure/biofertilizer	Sesbania	Rice	Oat	Maize	**Sesbania**
44	DDT stands for	dichloro-diphenyl trichloroethane	dichloro-triphenyl dichloroethane	Dichlorino triammounium methane	difluoro-diphenyl-tribromobutane	**dichloro-diphenyl trichloroethane**
45	DDT (dichloro-diphenyl trichloroethane: $C_{14}H_9Cl_5$) is a form of	insecticide	herbicide	pesticides	parasiticides	**insecticide**

46	Ammonia fertilizers are made by two components, they are	ammonia and hydrogen	ammonia and nitric acid	nitrogen and hydrogen	nitrogen and water	**ammonia and nitric acid**
47	If there is lack of nitrogen in soil, plants turn	red	orange	blue	to be stunted	**to be stunted**
48	Blue baby syndrome is due to	deficiency of fluorine in water	excess of nitrate in water	deficiency of fluorine and calcium in water	excess of iron in water	**excess of nitrate in water**
49	Greener synthetic methods should be carried out under the conditions	Ambient temperature and Pressure	High temperature	Low Temperature	High pressure.	**Ambient temperature and Pressure**
50	Microwave radiation is also called as	Ultraviolet radiation	Infrared radiation	Electromagnetic radiation	Radiofrequency radiation	**Electromagnetic radiation**
51	The microwave heating the molecules with excess potential energy is converted into kinetic energy through	Collision among the molecules	Interaction among the molecules	No interaction among the molecules	Vibration Collision among the molecules	**Collision among the molecules**
52	_______________ is fulfilling the needs of the present generation without compromising the ability of future generatio	Sustainability	Green chemistry	Life Cycle Assessment	Recycling	**Sustainability**
53	In a reaction the auxiliary substance is	Reactants	Products	catalyst	solvent	**solvent**
54	How many Principles of Green Chemistry	15	12	10	5	**12**
55	The selective absorption of microwaves	10^{9}-10^{11} HZ	10^{8}-10^{10} HZ	10^{7}-10^{9} HZ	10^{9}-10^{12} HZ	**10^{9}-10^{11} HZ**
56	A substance expanding to fill its container like a gas but with a density like that of a liquid.	Super critical carbon di oxide	Buffer solution	For respiration of plants	Liquid aerosol	**Super critical carbon di oxide**
57	Super critical carbon dioxide is used in the	Chemical extraction	Green house gas	With denaturation	As an animal feed	**Chemical extraction**

58	Ultrasound energy is a type of	electrical energy	chemical energy	mechanical energy	kinetic energy	**mechanical energy**
59	Solvent doesn't used in the reaction is called	Elimination reaction	Substitution reactions	Addition reaction	Solvent less reaction	**solventless reaction**

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
DEPARTMENT OF SCIENCE AND HUMANITIES

GREEN CHEMISTRY

UNIT II -ATOM EFFICIENT PROCESSES

	Questions	opt 1	opt 2	opt 3	opt 4	**Answer**
1	Synthetic methods should be designed to minimize incorporation of all materials used in the process in to final called	atom economy	prevention	waste	product	**atom economy**
2	Addition reactions give	90% atom economy	75% atom economy	50% atom economy	100% atom economy	**100% atom economy**
3	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**
4	Benzene, a _______ substance, is an important industrial solvent used in the production of pharmaceuticals, plastics, and dyes?	Odorless	Non-flammable	Biodegradable	Carcinogenic	**Carcinogenic**
5	The constituent in Deals – alder reaction	dienes	allyl halides	vinyl halide	all the above	**all the above**
6	Which of the following reaction gives 100% atom economy	clemmenson reduction	elimination reaction	diels alder reaction	aldol condensation	**diels alder reaction**
7	What is the percentage atom economy for elimination reaction?	46.10%	36.30%	56.30%	23.50%	**36.30%**
8	Diels alder reaction is a	[3+1] cycloaddition	[4+2] cycloaddition	[2+2] cycloaddition	[2+2] cycloaddition	**[4+2] cycloaddition**
9	Diels alder reaction is a	4π-electron system	2π-electron system	6π-electron system	3π-electron system	**4π-electron system**
10	Which of the following process where a quaternary amine is reacted to create a Tertiary amine and an alkene by treatment with excess methyl iodide followed by treatment with silver oxide, water, and heat	diels alder reaction	retro-Diels–Alder reaction	Simmons-Smith Reaction	Hofmann elimination	**Hofmann elimination**
11	The Diels–Alder reaction is an	organic chemical reaction	medicinal chemistry	green chemistry	environmental chemistry	**organic chemical reaction**

12	The Diels–Alder reaction is specifically a	[4+2] cycloaddition	[2+2] cycloaddition	[3+5] cycloaddition	[4+4] cycloaddition	**[4+2] cycloaddition**
13	Which of the following is formed between a conjugated diene and a substituted alkene, commonly termed the dienophile, to form a substituted cyclohexene system	Diels–Alder reaction	Hofmann elimination	retro-Diels–Alder reaction	Simmons-Smith Reaction	**Diels–Alder reaction**
14	The Diels-Alder reaction is a conjugate addition reaction of a conjugated diene to an alkene (the dienophile) to produce a	cyclobutane	cycloheptane	cyclopentane	Cyclohexene	**Cyclohexene**
15	Which is a chemical reaction that removes a carboxyl group and releases carbon dioxide?	Decarboxylation	demethylation	dehydration	dehydrogenation	**Decarboxylation**
16	The Hoffmann elimination under microwave irradiation yield is	85%	90%	97%	80%	**97%**
17	Primary alcohols can be oxidized to form	aldehydes and hydrocarbons	carboxylic acid and hydrocarbons	aldehyde and carboxylic acids	ketones and carboxylic acids	**aldehyde and carboxylic acids**
18	secondary alcohols normally terminates at the	aldehyde	alcohol	ester	ketone	**ketone**
19	Tertiary alcohols are resistant to	reduction	Oxidation	methylation	carboxylation	**Oxidation**
20	The oxidation of a primary alcohol at the aldehyde level is possible by performing the reaction in	absence of water	presence of water	absence of alcohol	presence of alcohol	**absence of water**
21	The indirect oxidation of primary alcohols to carboxylic acids normally proceeds via the corresponding aldehyde, which is transformed via an aldehyde hydrate by	reaction with alcohol	reaction with ester	reaction with water	reaction with ether	**reaction with water**
22	In which reactions one atom is replaced by another atom	Substitution reactions	Addition reactions	Rearrangement reactions	Elimination reactions	**substitution reaction**
23	The reaction involve rearrangement of atoms that make up a molecule is	Rearrangement reactions	Substitution reactions	Elimination reactions	Addition reactions	**rearrangement reaction**
24	In which reaction two atoms or groups of atoms are lost from the reactant to form a pi bond?	Elimination reaction	Substitution reactions	Addition reaction	Rearrangement reactions	**elimination reaction**

25	Reversible reactions in which a compound with two pi electrons are used to form a sigma bond is	Cycloaddition reactions	Electrocyclic reactions	Sigmatropic rearrangements	Addition reactions	**electrocyclic reaction**
26	Hoffmann elimination leads to formation of	olefin	alkanes	alcohols	acids	**olefin**
27	The formation of olefins by heating quaternary ammoniummhydroxides, this reaction known as	knoevenagel condensation	claisen condensation	perkin condensation	Hofmann elimination	**Hofmann elimination**
28	In Hoffmann elimination, the resulting yield of olefins are prepared from	sodium hydroxide	potassium hydroxide	ammonium hydroxide	quaternary ammonium hydroxide	**quaternary ammonium hydroxide**
29	The solvent used in Hoffmann elimination under microwave irradiation is	H_2O-$CHCl_3$	H_2O-CCl_4	CH_3OH-$CHCl_3$	CH_3OH-CCl_4	**H_2O-$CHCl_3$**
30	The compound having a double bond or triple bond called	dienophile	free radical	carbanion	carbocation	**dienophile**
31	Dienophiles are	2π-electron system	4π-electron system	3π-electron system	6π-electron system	**2π-electron system**
32	2π-electron system present in	nucleophile	electrophile	dienophile	free radical	**dienophile**
33	In Diels Alder reaction how many sigma bonds are formed	2	1	4	5	**2**
34	How many π-bonds are expenses in Diels Alder reaction	4	1	2	3	**2**
35	Diels alder reactions are highly	stereospecific	regiospecific	both stereospecific and regiospecific	none of the above	**regiospecific**
36	Disodium iminodiacetate is an essential reactant in manufacturing of	pesticides	fertilizers	insecticides	herbicides	**herbicides**
37	The green synthesis of disodium iminodiacetate is prepared from	ethylamine	diethylamine	diethanol amine	dimethanol amine	**diethanol amine**

38	The catalyst used in the green synthesis of disodium iminodiacetate is	Cu	Zn	Fe	Sn	**Cu**
39	The conventional synthesis of disodium iminodiacetate also known as	Williamson syntheisi	Perkin syntheis	Strecker synthesis	Claisen synthesis	**Strecker synthesis**
40	A typical reaction which has been carried out in aqueous phase is the	Diels-Alder reaction	Mannich reaction	Knoevengal condensation	Friedel-crafts reaction	**Diels-Alder reaction**
41	The reactants are stirred in a suitable solvent with a suitable adsorbent or solid support is	Solid phase organic synthesis without any solvent	Solid supported organic synthesis	Aqueous phase reaction	Electrocyclic synthesis	**solid supported organic synthesis**
42	The atom economy of all addition reactions are	100%	10%	40%	60%	**100%**
43	The atom economy of all rearrangement reactions are	100%	10%	Reductive process	10%	**100%**
44	The atom economy for the conventional synthesis of ibuprofen	100%	10%	Very high temperature and low pressure	40%	**40%**
45	The atom economy for the greener synthesis of ibuprofen	100%	10%	Catalyst percentage	77%	**77%**
46	% atom economy is used to	Measure the unwanted product produced in a reaction	Identify the Solvent percentage	identify impurities in a reaction	Feasibility of a reaction	**Measure the unwanted product produced in a reaction**
47	% atom economy is high for the following reaction	Addition reaction	Elimination reaction	Substitution reaction	Fusion reactions	**Addition reaction**
48	% atom economy is high for the following reaction	Rearrangement reaction	Elimination reaction	Substitution reaction	Fusion reactions	**Rearrangement reaction**
49	% atom economy is low for the following reaction	Rearrangement reaction	Elimination reaction	Addition reaction	Fusion reactions	**Elimination reaction**
50	% atom economy is low for the following reaction	Rearrangement reaction	Substitution reaction	Addition reaction	Fusion reactions	**Substitution reaction**

51	How many routes to synthesis ibuprofen	2	3	4	1	**2**	
52	Which medication is used in the nonsteroidal anti-inflammatory drug (NSAID) class that is used for treating pain, fever, and inflammation	Ibuprofen	paracetamol	aspirin	penicillin	**Ibuprofen**	
53	Ibuprofen is a	Analgesic	polymer	Antipyretic	Plastic material	**Analgesic**	
54	In the greener synthesis of ibuprofen which is not used as a catalyst	HF	Raney Ni	Pd	Aluminium chloride	**HF**	
55	Which is used in the Strecker synthesis	Formaldehyde	Diethanol amine	DMC	Potassium carbonate	**Formaldehyde**	
56	The raw material used in the greener synthesis of Disodium iminoacetate	Formaldehyde	HCN	Ammonia	Diethanolamine	**Diethanolamine**	
57	In the conventional method for the preparation of ibuprofen, the atom economy is	10%	77%	50%	40%	**40%**	
58	Example for a anti-inflammatory drug is	Ibuprofen	MMA	DMC	DMS	**Ibuprofen**	
59	Disodium iminodiacetate is an essential reactant in manufacturing of	pesticides	fertilizers	insecticides	herbicides	**herbicides**	
60	Which of the following act as catalysis for Williamson’s etherification process?	HCl	NaCl	$KMnO_4$	H_2SO_4	**H_2SO_4**	

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
DEPARTMENT OF SCIENCE AND HUMANITIES

GREEN CHEMISTRY

UNIT III -BIOTECHNOLOGY AND GREEN CHEMISTRY

	Questions	opt 1	opt 2	opt 3	opt 4	**Answer**
1	Application of biotechnology procedures in agricultural field is classified as	White biotechnology	Blue biotechnology	Green biotechnology	Red biotechnology	**Green biotechnology**
2	Bacteria Bacillus Polymysea is used to produce	antibiotic	anti-inflammetry	antipyretic	antiseptic	**antibiotic**
3	Fungus Penicillium notatum is uded to produce	antibiotic	antipyretic	anti-inflammetry	antiseptic	**antipyretic**
4	Polymyxin is produced from	Fungus Penicillium notatum	E-Coli	Armillaria gallica	Bacteria Bacillus Polymysea	**Bacteria Bacillus Polymysea**
5	Penicillin is produced from	E-Coli	Fungus Penicillium notatum	Armillaria gallica	Bacteria Bacillus Polymysea	**Fungus Penicillium notatum**
6	The process of cleaning up the hazardous substance into non-toxic compounds is called	Bioremediation	Biotransformation	Biomarker	Biosensing	**Bioremediation**
7	The changes that takes place in the biology of the environment which are changes of the complex compound to simple non-toxic to toxic is	Biosensing	Bioremediation	Biotransformation	Biomarker	**Biotransformation**
8	A chemical that helps to measure the level of damage caused	Bio-marker	Bioinformatics	bioremediation	biosensing	**Bio-marker**
9	The use of living microorganism to degrade environmental pollutants is called	Microremediation	Nanoremediation	Bioremediation	Biomagnification	**Bioremediation**
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 following is often referred to as the universal solvent and is a preferred green solvent?	Water	Methanol	Ethyl Acetate	Benzene	**Water**
12	What term is used to describe the process by which a synthetic procedure is developed such that it is suitable for a production plant?	Plant development	Product development	Process development	Production development	**Process development**

13	Which of the following solvents is unacceptable on large scale?	Heptane	Diethyl ether	Xylene	Dimethoxyethane	**Diethyl ether**
14	Which of the following reagents is acceptable on large scale	Palladium chloride	Sodium dithionite	Pyridinium chlorochromate	Tin chloride	**Tin chloride**
15	Which of the following solvents can not be bio-derived?	Heptane	DCM	Toluene	Ethanol	**Heptane**
16	This ‘green’ chemical is used in household cleaners to remove stains and is also a favorite dressing on salads!?	Vinegar (acetic acid)	Citric acid	Hydrochloric acid (HCl)	water	**Vinegar (acetic acid)**
17	Enzymes that catalyze decarboxylations are called	dehydraxylase	dehydrogenase	decarboxylases	demethylase	**decarboxylases**
18	Separation of the reaction components from the starting material is much simpler than with	Chemically unstable	Low cost	flammable	Not readily available	**Low cost**
19	Green chemistry, also called	sustainable chemistry	medicinal chemistry	environmental chemistry	synthetic chemistry	**sustainable chemistry**
20	Which is an area of chemistry and chemical engineering focused on the designing of products and processes that minimize the use and generation of hazardous substances	medicinal chemistry	environmental chemistry	synthetic chemistry	Green chemistry	**Green chemistry**
21	An example of green chemistry is?	Recycled carpet	A product made on Earth Day	A sublimation reaction	Bio-plastics	**Bio-plastics**
22	Green chemistry aims to?	products and process that maximize profits	chemical products and processes that reduce or	products and processes that work most	Utilize non-renewable energy	**products and processes that reduce or eliminate the use and generation of**
23	One of the raw materials used in the preparation of Nylon-6,6 is	Adipic acid	succinic acid	tartaric acid	lactic acid	**Adipic acid**
24	In conventional method for the preparation of Adipic acid, the raw material used is	ethanol	Non renewable source	propanol	Plant feedstock	**Non renewable source**
25	D-glucose is used to prepare	Ethanoic acid	adipic acid	citric acid	crotonic acid	**adipic acid**
26	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**

27	The threshold concentration of sulphur dioxide in any industrial activity should not be permitted beyond	2ppm	3ppm	4ppm	5ppm	**5ppm**
28	The threshold limit of benzene is	15ppm	20ppm	25ppm	30ppm	**25ppm**
29	Which of the following is used as antiknock compound in gasoline?	tetramethyl lead	tetraethyl lead	trimethyl lead	triethyl lead	**tetraethyl lead**
30	Which of the following is a fermentation product of molasses?	Methano	Formaldeyde	Ammonia	Acetone	**Acetone**
31	Green chemistry can reduce all but which of the following?	Cost	Risk & hazard	Awarness	Waste	**Awarness**
32	Heart of green chemistry is	to maximize the waste products formation	to minimize the waste products formation	to increase the toxic materials	materials and waste products formation	**to minimize the waste products formation**
33	During thunderstorms, water dissolves	dust particles	HCl	nitric acid	clouds	**nitric acid**
34	Maximum amount of ozone (O3) is present in	troposphere	stratosphere	mesosphere	thermosphere	**stratosphere**
35	Upset caused in natural balance of concentration of greenhouse gases is called	pollution	global warming	atmospheric poisoning	earth heating	**global warming**
36	Branch of chemistry dealing with plantation and overcoming greenhouse effect is	Biochemistry	Organic chemistry	Environmental chemistry	Inorganic chemistry	**Environmental chemistry**
37	Gas responsible for global warming is	oxygen	carbon dioxide	carbon monoxide	nitrogen	**carbon dioxide**
38	Ozone (O3) comprises of	one oxygen atom	2 oxygen atoms	3 oxygen atoms	4 oxygen atoms	**3 oxygen atoms**
39	An example of green chemistry is?	Recycled carpet	PVC	Bakelite	Bio-plastics	**Bio-plastics**
40	For green chemistry raw material should be	non - renewable	renewable	conventional	economical	**renewable**

41	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	largest component (by mass) of a process	**they make up the largest component (by mass) of a process**
42	Which can provide green technology solutions for a sustainable future?	Inorganic chemistry	Textile chemistry	Physical chemistry	Green chemistry	**Green chemistry**
43	Which of the following gases is not a green house gas?	CO	O3	CH4	H2O vapour	**CO**
44	Adipic acid is otherwise called as	hexanedioic acid	pentadioic acid	propadioic acid	butadioic acid	**hexanedioic acid**
45	Bio-polymers exemplify Green Chemistry Principle # 10, which is?	Catalysis	Prevent waste	Benign solvents & auxiliaries	Design for degradation	**Design for degradation**
46	Green chemistry improves --- of chemical manufacturers	Competitivenes s	Easiness of production	services	chemicals	**Competitiveness**
47	Bio ethanol is denatured alcohol that is also called as	Ethylene	Methylated spirit	Ethylene glycol	Methylene	**Methylated spirit**
48	A biocatalyst works under	a mild reaction condition	High temperature reaction condition	High pressure	High pressure and high temperature	**a mild reaction condition**
49	A biocatalyst works under	Physiological PH	High temperature reaction condition	High pressure	High pressure and high temperature	**Physiological PH**
50	A biocatalyst works under	Physiological temperature	High temperature reaction condition	High pressure	High pressure and high temperature	**Physiological temperature**
51	Example for a biocatalyst	Enzymes	Raney Nickel	Zeolites	metallic salts	**Enzymes**
52	Example for a biocatalyst	enzymes	Metallic salts	Raney Nickel	Coordination compounds	**enzymes**
53	Using a biocatalyst in a reaction makes it	Environmentally friendly	unattractive	Economically unviable	Environmentally unviable	**Environmentally friendly**
54	Using a biocatalyst in a reaction makes it	Environmentally un friendly	unattractive	Economically unviable	Environmentally viable	**Environmentally viable**

55	The aerobic digestion of sewage is used to produce	Biomass	Biofuels	Synthetic fuels	Metal articles	**Biofuels**
56	The production of bio ethanol is by fermenting the _________ and starch components	Acid	Milk	Sugar	Alcohol	**Sugar**
57	_________ is called as the bio gas.	Bio ethanol	Bio methane	Bio diesel	Bio butanol	**Bio methane**
58	The percentage of carbondioxide in the bio methane is ____________	30-40	32-43	35-45	55-60	**32-43**
59	Biotechnology deals with	increase pollutant level	production of toxic chemicals	pollution prevention	increase waste product	**pollution prevention**

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
DEPARTMENT OF SCIENCE AND HUMANITIES
GREEN CHEMISTRY
UNIT IV -RENEWABLE RESOURCES

	Questions	opt 1	opt 2	opt 3	opt 4	**Answer**
1	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**
2	Lignin,switch grass,and cellulose are all types of?	Enzymes	Catalysts	Bio-based feedstock's	Anti-cancer compounds	**bio based feedstocks**
3	An example for a renewable resource	Petroleum	Crude oil	Diesel	Biomass	**Biomass**
4	Soybean is used to replace traditional inks in printer cartridges,highlighting which of the green chemistry principles?	Atom economy	Use of renewable feedstock's	Reduce derivatives	Prevent waste	**Use of renewable feedstock's**
5	Which are considered as renewable starting materials ?	CO_2	methane gas	CO	CO_2 & methane gas	**CO_2 & methane gas**
6	Known deposits of a material that can be extracted profitably are called	resources.	undiscovered reserves.	identified deposits.	reserves.	**reserves.**
7	Which of the following is the most abundant fossil fuel?	oil	natural gas	coal	gasoline	**coal**
8	Which of the following is not a renewable energy source?	biomass conversion	solar	hydroelectric	oil	**oil**
9	What are the main constituents of natural gas?	CO	CO2	CH4 & C_2H_6	NO_2	**CH4 & C_2H_6**
10	In conventional method for the preparation of Adipic acid, it produces	N_2O	N_2O_2	NO	NO_2	**N_2O**
11	N_2O is produced during the preparation of	Adipic acid	Succinic acid	Tattaric acid	Lactic acid	**Adipic acid**
12	N_2O is produced during the preparation of adipic is a	Greenhouse gas	Laughing gas	Environmentally friendly gas	Dry liquid	**Greenhouse gas**
13	N_2O is produced during the preparation of adipic is a	Ozone depleting gas	Laughing gas	Environmentally friendly gas	Dry liquid	**Ozone depleting gas**
14	Which is the 12 Principles of Green Chemistry?	Waste prevention	Use of renewable feedstocks	Use of catalysis	Safer solvents	**Use of renewable feedstocks**
15	We must use feedstock derived from	annually renewable resources	Chemicals	Organic compounds	animals	**annually renewable resources**
16	An example of chemical toxics prevention is?	Removing water from industrial reactions	Eliminating the formation of chlorinated organics in paper	Utilizing ammonia instead of vinegar	Monitoring BPA (Bisphenol A) in plastic bottles	**formation of chlorinated organics in paper**
17	How can be citric acid produced other than from lemons?	Aerobic fermentation of starch	Anaerobic fermentation of starch	Aerobic fermentation of glucose	Anaerobic fermentation of glucose	**Aerobic fermentation of starch**
18	Which one of the following is an example of starch crops biomass feed stocks?	Sugar cane	Wheat straw	Corn stover	Orchard prunings	**Sugar cane**
19	In the greener method for the preparation of adipic acid the raw material used is	benzene	coal	petroleum	d-glucose	**d-glucose**
20	d-glucose is used to prepare	hexanedioic acid	Succinic acid	Tattaric acid	Lactic acid	**hexanedioic acid**
21	d-glucose is used to prepare adipic acid is a	Renewable source	Non-renewable source	Environmentally friendly gas	Biological catalyst	**Renewable source**

22	Green propellents are	Low toxicity	Low energy liquid	low efficiency	low performance	**Low toxicity**
23	Green propellent is	safer for the environment	decreases payloads capacity	hazardous to environment	disable to longer missions	**safer for the environment**
24	A rocket propellent consists	oxider	a fuel and oxidizer	a fuel	a fuel and reducer	**a fuel and oxidizer**
25	Enzymes which breakdown proteins	Lipases	cellulases	amylases	proteases	**proteases**
26	Enzymes which breakdown cellulose	cellulases	proteases	amylases	Lipases	**cellulases**
27	Enzymes which breakdown starch into simple sugars	amylases	cellulases	proteases	amylases	**amylases**
28	In conventional method for the preparation of Adipic acid, it uses the catalyst	Ni-Al_2O_3 catalyst	C0 -Al_2O_3 catalyst	Raney Nickel	palladium	**Ni-Al_2O_3 catalyst**
29	The catalyst used for the preparation of adipic acid from d-glucose is	E.Coli	Pen-acylase	Environmentally friendly gas	zymase	**E.Coli**
30	Glucose is treated with acid which gives	sorbital	hydroxymethyl furfural	Vitamin C	acetic acid	**hydroxymethyl furfural**
31	Fermentation of glucose yields	Ethanol	hydroxymethyl furfural	sorbital	amylases	**Ethanol**
32	During the fermentation of glucose which produce	Lactic acid	tartaric acid	glutamic acid	citric acid	**Lactic acid**
33	Biomass refers to	synthetic resources	liquid nitrogen	solid carbonaceous material	gasoline	**solid carbonaceous material**
34	Bulky biomass is reduced to a better volume to weight ratio by compressing in a die at a high T & P.	Combustion	Thermal -chemical conversion	Bio-chemical conversion	Densification	**Densification**
35	Biomass conversion technology has	4 types	7 types	2 types	6 types	**4 types**
36	Conversion of a solid biomass into a gaseous fuel	liquification	gasification	pyrolysis	composting	**gasification**
37	The waste plastics are converted into liquid fuel by	pyrolysis	cracking	hydrolysis	incineration	**pyrolysis**
38	Growing more trees help to	Reduce oxygen in the environment.	Increase carbon dioxide in the environment	Reduce carbon dioxide only in the environment	Reduce CO2 and increase O2 in the environment	**Reduce CO2 and increase O2 in the environment**
39	Electricity production is considered green energy if it is created	Without causing any harmful environment impact	In the Rocky Mountains	Only at night	By cutting down old growth forests	**Without causing any harmful environment impact**
40	Green chemistry is also called as	Environmental chemistry	organic chemistry	life chemistry	sustainable chemistry	**sustainable chemistry**
41	Power alcohol is ------------ than petrol	bad product	less efficient	costlier	cheaper	**cheaper**
42	What is the colour of the biodiesel?	orange	light yellow	dark orange	light brown	**light yellow**
43	The natural gas along with the petroleum is called	water gas	oil gas	wet gas	heavy oil	**wet gas**
44	d-glucose is used to prepare adipic acid is a	Renewable source	Non-renewable source	Environmentally friendly gas	Biological catalyst	**Renewable source**
45	The catalyst used for the preparation of adipic acid from d-glucose is	E.Coli	Pen-acylase	Environmentally friendly gas	zymase	**E.Coli**

46	d-glucose is used to prepare adipic acid is manufactured from	Corn starch	Animal protein	Bacteria	Animal fats	**Corn starch**
47	d-glucose is used to prepare adipic acid is manufactured from	Agricultural wastes	Animal protein	petroleum	Animal fats	**Agricultural wastes**

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
DEPARTMENT OF SCIENCE AND HUMANITIES

GREEN CHEMISTRY

UNIT V -CATALYSIS IN GREEN CHEMISTRY

	Questions	opt 1	opt 2	opt 3	opt 4	**Answer**
1	Which facilitate transformation and the conversions can be affected in short duration of time and consume less energy?	Catalysts	Selection of starting materials	Percentage atom utilization	Evaluating the type of reaction	**Catalysts**
2	Ionic liquids are good solvents for a wide range of	Inorganic materials	organic materials	Inorganic and organic materials	Physio-organic materials	**inorganic and organic materials**
3	Which of the following statements is false concerning cyclopropanation reactions?	The Simmons-Smith reagent generates a diiodo carbenoid which adds to alkenes.	Diazomethane can be used to generate methylene, but is not very useful in synthesis	Dichlorocarbene reacts with alkenes to give good yields of dichlorocyclopropane derivatives.	benzene reacts with chlorine	**The Simmons-Smith reagent generates a diiodo carbenoid which adds to alkenes.**
4	Toluene can be oxidized to produce what?	crotonaldehyde	Benzene	O-xylene	methyl benzene	**O-xylene**
5	Under which temperature, with a mild catalyst does toluene oxidize to benzaldehyde?	High	Moderate	Low	ambient	**High**
6	The oxidation of toluene depends on which condition?	Catalyst	pressure	mass	super cooled	**Catalyst**
7	The oxidation of toluene do not depends on which condition?	Catalyst	Temperature	Oxygen ratio	pressure	**pressure**
8	What is produced by dehydrogenating ethylbenzene over a zinc oxide catalyst?	Benzaldehyde	Styrene	Nylon-6	Benzoic acid	**Styrene**
9	Conversion of an aldehyde to an alcohol is generally known as	Reduction	Oxidation	Esterification	Polymerisation	**Reduction**
10	Which of the following statements about alcohols is incorrect?	Tertiary alcohols have lower boiling points than primary alcohols with an equivalent	Alcohols undergo nucleophilic substitution.	Tertiary alcohols undergo dehydration more readily than primary alcohols	Tertiary alcohols are metabolised in the body to ketone	**Tertiary alcohols are metabolised in the body to ketones**
11	Which of the following alcohols would be oxidised to propan-2-one?	ethanol	propan-2-ol	2-methylpropan-2-ol	butan-1-ol	**propan-2-ol**
12	Propan-2-one will get oxidized to give	aldehyde	ketone	alcohol	acid	**alcohol**
13	For methylation reaction the greener alternative is	Methyl halides	Dimethyl sulfate	Dimethyl carbonate	Methyl oxalate	**Dimethyl carbonate**
14	Methylation of active methylene group can be carried out by a greener reagent	Methyl halides	Dimethyl sulfate	Dimethyl carbonate	Methyl oxalate	**Dimethyl carbonate**
15	Dimethyl carbonate can be used as a greener reagent for the methylation of	Active methylene group	Methyl groups	Benzene ring	Double bonds	**Active methylene group**
16	Which one of the following example for green oxidants?	chlorides	chromates	permangnates	oxygen	**oxygen**

17	Example for green oxidants	Hydrogen peroxides	chromates	permangnates	iodides	**Hydrogen peroxides**
18	Which of the following enzyme groups can catalyse oxidation reactions?	phosphorylases	isomerases	hydrolases	dehydrogenases	**dehydrogenases**
19	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.**
20	Which of the following is an extracellular enzyme?	catalase	DNA polymerase	keratin	trypsin	**trypsin**
21	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**
22	Which type of enzyme catalyses the conversion of a dipeptide into two separate amino acids?	decarboxylase	dehydrogenase	hydrolase	oxidoreductase	**hydrolase**
23	A catalyst is	a reactant in a chemical reaction.	a product in a chemical reaction.	speeds up a reaction without being consumed in	increases the energy of the products.	**speeds up a reaction without being consumed in the**
24	Which of the following is not a category of catalysis?	Homogeneous	Heterogeneous	Artificial	Enzymatic	**Artificial**
25	Which is a key technology to achieve the objectives of sustainable (green) chemistry?	reagents	Catalysis	solvents	none of these	**Catalysis**
26	The chemical formula of zeolite is	$FeSO_4.7H_2O$	$Al_2(SO_4)_3$	$Na_2O.Al_2O_3.xSiO_2.yH_2O$	Na_2Al_2O	**$Na_2O.Al_2O_3.xSiO_2.yH_2O$**
27	Natrolite is an example of	Natural zeolite	synthetic zeolite	Calgon	Colloid	**Natural zeolite**
28	Which of the following is the greenest solvent?	Formaldehyde	benzene	Ethanol	water	**Water**
29	Which one belongs to a green oxidants?	chromates	permanganates	iodides	oxygen	**oxygen**
30	The process in which catalyst has a different phase to a reaction mixture is known as	homogenous catalysis	Heterogenous catalysis	Hypergenous catalysis	Hypogenous catalysis	**Heterogenous catalysis**
31	The color of natural zeolite is	Grey	Green	Black	Blue	**Green**
32	Natrolite is an example of	synthetic zeolite	natural zeolite	calgon	colloid	**natural zeolite**
33	Which of the following is an example of homogeneous catalysis?	Enzyme catalysis	Hardening of animal and vegetable oils	Haber's process	Cracking of heavy oils for synthesis of gasoline	**Enzyme catalysis**
34	Which of the following act as catalysis for Williamson's etherification process?	HCl	NaCl	$KMnO_4$	H_2SO_4	**H_2SO_4**
35	Which of the following process is used for the manufacturing of acetic acid	Bosch's process	Deacon's process	Vinegar process	Chamber process	**Vinegar process**
36	Which of the following process is used for the preparation of sulphuric acid?	Ostwald's process	Bergius process	Deacon's process	Chamber process	**Chamber process**

37	Process in which catalyst has a different phase to a reaction mixture, this process is known as	homogenous catalysis	heterogeneous catalysis	hypergeneous catalyst	hypogenous catalyst	**heterogeneous catalysis**
38	Changes in oxidation number of ions which are involved in catalysis is done in	homogenous catalysis	heterogeneous catalysis	hypergeneous catalyst	hypogenous catalyst	**homogeneous catalysis**
39	Which factor can decrease the rate of a chemical reaction?	high pressure	low pressure	low activation energy	high concentration of reactants	**low pressure**
40	How does a catalyst work?	by decreasing the pressure of a chemical reaction	by decreasing the activation energy of a reaction	by increasing the concentration of reactants in a reaction	by increasing the temperature of a chemical reaction	**by decreasing the activation energy of a reaction**
41	Which component is affected when a catalyst is added to a chemical reaction?	the amount of the substrate	the amount of product	the activation energy	the concentration of reactants	**the activation energy**
42	What happens when a catalyst is added to a system at equilibrium?	The reaction follows an alternative pathway of lower activation energy	The heat of reaction decreases	The rate of chemical reaction decreases	The potential energy of the reactants decreases.	**The reaction follows an alternative pathway of lower activation energy**
43	The role of a catalyst is to change	gibbs energy of reaction	enthalpy of reaction	activation energy of reaction	equilibrium constant	**activation energy of reaction**
44	Enzyme catalysis is an example of?	Auto catalysts	heterogeneous catalysis	homogenous catalysis	Induced catalyst	**heterogeneous catalysis**
45	Platinum is an example of?	Oxiation catalyst	auto catalyst	induced catalyst	negative catalyst	**Oxiation catalyst**