KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)

(Established Under Section 3 of UGC Act 1956)

Coimbatore – 641 021.

SYLLABUS

DEPARTMENT OF CHEMISTRY

Name of the Staff : **Dr. M. Makeswari**
Department : **Chemistry**
Title of the Paper : **Green Methods in Chemistry**
Paper Code : **18CHU404A**
Class : **II-B.Sc-Chemistry**
Year and Semester : **II Year and IV-Semester**

Chemistry **2018-2019**

Semester-IV

18CHU404A **GREEN METHODS IN CHEMISTRY** **3H 3C**

Instruction Hours/week:L:3 T:0 P:0Marks: Internal:40External: 60 Total:100

End semester Exam:3hrs

Course objectives

This course enables the students to

1. Understand the twelve principles of green chemistry
2. Understand the catalysis and alternate sources of energy.
3. Understand the process involved in the real word cases likeSurfactants for CO_2, environmentally safe marine antifoulant and plastic (poly lactic acid) made from corn.

Course outcome

The students understood

1. The twelve principles of green chemistry
2. The catalysis and alternate sources of energy.
3. The process involved in the real word cases likeSurfactants for CO_2, environmentally safe marine antifoulant and plastic (poly lactic acid) made from corn.

Methodology

Blackboard teaching, Powerpoint presentation and group discussion.

UNIT I

Theory and Hand-on Experiments

Introduction: Definitions of Green Chemistry. Brief introduction of twelve principles ofGreen Chemistry, with examples, special emphasis on atom economy, reducing toxicity,green solvents,

UNIT II

Green Chemistry and catalysis and alternative sources of energy, Greenenergy and ustainability

Green energy(microwave,ultra sound and sonachemist).

UNIT III

The following Real world Cases in Green Chemistry should be discussed:

Surfactants for carbon dioxide – Replacing smog producing and ozone depletingsolvents with CO_2 for precision cleaning and dry cleaning of garments.

UNIT IV

Designing of environmentally safe marine antifoulant.Rightfit pigment: Synthetic azo pigments to replace toxic organic and inorganicpigments.

UNIT V

An efficient, green synthesis of a compostable and widely applicable plastic (polylactic acid) made from corn.

Suggested Readings

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

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LESSION PLAN
DEPARTMENT OF CHEMISTRY
II B. Sc CHEMISTRY

STAFF NAME : **Dr. M. Makeswari**
SUBJECT NAME : **GREEN METHODS IN CHEMISTRY**
SUB. CODE : **18CHU404A**
SEMESTER : **IV**
CLASS : **II- B. Sc-CHEMISTRY**

S. No	**Lecture Duration Period**	**Topics to be Covered**	**Support Material/Page Nos**
		UNIT-I	
1	1	Introduction to Green Chemistry, Definitions of Green Chemistry	T1: 1, R1: 2-4,
2	1	Brief introduction of twelve principles of Green Chemistry	R1: 1-5, T2: 10-25
3	1	Atom economy- Examples	T2: 12-14
4	1	Reducing toxicity	T1: 1-5
5	1	Green solvents	T1 215-226, T_2: 25-26
6	1	Revision and Discussion of important questions	
	Total No of Hours Planned For Unit 1= 06		
1	1	Green Chemistry and catalysis	T1:109-120; T2: 86-95
2	1	alternative sources of energy	T1: 497-499
3	1	Green energy and sustainability	T1:477-512, T2:59
4	1	Green energy- Microwave energy	T1: 495
5	1	Ultra sound and sonochemist	T1: 496-499
6	1	Revision and discussion of important questions	

	Total No of Hours Planned For Unit II=06		
		UNIT-III	
1	1	Real world cases in green chemistry	R1: 4-8; 51-53
2	1	Replacing smog producing solvents	T1:217-218
3	1	Replacing ozone depleting solvents	T1:217-218
4	1	CO_2 as a solvent for precision cleaning	T1: 215-223
5	1	CO_2 for dry cleaning of garments	T1:226-230
6	1	Revision and discussion of important questions	
	Total No of Hours Planned For Unit III=06		
		UNIT-IV	
1	1	Designing of environmentally safe marine antifoulant.	T1: 81-83
2	1	Right fit pigment: Synthetic azo pigments to replace toxic pigments	R1: 55-58
3	1	Replacement of toxic organic pigments	R1: 56-58
4	1	Replacement of toxic inorganic pigments	R1: 53-56
5	1	Revision and discussion of important questions	
	Total No of Hours Planned For Unit IV=05		
		UNIT-V	
1	1	An efficient green synthesis of a compostable plastics	R1: 9-10
2	1	Synthesis of Poly Lactic acid	R1: 11-14
3	1	Widely applicable plastic made from corn	R1-12-15
4	1	Revision and discussion of important questions	
5	1	ESE question paper discussion	
6	1	ESE question paper discussion	
7	1	ESE question paper discussion	
	Total No of Hours Planned for unit V=07		
Total Planned Hours	**30**		

TEXT BOOK

T1: Matlack, A.S. (2010). *Introduction to Green Chemistry*. Marcel Dekker.

T2: James Clark, Duncan Macquarrie, (2002). *Handbook of Green Chemistry and Technology*. Blackwell Science Ltd

REFERENCE BOOK

R1: Cann, M.C. & Connely, M.E. (2000). *Real-World cases in Green Chemistry*, American Chemical Society. Washington.

UNIT I

SYLLABUS

Introduction: Definitions of Green Chemistry. Brief introduction of twelve principles of Green Chemistry, with examples, special emphasis on atom economy, reducing toxicity, green solvents.

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, the topic of thisbook.

Green chemistry

1. The term *green chemistry* was coined by Paul Anastas in1991.
2. It is also called as sustainablechemistry
3. It is a philosophy of chemical research and engineering that encourages the design of productsandprocessesthatminimizetheuseandgenerationofhazardoussubstances.
4. Green chemistry seeks to reduce and prevent pollution at itssource.

5. Green chemistry applies to organic chemistry, inorganic chemistry, biochemistry, analytical chemistry, and even physicalchemistry.
6. It seems to focus on industrial applications. The focus is on minimizing the hazard and maximizing the efficiency of any chemicalchoice.

What is Green Chemistry?

Green chemistry is a pro-active approach to pollution prevention. It targets pollution at the design stage, before it even begins. If chemists are taught to develop products and materials in a manner that does not use hazardous substances, then much waste, hazards and cost can be avoided. Green Chemistry is designing chemical products and processes that reduce or eliminate the use and/or the generation of hazardoussubstances.

Green Chemistry seeks to design out hazard.

Green Chemistry is the ONLY science which focuses on the intrinsic hazard of a chemical or chemical process. It seeks to minimize or eliminate that hazard. Traditional approaches to pollution prevention focus on mitigating the hazard or end-of-pipe pollution prevention controls. These traditional technologies focus on limiting the exposure of a hazardous material. Green chemistry goes to the root of the problem and aims to eliminate the hazard itself.

How does Green Chemistry design out hazards?

By teaching chemists about what makes a molecule toxic (to the environment and to humans). Not one University in the U.S. requires their Ph.D. students in chemistry to know anything about toxicity and environmental impact. Chemists are simply not taught how to design safer chemicals and chemical processes. Green Chemistry focuses to merge toxicity with the knowledge of synthetic design of molecules in order to create the next generation of safe chemicals and products. It is a revolutionary way of teaching chemistry and is a change in mindset rather than a separate field ofstudy.

Green Chemists invents alternatives when alternatives do not exist.

There are many groups and organizations who aim to help industries design more sustainable products and processes. Many of the organizations use existing benign alternatives which currently exist. What happens when no benign alternative exists? This is where Green Chemistry comes into play.As Green Chemists, we focus on designing new, benign alternatives to current chemical and products and ensuring that the next generation of products and processes are developed in a sustainable way to beginwith.

Green Chemists is NOT a policy-based approach to pollution prevention.

Green Chemistry was developed out of a union between interests in industry and the government. It has been found that Green Chemistry can make a significant economic impact in industry. Due to the many existing laws and regulations, the cost of using a hazardous material is extremely high for an industry. It costs more to buy, store, dispose of, transport and use (due to PPE used) a hazardous chemical. If they can use safer chemicals to make safer products, the economic benefit is tremendous. Green chemistry is designed to be a non-policy based approach to pollution prevention. The economic benefit, along with other benefits such as community relations and new employee recruitment, make Green Chemistry a very attractive alternative for industries. For some "real-world" examples of Green Chemistry technologies see the Presidential Green Chemistry Challenge Award given through the EPA and the ACS Green ChemistryInstitute.

What is the difference between Environmental Science and Green Chemistry?

Both areas of study seek to make the world a better place. The two are complimentary to each other. Environmental Science identifies sources, elucidates mechanisms and quantifies problems in the earth’s environment. Green Chemistry seeks to solve these problems by creating alternative safe technologies. Green Chemistry is not Environmental Chemistry. Green Chemistry targets pollution prevention at the source, during the design stage of a chemical product or process, and thus prevents pollution before it begins.

Is Green Chemistry more expensive than traditional Chemistry?

No. A simplified analysis of the cost structure associated with any chemical process takes into account the cost of materials, equipment and the human resources necessary. But, in reality, disposal, treatment and regulatory costs associated with the buying, using and generating hazardous materials involves numerous hidden costs. When you buy and use a hazardous material you are paying for it twice, once when you use it and once when you get rid of it. It makes sense that if you use materials that are non-hazardous and thus have minimal regulatory or disposal costs associated with them, the benefit to the economic bottom line is obvious. The Presidential Green Chemistry Challenge Award has provided illustrations of several examples where industry has not only accomplished goals of pollution prevention, but has achieved significant economic benefitssimultaneously.

Green Chemistry: Combining Sustainable Product Design with Economic Development.

Sustainable design and economic development do not have to be mutually exclusive. Green chemistry is an innovative way of approaching pollution prevention. By focusing on the materials scientists and chemists who develop new materials, we can prevent pollution before it even begins. It is not a policy-based program, but rather a new way of teaching chemistry so that the scientist designing the next generation of materials will have the tools necessary to make benign products from benign, sustainable rawmaterials.

Difference between Green chemistry and Environmental chemistry

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

Recent key developments in green chemistry:

1. Use of supercritical carbon dioxide as greensolvent,
2. Use of aqueous hydrogen peroxide for cleanoxidations
3. Use of hydrogen in asymmetricsynthesis.
4. On water reactions,and
5. Dry mediareactions.

The symptoms of good product design

Designing safer, economical, and efficacious processes and products.

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

What is Sustainability

Sustainability is most commonly defined as:

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

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

Nobel Prize for Green Chemistry

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

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

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 naturalresources.
2. Many feedstocks for the production of chemicals are based on petroleum, which is nota

renewable resource.

In order to address the following points :

1. What alternatives can be developed andused.
2. we must ensure that future generations can also use these newalternatives.
3. "Sustainability" is a concept that is used to distinguish methods and processes that can ensure the long-term productivity of the environment, so that even subsequent generations of humans can live on this planet. Sustainability has environmental, economic, and social dimensions.

Paul Anastas of the U.S. Environmental Protection Agency formulated some simple rules of thumb for how sustainability can be achieved in the production of chemicals - the "Green chemical principles":

The principles cover such concepts as:

- the design of processes to maximize the amount of raw material that ends up inthe product;
- the use of safe, environment-benign substances, including solvents, wheneverpossible;
- the design of energy efficientprocesses;
- the best form of waste disposal: not to create it in the firstplace.

The 12 principlesare:

1. It is better to prevent waste than to treat or clean up waste after it isformed.
2. Synthetic methods should be designed to maximize the incorporation of allmaterials used in the process into the finalproduct.
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 whenused.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature andpressure.

7. A raw material or feedstock should be renewable rather than depletingwherever technically and economicallypracticable.
8. Reduce derivatives - Unnecessary derivatization (blocking group, protection/ deprotection, temporary modification) should be avoided wheneverpossible.
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 donot 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 hazardoussubstances.
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 tp 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

It is better to prevent waste than to treat or clean up waste after it has been created.

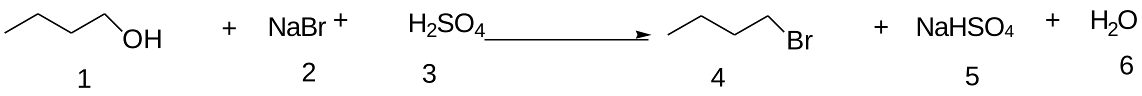
An often-used measure of waste is the E-factor, which relates the weight of waste coproduced to the weight of the desired product. More recently, the ACS Green Chemistry Institute Pharmaceutical Round table has favoured process mass intensity, which expresses a ratio of the weights of all materials (water, organic solvents, raw materials, reagents, process aids) used to the weight of the active drug ingredient produced. This is an important focus because of the historically large amount of waste coproduced during drug manufacturing. However, when companies apply green chemistry principles to the design of the process, dramatic reductions in waste are often achieved, sometimes as much as ten-fold.

2. AtomEconomy

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 ChemicalSyntheses

> 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 beused.

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 bydesign.

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 safermolecules.

4. Designing SaferChemicals

Chemical products should be designed to affect their desired function whileminimizing theirtoxicity.

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 andAuxiliaries

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 thatcounts.

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. Design for EnergyEfficiency

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

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 theflask.

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 RenewableFeedstocks

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 50years.

8. ReduceDerivatives

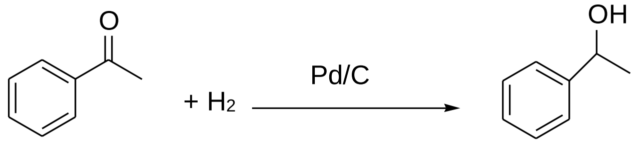
Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

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. 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 ofthe 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 greenchemistry.

10. Design forDegradation

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 mustoccur 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 continuestoday.

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 productformulation.

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 moreensured.

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 processanalytical 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 AccidentPrevention

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 highlightedinOSHA’snewTransitioningtoSaferChemicalsToolkitillustratesthe 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.

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

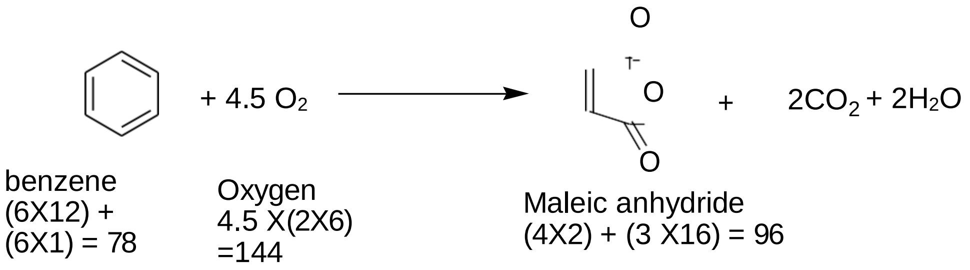
$$\text{Atomeconomy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in reactants}} \text{ X } 100\%$$

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.

Examples

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

Maleicanhydridefrombenzene



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.

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

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.

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

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.

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

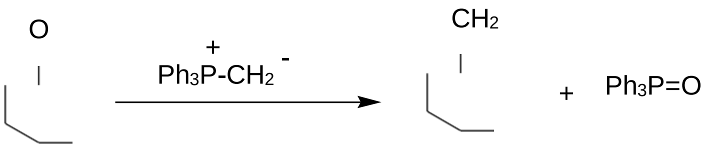
(12X6) +
(1X6)= 78

(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%.

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

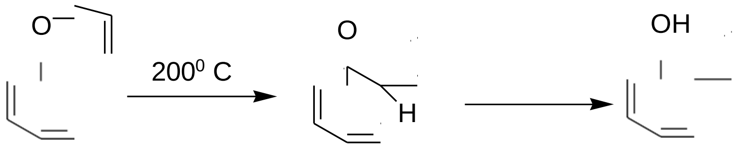
Wittig reaction

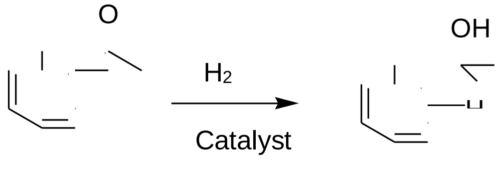


$$\text{Atom economy} = \frac{96}{98 + 276} = 25.7\%$$

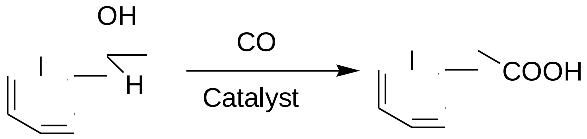
Rearrangements (100% atom economy)

Claisen rearrangement



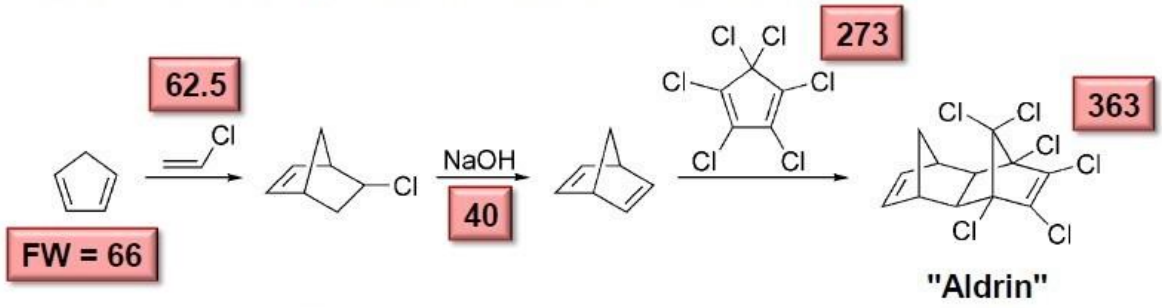


Hydrogenation



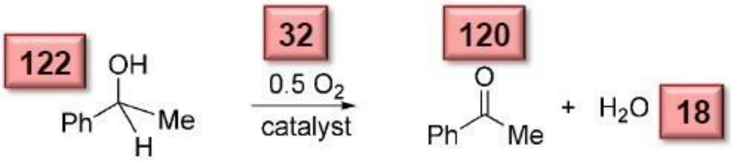
Carbonylation

Cycloadditions, e.g. Diels-Alder (100% atom economy)



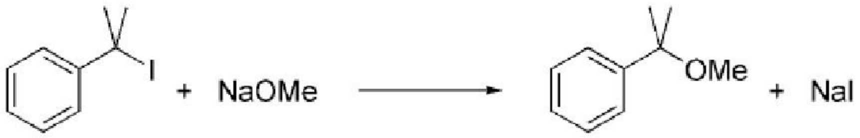
Overall atom economy = 363 / (66 + 62.5 + 40 + 273)
= 82.2 %

Oxidations

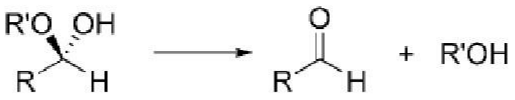


Atom economy = 120 / (122 + 16) = 87.0 %

Substitutions



Eliminations



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.

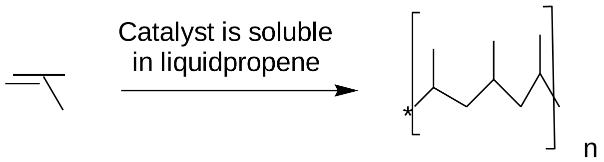
The main alternatives to organic solvents are

1. Solvent freeprocesses
2. Waste basedchemistry
3. Use of super critical fluids (particularly water andCO_2)
4. Ionicliquids
5. Fluorous biphasicsystems

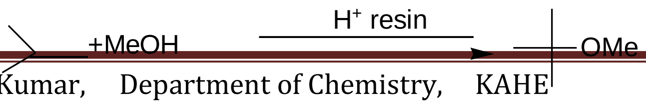
There are several ways in which organic solvents may be replaced and a good argument can often be made for doing so on green chemistry grounds. However, it is important to remember that changing solvents may require additional energy (e.g. stronger heating), and organics may still be needed for work-up/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

Many high-volume chemicals are already produced without solvents

e.g. polymerization of propene (Catalyst is soluble in liquid phase)



Synthesis of MTBE: (Fuel additive in USA): Liquid phase reaction (90 C, 8 atm)



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 overcomeusing microwaves)
3. Fewer solvent-free examples exist for finechemicals/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 fororganics.

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 usesdichloromethane)
2. Extraction of fatty acid glycerides fromcrisps
3. Dry cleaning (traditional method usesC_2Cl_4)
4. Spraypainting.

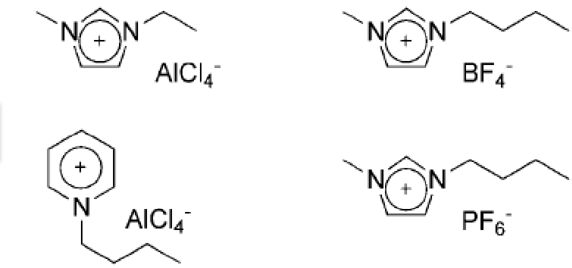
The advantages are

Non-toxic, readily removed (and recyclable), Non-flammable, low viscosity (fast diffusion), CO_2 is cheap. The disadvantages are highpressure 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

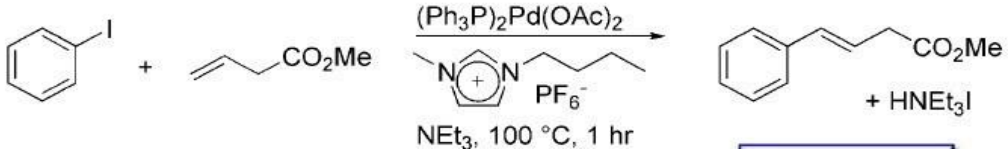


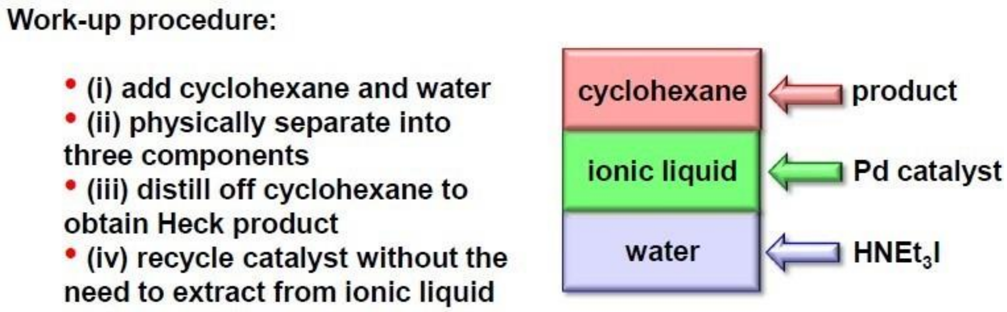
Advantages are

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.

Pd-catalysed Heck arylation





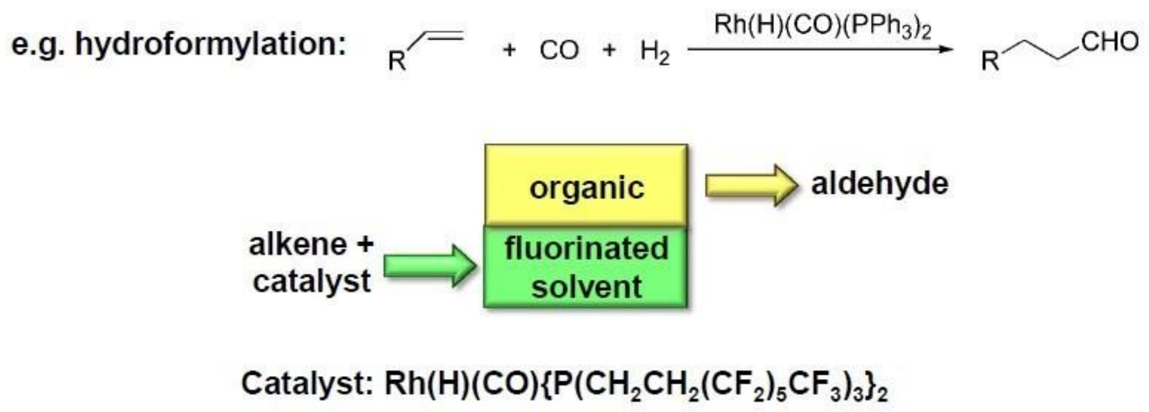
Work-up procedure:

- **(i) add cyclohexane and water**
- **(ii) physically separate into three components**
- **(iii) distill off cyclohexane to obtain Heck product**
- **(iv) recycle catalyst without the need to extract from ionic liquid**

Fluorousbiphasics

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



POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What is GreenChemistry?
2. Why do we need GreenChemistry?
3. Write a comparative statement on green chemistry and syntheticchemistry.
4. What are the economic benefits of Green Chemistry?
5. What is the goal of the Green ChemistryInitiative?
6. Give one example to 100% atomeconomy?
7. What is meant by GreenChemistry?
8. What are the educational challenges lying behind the GreenChemistry?
9. What is the difference between Environmental Science and GreenChemistry?
10. Is Green Chemistry more expensive that traditionalChemistry?
11. What is meant by Less Hazardous ChemicalSynthesis
12. Explain the greener reagents with twoexamples.
13. How do you evaluate the chemical reactions according to their yield andatom efficiency?

14. Why are reactions performed usingsolvents?
15. What is meant by Non-organic solvents? Giveexamples.
16. What are fluorous solvents. Give twoexamples.
17. What are the advantages in carrying out the reactions using a micro waveoven

PART C (8 Mark Questions)

1. What is green Chemistry? What are the twelve principles of greenchemistry
2. “Green Chemistry is important in alternate reactionpathways”-Explain
3. How does the Green Chemistry Initiative differ from traditional efforts toreduce pollution?
4. Explain the following reactions with special reference to green chemistry. (a)Aldol condensation (b) Diels-Alderreaction
5. Explaintheadvantagesandlimitationsofsolventlessreactions.Givesomeexamples for solid statereactions.
6. Write notes on organic reactions in aqueousmedia.
7. What are the tools used in the green chemistry
8. Comment on “designing safer chemicals” in greenchemistry
9. Explain an atom efficient Process taking an Elimination reaction as anexample

DEPARTMENT OF CHEMISTRY

Online questions (Multiple choice questions)

GREEN METHODS IN CHEMISTRY (18CHU404A)

UNIT I

S.No	Question	Option 1	Option 2	Option 3	Option 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 'costlier' products to entice customers	Non- compliance with environmental legislation	Avoiding solvents	Reduced costs associated with waste treatment and disposal
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 of the following is the greenest solvent?	Formaldehyde	Benzene	Ethanol	Water	Water
10	An example for green chemistry is ?	Recycled carpet	A product made on earth day	A sublimation reaction	Bio plastics	Bio plastics
11	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
12	Green chemistry can reduce all but not one among the following?	Cost	Risk & hazard	Awarness	Waste	Awarness
13	Green chemistry synthesis could also involve which of the following?	High temperature	Dichloromethane	Fossil fuels	Microwave	Microwave
14	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
15	When discussing sustainability and green chemistry often used moral arguments and	Environment	Technology	Politics	Ethics	Ethics
16	Which of the following term is used in the 'Sustainability triangle'?	Micro-economics	Planet	Social responsibility	economics	Social responsibility
17	The term used to measure a product or person's environmental impact is?	Handprint	Co2 print	Footprint	Hazardous print	Footprint
18	In which reactions one atom is replaced by another atom	Substitution reactions	Addition reactions	Rearrangement reactions	Elimination reactions	Substitution reactions
19	The reaction involve rearrangement of atoms that make up a molecule is	Rearrangement reactions	Substitution reactions	Elimination reactions	Addition reactions	Rearrangement reactions
20	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 reactions
21	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 reactions
22	Solvent doesn't used in the reaction is called	Elimination reaction	Substitution reactions	Addition reaction	Solvent less reaction	Solvent less reaction
23	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 act of 1990

24	In 1998, this state signed green chemistry legislation promising to remove politics from the evaluation of disputed chemicals?	Oregon	California	Newyork	Florida	California
25	The following is often referred to as the universal solvent and is a preferred green solvent?	Water	Methanol	Ethyl acetate	Benzene	Water
26	A chemical process with an E-Factor of 1 creates less waste than an E-Factor of	21	25	22	23	25
27	Lignin,switch grass,and cellulose are all types of?	Enzymes	Catalysts	Bio-based feedstock's	Anti-cancer compounds	Bio-based feedstock's
28	Which is an excellent 'green' solvent as well as a greenhouse gas?	Methanol	CFCs	Carbonmonoxide	Carbondioxide	Carbondioxide
29	Which one interfere with hormone systems in animals and humans and are abbreviated EDC's ?	Endocrine destructive components	Energy disrupting chemicals	Endocrine disrupting chemicals	Enzyme destructive components	Endocrine disrupting chemicals
30	Which can provide green technology solutions for a sustainable future?	Inorganic chemistry	Textile chemistry	Physical chemistry	Green chemistry	Green chemistry
31	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
32	Bio-polymers exemplify green chemistry principle #10,which is ?	Catalysis	Prevent waste	Benign solvents & auxiliaries	Design for degradation	Design for degradation
33	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
34	Who was the co-founder of the worldwide green chemistry movement and the first director of the green chemistry institute ,now part of ACS?	Joseph breen	Albert einstein	John warner	Paul anastas	Paul anastas
35	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	Water	Vinegar(acetic acid)
36	Who was instrumental in winning a	Leonardo dicaprio	George clooney	Erin brockovich	Angelina jolie	Erin brockovich

	1996 legal settlement of $333 million for the california town of Hinkley due to chromium in its drinking water?					
37	Used to indicate the level of contaminants present , the term 'PPM' means?	Parts - per-micron	Parts-per-million	Parts-per-mass	Parts-per-molecule	Parts-per-million
38	The term missing in Risk=Hazard×?	Exposure	Cancer	Benign	Reactivity	Exposure
39	The following term refers to the relative proportion of chemical components?	Togetherness	Stoichiometry	Metric	Colligative	Stoichiometry
40	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	Eliminating the formation of chlorinated organics in paper
41	TRI is used by the EPA to track pollution prevention.TRI stands for?	Total reporting inventory	Total release impact	Toxic release inventory	Toxic release impact	Toxic release inventory
42	Which are considered as renewable starting materials ?	Co2	methane gas	Co	Co2 & methane gas	Co2 & methane gas
43	There should be maximum incorporation of the starting materials and reagents into the final product ? It refers to	Percentage atom utilization	Atom economy	Use of renewable feedstocks	Design for energy efficiency	Percentage atom utilization
44	The reaction involved must be evaluated with regard to its environmental impact or consequences is	Evaluating the type of the reaction involved	Percentage atom utilization	Selection of starting materials	Use of renewable feedstocks	Evaluating the type of the reaction involved
45	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
46	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
47	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
48	A typical reaction which has been	Diels-Alder reaction	Mannich reaction	Knoevengal	Friedel-crafts	Diels-Alder reaction

	carried out in aqueous phase is the			condensation	reaction	
49	Which should be avoided as far as possible ,since they generate wastes?	Use of catalyst	Use of microwave	Use of protecting group	Selection of appropriate solvent	Use of protecting group
50	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
51	Heart of green chemistry is	to maximize the waste products formation	to minimize the waste products formation	to increase the toxic materials	to increase toxic materials and waste products formation	to minimize the waste products formation
52	PFC is abbreviated as	Perfluoro carbons	Perfluoro carbonyls	Perfluoro carboxyls	Perfluoro chlorine	Perfluoro carbons
53	Environmental factor of petroleum refining is	one	two	four	Zero	Zero
54	Which deals with envionmentally benign chemical synthesis with a view to devise pathways for the prevention of pollution?	Textile chemistry	Inorganic chemistry	Physical chemistry	Green chemistry	Green chemistry
55	The substitution reactions are less atom economical than	rearrangement or addition reactions	addition or elimination reactions	elimination or rearrangement reactions	Pericyclic or addition reactions	Rearrangement or addition reactions
56	The hydration of alkynes gives	aldehydes	ketones	Carboxylic acids	Aldehydes or ketones	Aldehydes or ketones
57	Hydrogenation of propene in presence of nickel catalyst gives	Toluene	Propane	Propyne	Propanol	Propane
58	Oxidation of toluene with KMno4 in presence of crown ether gives	Benzoic acid	Benzyl cyanide	Benzyl chloride	Oxalic acid	Benzoic acid
59	Bromination of propene gives	1,2-Dibromopropane	1,3-Dibromopropane	1,2-Dibromopropanol	Propane	1,2-Dibromopropane
60	Benzyl chloride reacts with KCN gives	Benzoic acid	Benzyl cyanide	Acetaldehyde	Butyl iodide	Benzyl cyanide
61	The nonpolar molecules fail to interact with the	Microwave radiation	Ultraviolet radiation	Infrared radiation	Radiofrequency radiation	Microwave radiation
62	Which type of molecules is fail in Microwave radiation	Polar molecules	Nonpolar molecules	Aprotic molecules	Proteic molecules	Nonpolar molecules

UNIT II

SYLLABUS

Green Chemistry and catalysis and alternative sources of energy, Green energy and sustainability

Catalysis

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 reactionmedia.

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 blendthe many advantages of heterogeneous catalysis with the versatility of homogeneouscatalysts.

Heterogeneous catalysts have several advantages compared to other catalytic processes

- they avoid formation of inorganicsalts
- they areregenerable
- easy to handle, safe to store and has long lifetime
- easy and inexpensive of recovery andrecycling
- the selectivity and activity of homogeneous catalysts under mild reaction conditionsis

unbeaten by their heterogeneous counter parts.

Green Catalysts

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 moleculeof catalyst can perform several transformations That allows scientists to get high yields from areaction 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. Stoichiometricreductionswithmetals(Na,Mg,Zn,Fe)andmetalhydridereagents ($LiAlH_4$,$NaBH_4$),
2. oxidations with permanganate, manganese dioxide and chromium(VI) reagentsand

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).

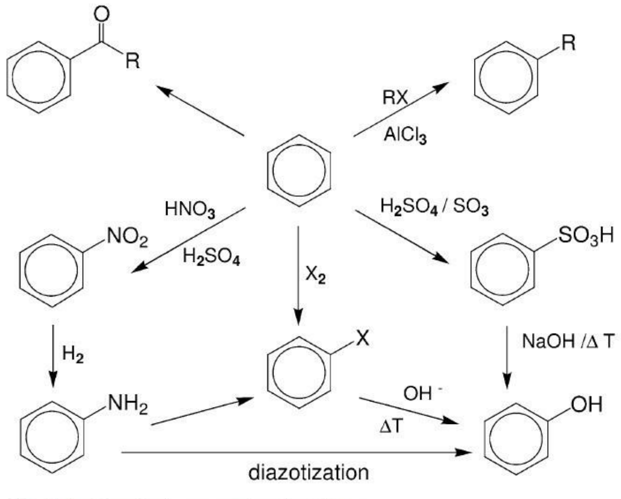
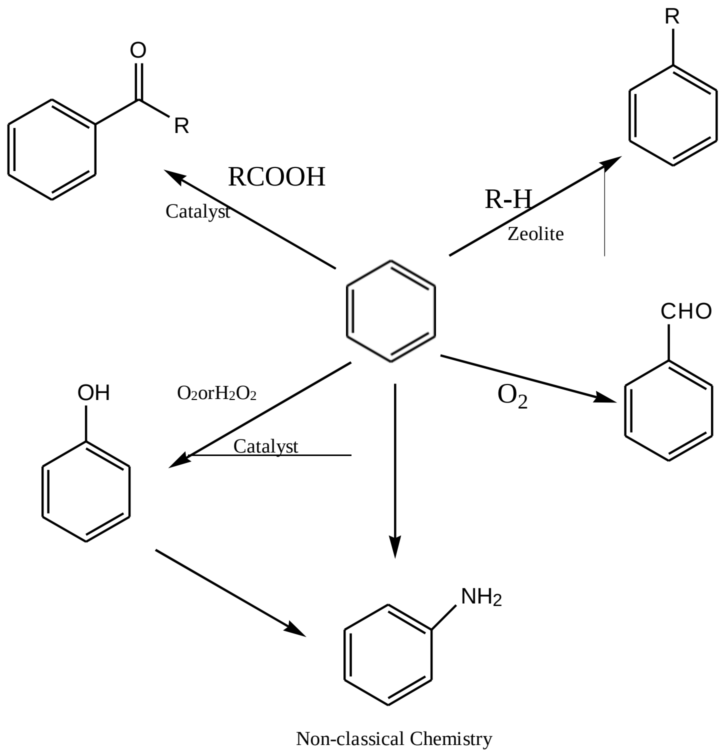


Fig. 1.4 Classical aromatic chemistry.

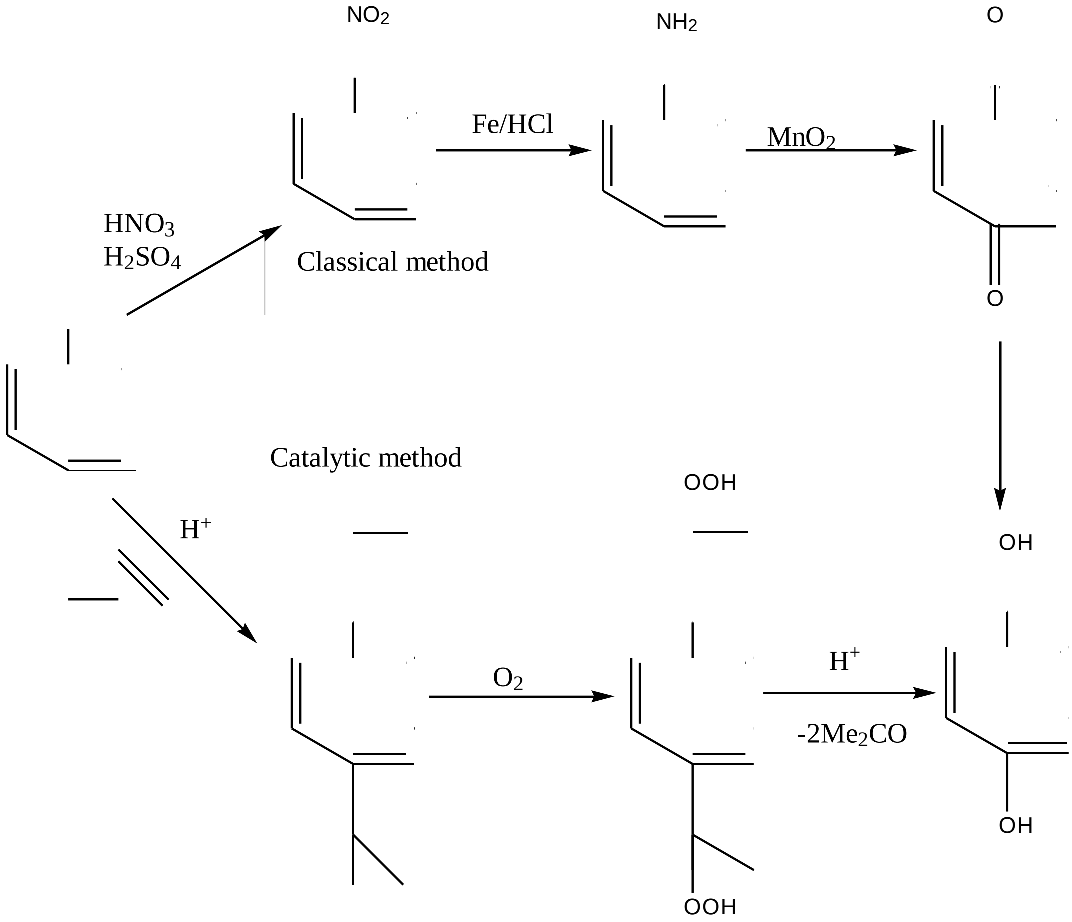
The solution is to substitute the classical stoichiometric methodologies with cleaner catalytic alternatives. Indeed, a majorchallenge in (fine) chemicals manufacture is to develop processes based on H_2, O_2, H_2O_2, CO, CO_2 and NH_3 as the direct source of H, O, C and N. Catalytic hydrogenation, oxidation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

The generation of large amount of inorganic salts can similarly be largely circumventedby replacing stoichiometric mineral acids, such as H_2SO_4, and Lewis acids and stoichiometric bases,suchasNaOH,KOH,withrecyclablesolidacidsandbases,preferablyincatalytic 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 hydrogenperoxide.



Biocatalysis has many advantages in the context of green chemistry, e.g. mild reaction conditions and often fewer steps than conventional chemical procedures because protection and deprotection of functional groups are often not required. Consequently, classical chemical procedures are increasingly being replacedby cleaner biocatalytic alternatives inthe fine chemicals industry.

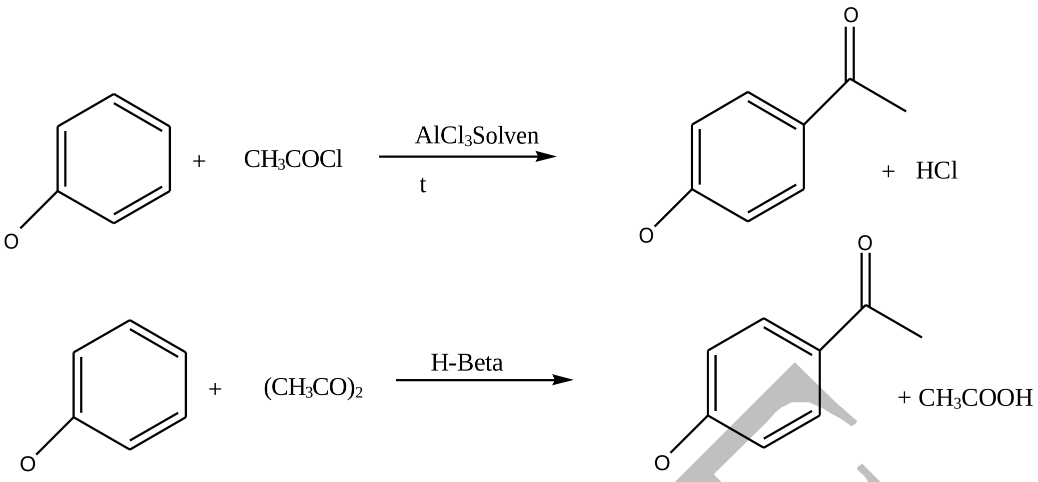
Catalysis by Solid Acids and Bases

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. Theirwidespread replacement by recyclable solid acids would afford a dramaticreduction in waste. Solid acids, such as zeolites, acidic clays and relatedmaterials, have many advantages in thisrespect.

1. They are trulycatalytic and can easily be separated from liquid reaction mixtures,avoiding the need for hydrolytic work-up, andrecycled.
2. Moreover, solid acids are non-corrosiveand easier (safer) to handle than mineral acids such as H_2SO_4 orHF.

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, togive *p*-methoxyacetophenone (Fig. 1.8). The original process used acetyl chloridein 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 ofproduct.

The catalytic alternative, in stark contrast, avoidsthe 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, consistingof 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 superiorto 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 organicsynthesis. Molecular hydrogen is a clean and abundant raw material and catalytichydrogenations 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 availableto the organic chemist. The scope of the reaction is very broad; mostfunctional groups can be made to undergo reduction, frequently in high yield,to any of several products. Multifunctional molecules can often be reduced selectivelyat any of several functions. A high degree of stereochemical control ispossible with considerable predictability, and products free of contaminatingreagents are obtained easily. Scale up of laboratory experiments to industrialprocesses presents little difficulty.”

Most of the above comments apply to heterogeneous catalytic hydrogenationsover supported Group VIII metals (Ni, Pd, Pt, etc.). Although catalytic hydrogenation is a mature technology that is widely appliedin industrial organic synthesis, new applications continue to appear, sometimesin 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 alkylationof an aldehyde has been reported. This avoids the coproductionof NaCl, which may or may not be a problem, depending on the productionvolume. Furthermore, the aldehydes may, in some cases, bemore readily available than the corresponding alkylchloride.

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 bulkpetrochemicals.

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.

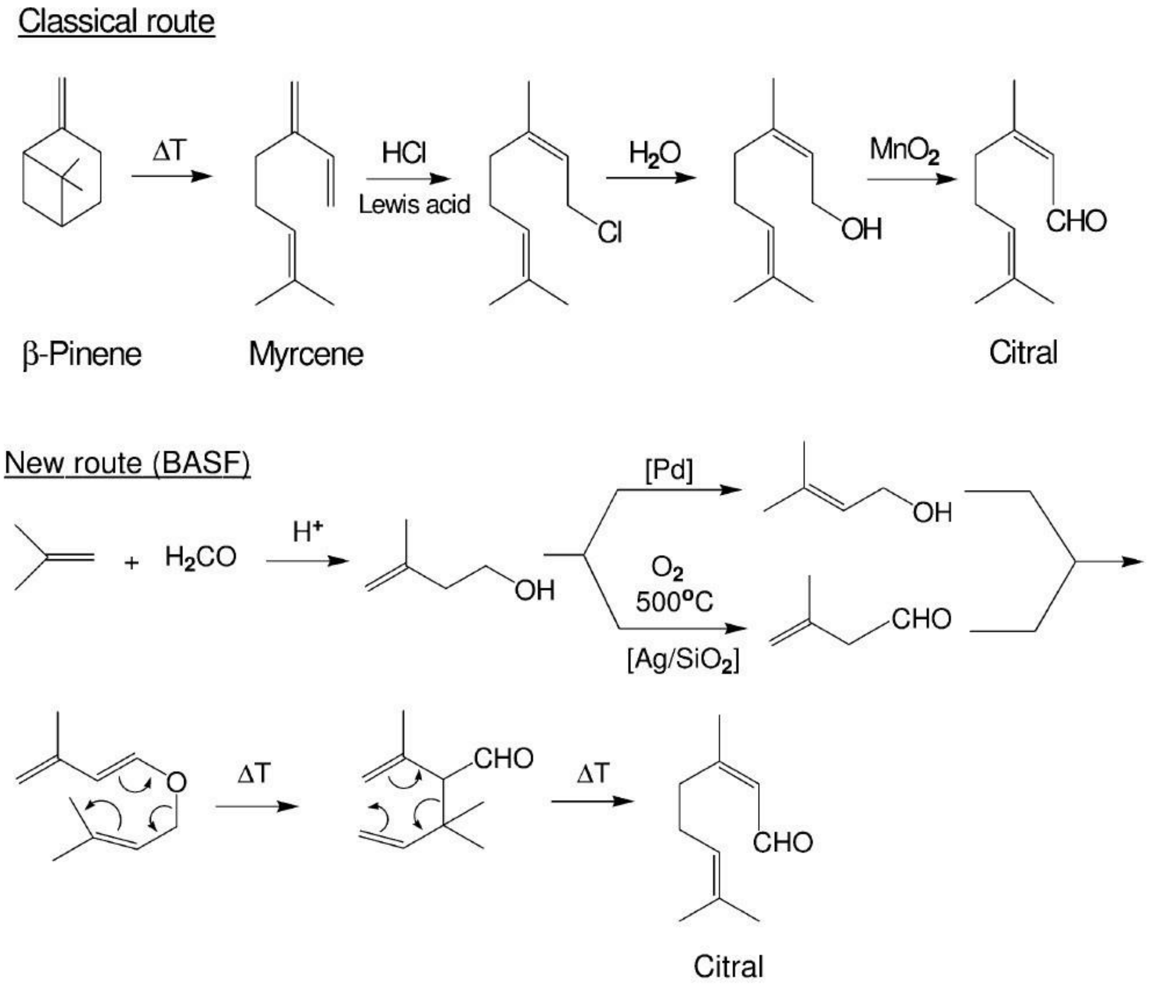
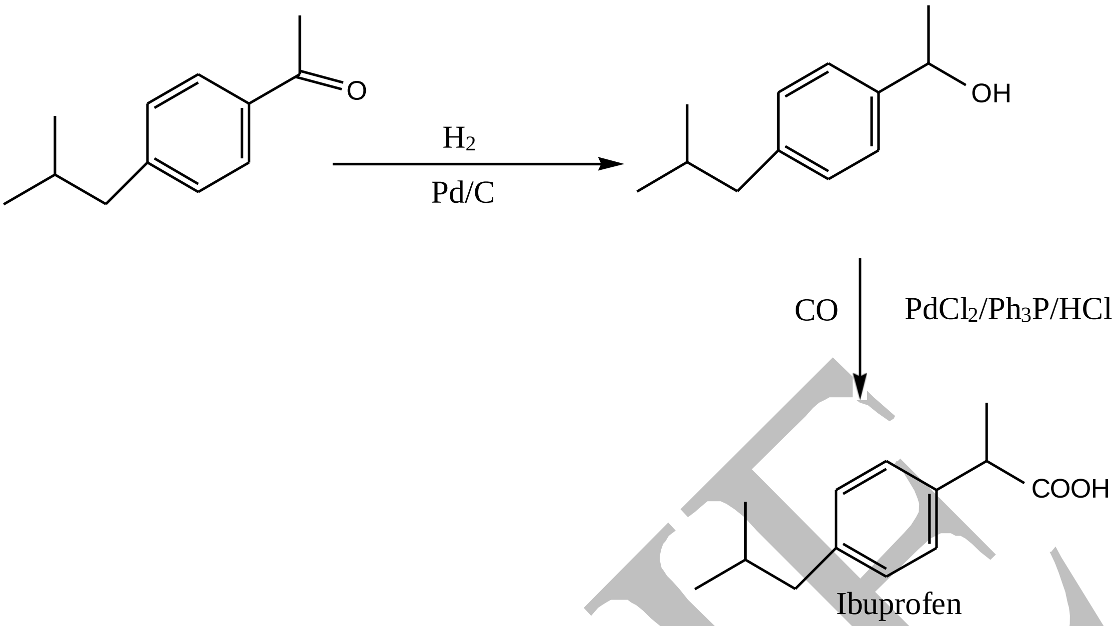


Fig. 1.19 Two routes to citral.

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.



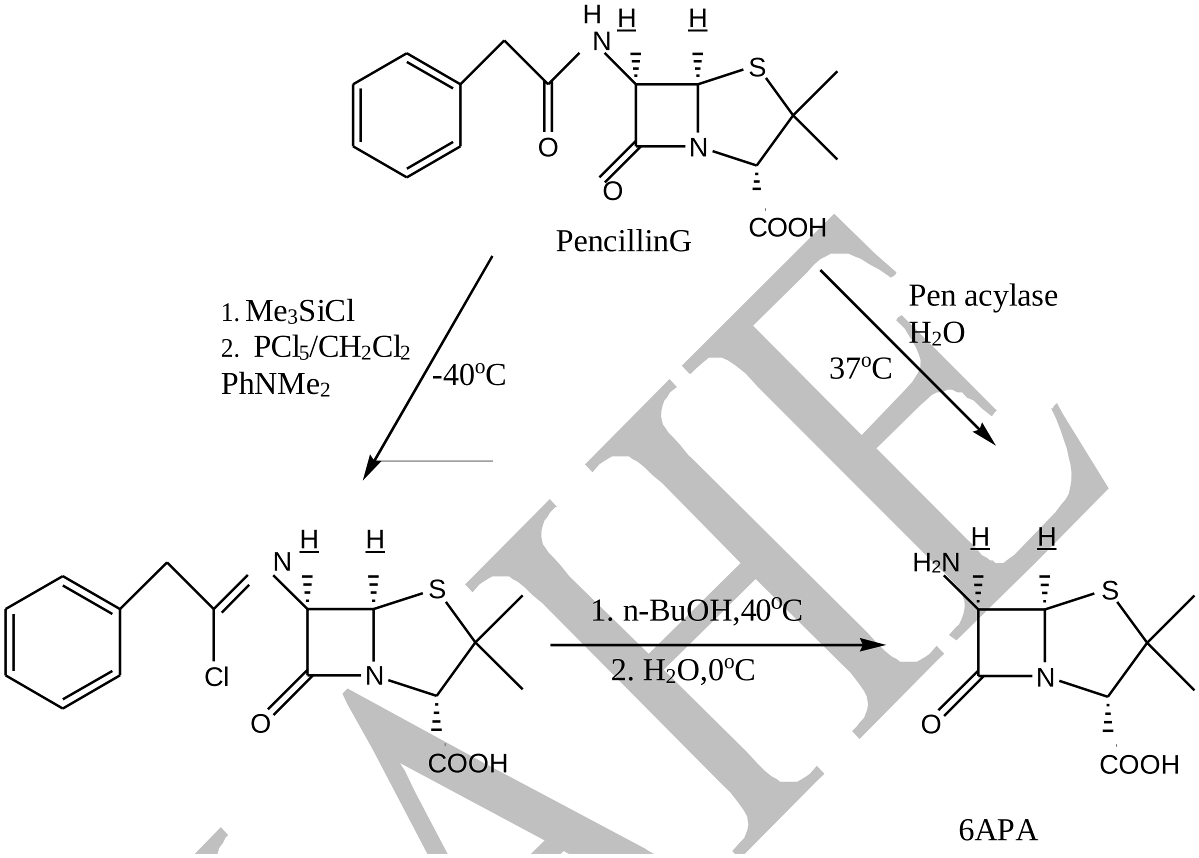
Ibuprofen

Biocatalysis

Biocatalysis has many attractive features in the context of green chemistry: mildreaction conditions (physiological pH and temperature), an environmentallycompatible catalyst (an enzyme) and solvent (often water) combined with highactivities and chemo-, regio- and stereoselectivities in multifunctional molecules.Furthermore, the use of enzymes generally circumvents the need for functionalgroup activation and avoids protection and deprotection steps required in traditionalorganic syntheses. This affords processes which are shorter, generate less waste and are, therefore, both environmentally and economically more attractivethan conventional routes.

An illustrative example of the benefits to be gained by replacing conventionalchemistry 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 chemicalprocedure was used for this hydrolysis (Fig. 1.37). It involved the use of environmentallyunattractive 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 requiredto produce 1 kg of6-APA.

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



Traditionally, transition metals like palladium, platinum, and ruthenium are used to build catalystsfor carbon-carbon bond-forming reactions However, these metals are expensive and in lowabundances in the Earth's crust. In some cases, the catalysts require large ligands to control theselectivity 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 moreavailable and sustainable metal: iron. Iron catalysts can carry out a wide range of crosscouplingreactions.

Another independent area of research isnanoscience. Attaching catalysts to magneticnanoparticles makes it easy for chemists to separate andrecycle the catalyst after a reactionOther types of catalysts can reduce safety risks Acidcatalysts attached to silica, for example, reducethe aqueous waste generated by quenching andneutralizing a reaction.

Phase transfer catalysts (oftenammonium salts) carry an insoluble reactant between the organic and aqueous phases in a mixture Chemistsused tetrabutylammonium bromide to catalyze thedisplacement of a chloride by a cyanide ion on a processscale The reaction releases heat, but the researchers couldcontrol the exotherm and prevent a temperature spike justby controlling the stirring speed.

Reducing Toxicity By Design

Toxicologists track how chemicals harm the body, by studying their effects on biochemical pathways, cells, and tissues They also uncover relationships between the dose of a chemical and its physical effect These dose-response relationships are part of risk assessment and hazard management plans But one principle of green chemistry aims to do more than manage risks; it challenges chemists to reduce a molecule’s toxicity during the design process, rather than managing the effects after a molecule has been synthesized.

Currently, it’s not possible to fully predict the toxicity of any new molecule But principles of toxicology can help chemists identify characteristics of a molecule that might impart toxicity (41) Certain molecular structures bind to metabolic enzymes Other electron-poor molecules are carcinogenic because they bind to DNA And fat-soluble molecules can accumulate infat cells and not be cleared from thebody.

Medicinal chemists can exploit some of these structures to help develop killer drugs specific for diseased cells Green molecular designers, however, want to avoid those structures, as they want to prevent a molecule from causing biological harm

Alternative energy sources for reactions

Running reactions can be energy intensive. When chemists boil a reaction, they simultaneouslycool the solvent vapours. The resulting droplets fall into the reaction so that the reaction neverruns dry. But this standard process requires energy to both heat and cool the reaction, inaddition to the water being constantly run through a condenser. Therefore, some green chemists look to new energy sources to drive reactions.Microwaveassisted reactions can be run in water at a small scale, often with accelerated rates due totemperature and pressure effects. Reactions to build oxygen-, nitrogen- or sulfur-containingrings common in medicinal chemistry can also be driven using microwaves. Alternatively, the energy from grindingreagents together using a mortar and pestle or a ball grinder can be enough to triggerareaction.

Ultrasound sonication is another energy source with useful applications such as deprotecting an amine, protecting hydroxyls on sugars, or reducing an α,β-unsaturated ketone in a steroid The sound waves create areas of high and low pressure, much like ripples in a pond, as they travel through liquid. Bubbles form in the low-pressure areas, collapse when they reach high-pressure regions, and send shockwaves through the reaction. Surprisingly, ultrasound sonication can influence the products of a reaction. When chemists stirred a suspension of benzyl bromide and alumina-supported potassium cyanide, they retrieved diphenylmethane, which contains two connected benzene rings, as the product of a Friedel-Crafts reaction. But when they sonicated the reaction, the cyanide ion replaced the bromine atom, giving benzyl cyanide as the product. The researchers suspect that the bubbles generated during sonication masked the metallic catalytic sites on the solid support.

In 1830, scientists discovered *photo-voltaic* compounds, which release energy when exposed to light. This discovery eventually led to the development of *solar cells and solar power*.

In 1839, William Robert Grove invented the first *hydrogen fuel cell*, which harnessed electricity from the reaction between hydrogen and oxygen.

In the late 1880, *hydroelectric power* first became commercially available in the United States, and solar power was discovered in Europe. Governments established the first energy departments shortly before the turn of the century.

In 1947, The first nuclear reactor project aimed at energy production was initiated in Brookhaven, New York.

In 1970, the US Environmental Protection Agency (EPA) was established. Damage to natural areas as a result of *energy harvesting* was one of the first issues addressed by the agency.

In 1976, Congress authorized a committee to examine the potential for the development of electric vehicles, with the goal of reducing dependence on fossil fuels.

Solar poweris the conversion of sunlightintoelectricity, either directly using *photovoltaics (PV)*, or indirectly using*concentrated solar power (CSP)*. Concentrated solar power systems use lenses or mirrors and tracking systems to focus a large area of sunlight into a small beam. Photovoltaics convert light into an electric currentusing the photovoltaic effect.

How can an organization use it? Public and private entities can take advantage of the benefits of solar power for business in a wide variety of ways:

- Install a commercial solar power system (rooftop equipment, field array orcarport) and become an owner/operator, lessee or participant in a solar power purchase agreement(PPA).
- Purchase solar energy that’s been generated by an offsitecommercial solarinstallation.
- Construct or retrofit a building to incorporate a solar hot water, cooling or ventilation system.

Wind power is the use of air flow through wind turbines to mechanically power generators for electricity. Wind power, as an alternative to burning fossil fuels, is plentiful, renewable, widely distributed, clean, produces no greenhouse gas emissions during operation, and uses little land.

Bioenergy

The term “biomass” refers to organic matter that has stored *energy* through the process of *photosynthesis*. It exists in one form as plants and may be transferred through the food chain to animals’ bodies and their wastes, all of which can be converted for everyday human use through processes such as *combustion*, which releases the *carbon dioxide* stored in the plant material.

Many of the *biomass fuels* used today come in the form of wood products, dried vegetation, crop residues, and aquatic plants. Biomass has become one of the most commonly used renewable sources of energy in the last two decades, second only to*hydropower* in the generation of electricity.

It is such a widely utilized source of energy, probably due to its low cost and indigenous nature, that it accounts for almost 15% of the world's total energy supply and as much as 35% in developing countries, mostly for cooking and heating.

Advantages of Biomass Energy includes:

1) Biomass used as a fuel reduces need for fossil fuels for the production of heat, steam, and electricity for residential, industrial and agriculturaluse.
2)Biomass is always available and can be produced as a renewable resource.
3)Biomass fuel from agriculture wastes maybe a secondary product that adds value to agriculturalcrop.
4) Growing Biomass crops produce oxygen and use up carbondioxide.
5) The use of waste materials reduce landfill disposal and makes more space foreverything else.
6) Carbon Dioxide which is released when Biomass fuel is burned, is taken inby plants.
7)Less money spent on foreignoil.

Disadvantages of Biomass Energy includes:

1)Agricultural wastes will not be available if the basic crop is no longer grown.
2)Additional work is needed in areas such as harvesting methods.
3) Land used for energy crops maybe in demand for other purposes, such asfaming, conservation, housing, resort or agriculturaluse.

This is a type of renewable energy derived from biomass to create heat and electricity (or to produce liquid fuels used for transportation, like ethanol and biodiesel). Biomass refers to any organic matter coming from recently living plants or animals. Even though bioenergy generates about the same amount of carbon dioxide as fossil fuels, the replacement plants grown as biomass remove an equal amount of CO_2 from the atmosphere, keeping the environmental impact relatively neutral. There are a variety of systems used to generate this type of electricity, ranging from directly burning biomass to capturing and using methane gas produced by the natural decomposition of organic material.

How can an organization use it? Depending on your operation, there are many ways to incorporate bioenergy into your sustainable energy plans:

- Organizations can convert to fleet vehicles that use biofuels such as ethanolor biodiesel.
- Manufacturing facilities can be equipped to burn biomass directly, producing steam captured by a turbine to generate electricity. In some cases, this process can powerthe facility as well as heating it. For example, paper mills can use wood waste to produce electricity and steam forheating.
- Farm operations can convert waste from livestock into electricity usingsmall, modularsystems.
- Towns can tap the methane gas created by the anaerobic digestion of organic waste in landfills and use it as fuel for generatingelectricity.

Geothermal Power

Energy from the Earth What could be more natural or plentiful? The source of geothermal power is the heat contained inside the Earth; heat so intense that it creates molten magma. There are a few different types of geothermal energy that can be tapped. “Some geothermal systems are formed when hot magma near the surface (1,500 to 10,000 meters deep) directly heats groundwater.” The heat generated from these hot spots flows outward toward the surface, manifesting as volcanoes, geysers, and hot springs.

Naturally-occurring hot water and steam can be tapped by energy conversion technology to generate electricity or to produce hot water for direct use. “Other geothermal systems are formed even when no magma is nearby as magma heats rocks which in turn heat deeply-circulating groundwater.” In order to maximize the energy gleaned from these so-called “hot dry rocks," geothermal facilities will often fracture the hot rocks and pump water into and from them in order to use the heated water to generate electricity.

Advantages of Geothermal Energy:

- **ReduceRelianceonFossilFuels**:Dependenceonfossilfuelsdecreaseswiththeincrease in the use of geothermal energy. With the sky-rocketing prices of oil, many countries are pushing companies to adopt these clean sources of energy. Burning of fossil fuels releases greenhouse gases which are responsible for globalwarming.
- **No Pollution** : This is one of the main advantage of using geothermal energy since it does not create any pollution and help in creating clean environment. Being the renewable source of energy, geothermal energy has helped in reducing global warming and pollution. Moreover, Geothermal systems does not create any pollution as it releases some gasesfrom deep within the earth which are not very harmful to theenvironment.
- **Direct Use** : Since ancient times, people having been using this source of energy for taking bath, heating homes, preparing food and today this is also used for direct heating of homes and offices. This makes geothermal energy cheaper and affordable. Although the initial investment is quite steep but in the long run with huge cost saving it proves quiteuseful.

How can an organization use it? Geothermal energy can be part of a commercial utility energy solution on a large scale, or be part of a sustainable business practice on a local level. Direct use of geothermal energy may include:

- Heating office buildings or manufacturingplants
- Helping to grow greenhouseplants
- Heating water at fishfarms
- Aiding with various industrial processes (e.g. pasteurizing milk)

Hydroelectric

Remaining waterwheels previously used to operate the gristmills and sawmills of early America are now largely functioning as historic sites and museums. Today, the kinetic energy of flowing rivers is captured in a much different way and converted into hydroelectricity. Probably the most familiar type of hydroelectric power is generated by a system in which dams are constructed to store water in a reservoir. When released, the water flows through turbines to produce electricity. This is known as “pumped-storage hydropower”—water is cycled between lower and upper reservoirs to control electricity generation between times of low and peak demand. Another type, called “run-of-river hydropower,” funnels a portion of river flow through a channel and does not require a dam. Hydropower plants can range in size from massive projects like the Hoover Dam to micro-hydroelectric power systems.

How can an organization use it? Direct use of hydroelectric power is naturally dependent on geographic location. Assuming a dependable waterway source is accessible and available, it could be used in the following ways:

- Micro-hydroelectric plants can be constructed to supply electricity to farm andranch operations or smallmunicipalities.
- Small towns can harness the energy of local waterways by buildingmoderately-sized hydroelectric powersystems.

Hydrogen

Hydrogen is the simplest (comprised of one proton and one electron) and most abundant element in the universe, yet it does not occur naturally as a gas on earth. Instead, it is found in organic compounds (hydrocarbons such as gasoline, natural gas, methanol and propane) and water (H_2O). Hydrogen can also be produced under certain conditions by some algae and bacteria using sunlight as an energy source. Hydrogen is high in energy, yet produces little or no pollution when burned. Hydrogen fuel cells convert the potential chemical energy of hydrogen into electricity, with pure water and heat as the only byproducts. However, practical and widespread commercialization of these fuel cells will likely be limited until costs come down and durability improves.

How can an organization use it? Almost all the hydrogen used in the United States is used in industry to refine petroleum, treat metals, produce fertilizer and process foods. In addition, hydrogen fuel cells are used as an energy source where hydrogen and oxygen atoms are combined to generate electricity. There are also currently a few hundred hydrogen-powered vehicles operating in the United States, a number that could increase as the cost of fuel cell production drops and the number of refueling stations increases. Other practical applications for this type of renewable energy include:

- Large fuel cells providing emergency electricity for buildings and remotelocations
- Marine vessels powered by hydrogen fuelcells

POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What is meant by a catalyst. Explain with anexample.
2. What arecatalysis.
3. What is meant by homogenous catalysis. Give anexample
4. What is meant by heterogenous catalysis. Give anexample.
5. What are the disadvantages of conventionalcatalysts.
6. What are the advantages of greencatalysts.
7. Explainwithasuitableexampletheadvantagesofagreencatalystanddisadvantages of a conventionalcatalyst.
8. Mention the advantages of solid statecatalysis.
9. What is meant by biocatalysis. Giveexamples.
10. Explain in detail about bioenergy.

PART C (8 Mark Questions)

1. Explain in detail about the alternative energy sources used for taking outgreener reactions.
2. Describe any four alternative energysources.
3. Write notes on 1. Wing energy 2. Hydroelectric energy 3. Geothermalenergy
4. What are the advantages and disadvantages of biomassenergy.
5. Explain different types of catalysis with suitable examples. What are the advantages of greencatalysts.
6. “Green Chemistry is sustainable chemistry”- Explain thestatement
7. Write the principles of sustainability of greenchemistry

DEPARTMENT OF CHEMISTRY

Online questions (Multiple choice questions)

GREEN METHODS IN CHEMISTRY (18CHU404A)

UNIT II

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	The catalyst used for asymmetric epoxidation	Mn(III) complex with a chiral ligand	Rh(I) complex with a chiral diphosphine ligand	$(Ph_3P)RhCl$	$Co_2(CO)_8$	Mn(III) complex with a chiral ligand
2	The catalyst used for asymmetric hydrogenation	Mn(III) complex with a chiral ligand	Rh(I) complex with a chiral diphosphine ligand	$(Ph_3P)RhCl$	$Co_2(CO)_8$	Rh(I) with a chiral diphosphine ligand complex
3	The catalyst used for hydrogenation of olefin	Mn(III) complex with a chiral ligand	Rh(I) complex with a chiral diphosphine ligand	$(Ph_3P)RhCl$	$Co_2(CO)_8$	$(Ph_3P)RhCl$
4	The catalyst used for hydrogenation of olefin	Mn(III) complex with a chiral ligand	Rh(I) complex with a chiral diphosphine ligand	Wilkinson’s catalyst	$Co_2(CO)_8$	Wilkinson’s catalyst
5	The catalyst used for hydroformylation of olefin	Mn(III) complex with a chiral ligand	Rh(I) complex with a chiral diphosphine ligand	$(Ph_3P)RhCl$	$Co_2(CO)_8$	$Co_2(CO)_8$
6	Mn(III) complexs with a chiral ligand are catalyst for	asymmetric epoxidation	Assymetric hydrogenation	Hydrogenation of olefins	Hydroformylation of olefin	asymmetric epoxidation
7	Rh(I) complex with a chiral diphosphine ligand are catalyst for	asymmetric epoxidation	Assymetric hydrogenation	Hydrogenation of olefins	Hydroformylation of olefin	Assymetric hydrogenation
8	$(Ph_3P)RhCl$ is a catalyst for	asymmetric epoxidation	Assymetric hydrogenation	Hydrogenation of olefins	Hydroformylation of olefin	Hydrogenation of olefins
9	$Co_2(CO)_8$ is a catalyst for	asymmetric epoxidation	Assymetric hydrogenation	Hydrogenation of olefins	Hydroformylation of olefin	Hydroformylation of olefin
10	Wilkinson’s catalyst is a catalyst for	asymmetric epoxidation	Assymetric hydrogenation	Hydrogenation of olefins	Hydroformylation of olefin	Hydrogenation of olefins
11	Monsanto synthesis is for the preparation of	Acetic acid	acetaldehyde	Ethyl acetate	propylene	Acetic acid
12	The catalyst used for the	Mn(III) complex	$[Rh(Co)_2I_2]$ complex	Wilkinson’s	$Co_2(CO)_8$	$[Rh(Co)_2I_2]$ complex

	synthesis of acetic acid by Monsanto synthesis is			catalyst		
13	Wacker process is used for the synthesis of	Acetic acid	acetaldehyde	Ethyl acetate	propylene	acetaldehyde
14	In heterogenous catalysis the catalyst will be in------- phase	Liquid	solid	gas	gel	solid
15	The advantage of heterogenous catalysis	lower effective concentration on surface	Special catalyst preperation technique is required	Easier catalyst seperation takes place	The reaction takes place slowly	Easier catalyst seperation takes place
16	The advantage of heterogenous catalysis	lower effective concentration on surface	Special catalyst preperation technique is required	Easier handling, stability and safety of the catalyst	The reaction takes place slowly	Easier handling, stability and safety of the catalyst
17	The disadvantage of heterogenous catalysis	Easy catalyst seperation	Easy handling, stability and safety of the catalyst	Easy catalyst recycling	Special catalyst preparation techinques are required.	Special catalyst preparation techinques are required.
18	In Green chemistry the role of catalysis is	Replace toxic reagents	Enable less efficient process	To have low atom economy	To increase the cost of the process	Replace toxic reagents
19	In biocatalysis the catalysts are	Enzymes	Transition metal ions	Alkali metals	Alkaline earth metals	Enzymes
20	In biocatalysis the solvent which is often used is	Chloroform	Ethanol	Water	Blood serum	Water
21	The catalyst used for manufacture of 6-aminopenicillanicacid (6-APA)	Penacylase	Invertase	Zymase	$Co_2(CO)_8$	Penacylase
22	Elements which are good catalysts and have ability to change their oxidation number are	transition elements	Noble gases	Alkali metals	Alkali earth metals	transition elements
23	The green catalyst used for Friedel-Crafts acylation is	Aluminium Chloride	Boron trifludoride	Zeolite beta	Zinc chloride	Zeolite beta
24	Zeolite beta is used as a green catalyst for	Friedel Crafts alkylation	Friedel Crafts Acylation	Mannich Reaction	Claisen condensation	Friedel Crafts Acylation
25	For the conventional Friedel-Crafts acylations the quantity	In the Stoichiometric quantity	Less than 1 gram	In Nanogram scale	In micrograms	In the Stoichiometric quantity

	of catalyst used is					
26	In the Friedel-Crafts acylations the original process used acetyl chloridein combination with 1.1 equivalents of $AlCl_3$, the amount of waster material generated per kg of the product is	4.5 kg	1.5 kg	2.5 Kg	1.2 Kg	4.5 kg
27	The catalyst used for the Friedel Crafts reaction in Conventional method is	Aluminium Chloride	Boron Silicates	Zeolite beta	Zinc chloride	Aluminium Chloride
28	The solvent used for the Friedel Crafts reaction in Conventional method is	Anisole	Chlorinated hydrocarbon	Toluene	Ethanol	Chlorinated hydrocarbon
29	In Béchamp reduction for the conversion of nitrobenzene to aniline the catalyst used is	Mn(III) complex with a chiral ligand	Rh(I) complex with a chiral diphosphine ligand	iron and hydrochloric acid	Cobalt complexes	iron and hydrochloric acid
30	Example for a metal hydride reagent	Sodium borohydride	$AlCl_3$	$ZnCl_2$	H_3PO_4	Sodium borohydride
31	Examples of highly atom efficient, low-salt processes.	Catalytic hydrogenation	Hofmann elimination	Dehydrogenation reaction	Nitration reactions	Catalytic hydrogenation
32	The greener reagent used for oxidation	Potassium permangnate	Potassium dichromate	Chromic acid	Catalytic oxidation with oxygen	Catalytic oxidation with oxygen
33	An alternate energy source for carrying out reactions	Microwaves	Green house gases	Ozone	Wind energy	Microwaves
34	An alternate energy source for carrying out reactions	Ultrasound sonication	Green house gases	Ozone	Wind energy	Ultrasound sonication
35	**Solar power** is the conversion of sunlight into electricity using	photovoltaics	Microwaves	Ultrasound sonication	Fuel cells	photovoltaics
36	**Solar power** is the conversion of sunlight into electricity using	concentrated solar power	Microwaves	Ultrasound sonication	Fuel cells	
37	The principle in concentrated solar power	power systems use lenses or mirrors and tracking systems to focus a large area of sunlight into a	convert light into an electric current	waves create areas of high and low pressure, much like ripples	Generate microwaves	power systems use lenses or mirrors and tracking systems to focus a large area of sunlight into a

		small beam		in a pond, as they travel through liquid		small beam
37	power systems use lenses or mirrors and tracking systems to focus a large area of sunlight into a small beam	concentrated solar power	Microwaves	Ultrasound sonication	photovoltaics	concentrated solar power
38	Substances which convert light into an electric current	concentrated solar power	Microwaves	Ultrasound sonication	photovoltaics	photovoltaics
39	waves create areas of high and low pressure, much like ripples in a pond, as they travel through liquid	concentrated solar power	Microwaves	Ultrasound sonication	photovoltaics	Ultrasound sonication
40	Air flow through wind turbines to mechanically power generators for electricity.	Hydroelectricity	Wind mill	Ultrasound sonication	photovoltaics	Wind mill
41	Example for a Nonrenewable energy source	Nuclear energy	Biomass energy	Ocean currents	Wind energy	Nuclear energy
42	Example for a renewable energy source	Nuclear fission	Nuclear fusion	Biomass energy	Fossil fuels	Biomass energy
43	Example for a renewable energy source	Nuclear fission	Nuclear fusion	Solar energy	Fossil fuels	Solar energy
44	Example for a conventional energy source	Wind energy	Ocean energy	Solar energy	Fossil fuels	Fossil fuels
45	Choose the conventional energy source	Wind energy	Ocean energy	Solar energy	Hydroelectricity	Hydroelectricity
46	Choose the Non-conventional energy source	Fossil fuels	Hydroelectricity	Atomic energy	Wind energy	Wind energy
47	Choose the Non-conventional energy source	Fossil fuels	Hydroelectricity	Atomic energy	Solar energy	Solar energy
48	Microwave radiation is selectively absorbed by	Non-polar molecules	Polar molecules	Neutral molecules	Gaseous molecules	Polar molecules
49	The vessels used in microwave heating	Teflon vessels	Pyrex glass vessels	Quartz glass vessels	Plastic containers	Teflon vessels
50	One among the advantages in using microwave irradiation for chemical reactions is	Quick reaction	We can reflux for longer hours	We can use halogenated hydrocarbons as	Recovery of products are not required	Quick reaction

				solvent		
51	One among the advantages in using microwave irradiation for chemical reactions is	Wont initiate a reaction quickly	Need not reflux for longer hours	We can use halogenated hydrocarbons as solvent	Recovery of products are not required	Need not reflux for longer hours
52	The frequency of microwaves to carryout chemical reactions is	20KHz to 100KHz	20KHz to 10KHz	10^9 to 10^{11} Hz	10^9 to 10^{11} MHz	10^9 to 10^{11} Hz
53	In sonochemistry the frequency of the waves are in the range	20KHz to 100KHz	20KHz to 10KHz	10^9 to 10^{11} Hz	110^9 to 110^{11} Hz	20KHz to 100KHz
54	Green chemistry synthesis could also involve which of the following	High Temperature	Dichloromethane	Fossil fuels	Microwaves	Microwaves
55	Green chemistry synthesis could also involve which of the following	High Temperature	Dichloromethane	Fossil fuels	Ultrasound waves	Ultrasound waves
56	Green and sustainable catalyst should not have	higher activity	higher selectivity	Difficulty of recovery from reaction medium	durability or recyclability	Difficulty of recovery from reaction medium
57	The waste generated in the manufacture of organic compounds consists primarily of	Inorganic Salts	Organic salts	Coordination compounds	Sludge	Inorganic Salts
58	Example for a solid acid which can be used as a green catalyst	Aluminium chloride	Sodium Borohydride	zeolites	Lithium Aluminium Hydride	zeolites
59	Example for a solid acid which can be used as a green catalyst	Aluminium chloride	Sodium Borohydride	Acidic Clays	Lithium Aluminium Hydride	Acidic Clays
60	Which is not related to a green catalyst	higher activity	higher selectivity	Difficult to recover from reaction medium	durability or recyclability	Difficult to recover from reaction medium

UNIT III

SYLLABUS

Design and Application of Surfactants for Carbon Dioxide; Making Carbon di oxide a Better Solvent in an Effort to Replace Solvents that Damage the Environment

Volatile Organic Compounds and Halogenated Organic Compounds

- xylene
- toluene
- benzene
- methylenechloride
- chloroform
- isopropylalcohol

Uses of Volatile Organic Compounds andHalogenated Organic Compounds

- Industrial types ofcleaning
    a. fluxremoval
    b. oil and grease removal from metalparts
    c. garmentcleaning
- Householdproducts
    a. stains and varnishes
    b. paintthinner
    c. fingernail polishremover
    d. adhesives
    e. furniturepolish
    f. hairspray

VOCs and Ozone Production

VOCs + NO + sunlight O_3 + HNO_3 + organic compounds

Halogenated Organic Compounds

- Carbon based compounds that contain halogen atoms such as fluorine, chlorine,and bromine.

- They include the chlorofluorocarbons (CFCs) and the hydrochlorofluorocarbons(HCFCs).

Chlorofluorocarbons (CFCs)

- Widely used for manyapplications
  a. refrigerants, propellants for aerosol, and blowingagents
  b. industrialcleaning

- Chemically unreactive, nontoxic and nonflammable

- Known to decompose in the stratosphere under theinfluence of high energy UVradiation

- These decomposition products catalyze reactions thatdeplete the stratospheric ozonelayer

- Significant increases in the intensity of harmful UVradiation reaching the surface of the earthresults

Hydrochlorofluorocarbons

- HCFCs are being used as temporary replacementsforCFCs.

- HCFCs do not have as great an ozone layerdepletingpotential.

- The carbon hydrogen bond in HCFCs makes them muchmore reactive than CFCsso…

- the vast majority of the HCFC molecules are destroyed inthetroposphere.

- This prevents most of the HCFC molecules from rising intothe stratosphere where they too would act to deplete theozonelayer.

Carbon Dioxide: An Alternative Solvent

- Preferable to VOCs and Halogenated OrganicCompounds

- Nonflammable, nontoxic, and chemicallyunreactive

- Available as a cheaply recovered byproduct from the production of ammonia andfrom natural gaswells

- The used carbon dioxide can easily be recovered, purified, andreused

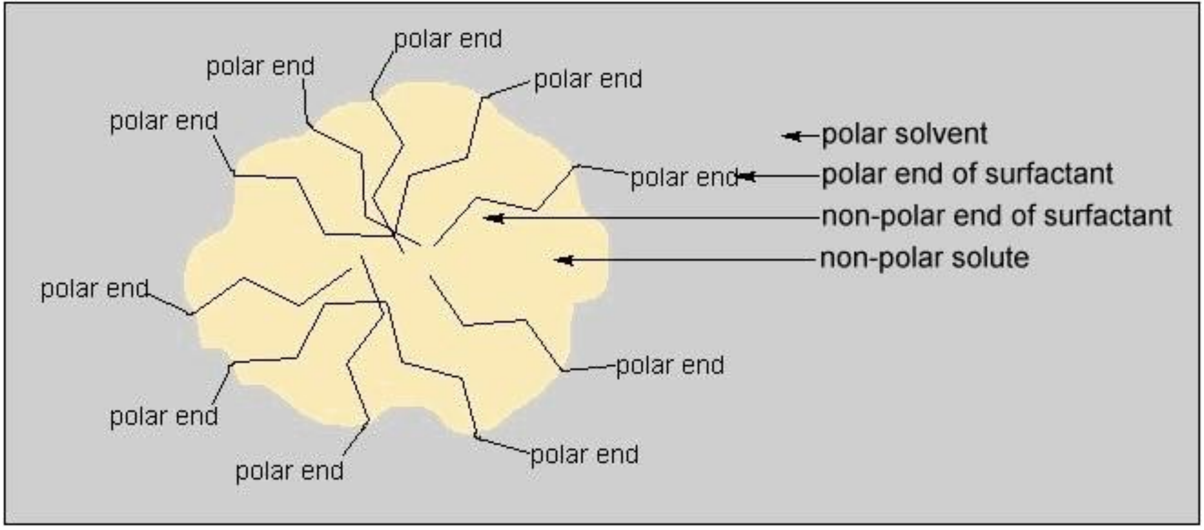
Solubility of Substances in CO2

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

Surfactants

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

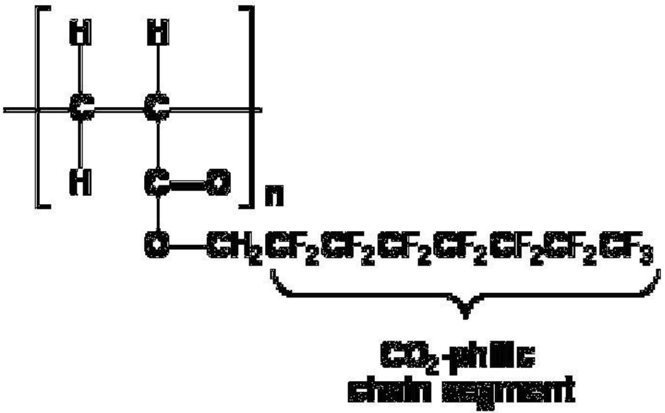
Micelle Structure of a Surfactant



A Surfactant for Liquid or Supercritical Fluid CO_2

- Musthave both CO_2-philic (CO_2loving) andCO_2-phobicfunctionality.

- In 1994, Joseph M. DeSimone of the University of North Carolina and North Carolina State University published his discovery that polymers such as that shown below are soluble in liquid or supercriticalCO_2

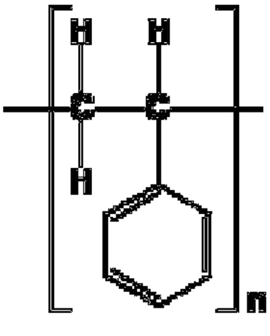


Polymers

- Molecule with a high molar mass (typically 10,000 to 10 6)
- Polystyrene is anexample:
- n is the number of times the structure in brackets repeats itself (onaverage)
- n is called the number average degree of polymerization and is usually≥1000

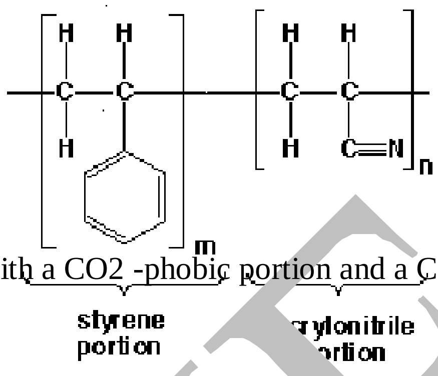
Copolymers

- A copolymer contains two different types of repeat units within the same polymerchain.
- A copolymer is not a blend of two different polymers, but instead the two monomers are covalently bonded along the length of thechain.
- Example of a copolymer of styrene andacrylonitrile:

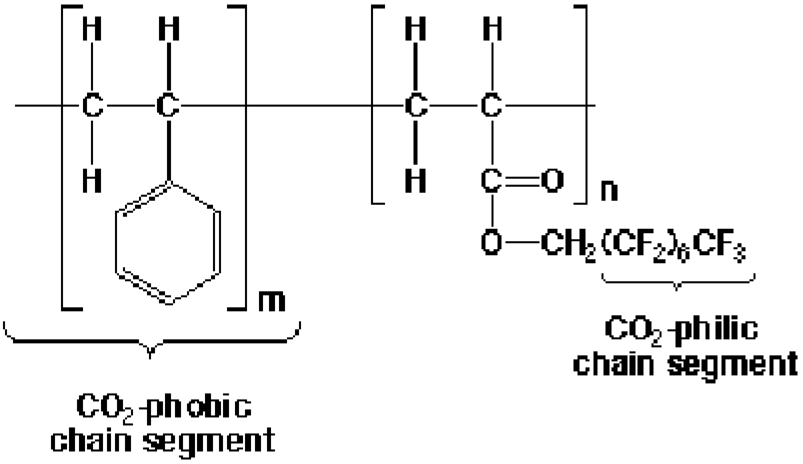


Possible Copolymer Sequencing Arrangements Using ‘S’ to represent the styrene monomers and ‘A’ to represent the acrylonitrile monomers: •Random Copolymer SASASAASASSAS •Block Copolymer SSSSSSAAAAAAA •Alternating CopolymerSASASASASASASA

Block Copolymers are Used to make a Surfactant for CO_2 •



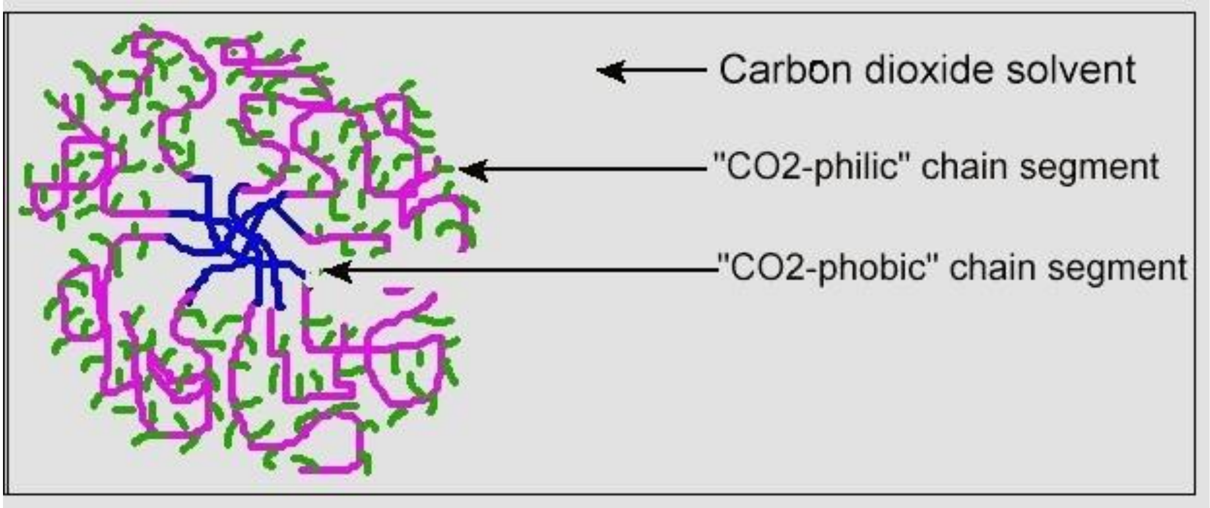
DeSimone synthesized copolymers with a CO_2 -phobic portion and a CO_2 -philic portion.



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

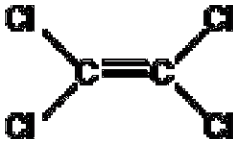
- 344 million lb of PERC were produced in the United States in1998.
- The dry cleaning industry uses approximately 50% of the PERC produced each year ~ 172 million pounds of thesolvent.

Mischell structure of co2 surfactant

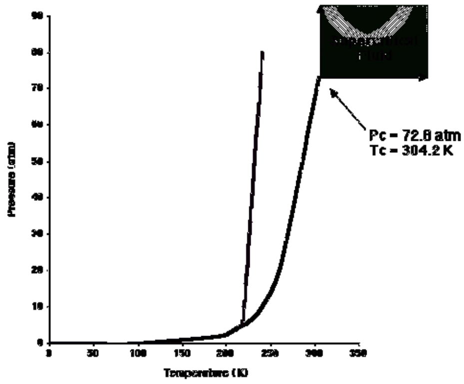


Current Use of CO_2 Surfactants--Green Chemistry in ACTION

- EPA has classified PERC as a groundwater contaminant and a potential human health hazard.
- PERC is a suspected human carcinogen and a known rodentcarcinogen.
- Breathing PERC for short periods of time can adversely affect the central nervoussystem.
- These effects are not likely to occur though at levels of PERC that are normally found in the environment, but people who work in the dry cleaning industry have the greatest risk for exposure.
- Micell Technologies, a company founded in 1995, has made the CO_2 surfactanttechnology availablecommercially.
- Micell'sMicareô system is a commercial washing machine that utilizes $CO_2$and a CO_2 surfactant instead of PERC, thereby eliminating the need forPERC.
- The franchise, Hangers, uses thistechnology.



Supercritical CO_2



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

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

Benefits can be realised if CO2 gas is pressurised to condense it to form a liquid. If exhaust gas CO2 were liquefied then perhaps it might find use as an industrial solvent; this article explores the possibilities for such applications. In fact, CO2 can also be produced in a very special form, a supercritical fluid, which has unique properties that are beneficial for many industrial applications. However, it can be seen that if CO2 could be trapped and used in liquid (supercritical) form then it could solve many of the problems that contribute towards The advantages of using supercritical fluids over normal liquid solvents can be realised once it is appreciated that solvent strength and density can be varied over a very wide range. This allows fine control over all physical properties such as viscosity, density, solubility parameter, dielectric constant and diffusivity though only modest changes in the temperature and pressure. Since the 1950s, the use of supercritical CO2 (scCO2) as a solvent has been investigated by academia and industry.

Although this ‘green’ scCO2 solvent has many desirable properties, technically speaking it is a very ‘weak’ solvent: the polarity, dielectric constant and dipole moment are less than that of most conventional organic solvents. Consequently, high-molecular-weight polymers,proteins and polar molecules are only sparingly soluble or even insoluble in scCO2. One effective way to make scCO2 able to dissolve high-molecularweight or polar compounds is by using suitable additives, or surfactants, to produce nanometresized domains in the scCO2 by forming micelles or microemulsions (Figure 1). The problem is the naturally very low solubilities of readily available surfactants with scCO2. Therefore, during the last two decades, many research groups have tried to design new surfactants compatible with scCO2. To date, the most effective compounds for this purpose contain high levels of fluorine in the molecules, which is needed to boost the solubility in scCO2 (Eastoe et al.,2006a). Unfortunately, fluorinated surfactants are not a good way to solve the problem, being both expensive and environmentally harmful. Some efforts have been made to investigate fluorine-free surfactants (Eastoe et al., 2006b) for CO2. The significance is that these surfactants are generally cheaper and less environmentally hazardous than the fluorinebearing analogues There is currently great interest in designing and understanding the nature of fluorine-free CO2-compatible hydrocarbon surfactants. Research has shown that branched and methylated surfactants and those with a ‘stubby’ molecular shape, can be used to stabilise water-in-CO2 (w/c) microemulsions (Figure 1), presumably because of higher solvation and lower intermolecular interactions. With the underlying philosophy and strategy previously explored, some success has been achieved at the University of Bristol with new CO2-philic hydrocarbon surfactants, including highly branched and oxygenated surfactants (Table 1) (Eastoe et al., 2006a; 2006b). The special aspects of the chemical structures that give rise to high solubility in scCO2 are described later in this chapter.

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

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

Design of hydrocarbon CO2-philic surfactants

Research efforts continued and it become apparent that, in order to advance the field, a basic understanding of solvation of the surfactant tails by CO2 was needed. The first spectroscopic evidence for specific CO2–surfactant interactions was obtained by Dardin, DeSimone and Samulski (1998). The results showed that favourable van der Waals intermolecular interactions take place between fluorinated surfactants and CO2, highlighting the importance of specific tail–fluid interactions. Even though arguments about the exact nature of the interactions between CO2 and fluorosurfactants continue, favourable interactions between surfactant tails and CO2 are understood to be the key factor in designing new surfactants for CO2.Liu et al. (2001) investigated the solubility of the hydrocarbon (fluorine-free) surfactant Dynol- 604 in scCO2 and microemulsion formation. (The molecular structure of Dynol-604 is a trade secret.) The results showed that Dynol-604 can dissolve in CO2 up to 5wt%. Water loading to generate reverse micelles in CO2–Dynol-604 mixtures was achieved up to 0.6wt% of added water by controlling pressure and temperature. The solubility and water-loading in scCO2 of the non-fluorinated Ls-36 and Ls-45 surfactants (Table 4) were studied by the same group. Comparing surfactant structures, Ls-36 has three hydrophilic ethylene oxide(EO) groups and six hydrophobic propylene oxide (PO) groups, whereas Ls-45 has four EO groups and five PO groups. The results showed that both surfactants are quite soluble in CO2, at approximately 4wt% (pressure 19–22MPa and temperature 37–47°C). Raveendran and Wallen (2002) reported that the specially modified acylated (Ac) sugars α- and β-1,2,3,4,6-pentaacetyl-D-glucose and β-1,2,3,4,6-pentaacetyl-D-galactose (Table 4) exhibit high solubilities inscCO2. The strategy for enhancing solubility involves using carbonyl groups in the Ac parts of the adapted solutes. The high solubility was attributed to Lewis acid–Lewis base interactions between CO2 and the CO2-philic sugars, with the carbonyl groups providing Lewis base functionality (Eastoe et al., 2006a). Specific beneficial interactions between CO2 and the carbonyl groups were confirmed by spectroscopic studies. The finding demonstrates favourable interactions betweenCO2 and acetylated groups, especially the pendent carbonyl parts. The design of efficient hydrocarbon CO2-philic surfactants can be achieved using the template of AOT (Table 1), a common commercially available surfactant that is frequently used for reverse micelle formation in a variety of organic solvents (Eastoe et al., 2006a). Unfortunately, normal AOT is incompatible with CO2, but by subtle modifications of the alkyl tails it can be coerced to dissolve in CO2 (Eastoe et al., 2001). This class of surfactants can be readily synthesised from inexpensive, commercially available reagents by a well-documented two-step reaction. The majorrationale in designing hydrocarbon surfactants is to increase the density of the terminal CO2-philic methyl groups. This is the region where CO2 comes into intimate contact with surfactant molecules, and optimising the surfactant–CO2 solvent intermolecular interactions in this ‘chain tip’ region is now known to be of key importance for generating CO2-soluble surfactants. Based on this approach, the twin-tailed, branched, hydrocarbon-based ionic surfactant AOT4 (Table 1) was designed and synthesised, and it was found to have good CO2 compatibility and to form dry reverse micelles in pure CO2 (50MPa, 33°C) (Eastoe et al., 2001). The results revealed that molecular structures with branched and pendent methyl groups (chain tips) serve to boost compatibility in scCO2.Furthermore, the methylation of chain tips and addition of carbonyl functional groups in the surfactant (Eastoe et al., 2006b) successfully lead to CO2 solubility with another new tri-chain hydrocarbon surfactant, TC14 (Table 1) (Hollamby et al., 2009). The tri-chain TC14 exhibited good compatibility with CO2 resulting in homogeneous, optically transparent solutions under mild conditions (15MPa, 25°C). Compared with the di-chain analogue AOT4, the introduction of third surfactant chain has a dramaticimprovement on surfactant–CO2 solvent intermolecular interactions, allowing the formation of reverse micelles in CO2 (Hollamby et al., 2009). Significantly, the addition of a third surfactant chain also improves the spacefilling efficiency of the surfactant tails, which is expected to favour formation of reverse micelles by providing better separation between CO2 and water across the interface (Mohamed et al., 2010). There are two main considerations if CO2-philic surfactants are to be commercialised: l the minimisation of raw material costs; l the reduction of working pressure, thereby reducing engineering demands on processing rigs and plant. Clearly, these are both of great importance for applications involving high volumes of scCO2. At current market prices and using scientific (notbulk) suppliers, the raw costs for di-CF4, the leading CO2-philic fluorosurfactant(Table 3), can be estimated at US$220 per gram. In contrast, the hydrocarbon analogues, loaded with terminal methyl groups, are much cheaper at around US$1 per gram for AOT4 and US$6 per gram forTC14.

POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What are Volatile Organic Compounds and Halogenated Organic Compounds.Give examples
2. What are the Uses of Volatile Organic Compounds and HalogenatedOrganic Compounds
3. Write notes on chlorofluoro hydrocarbons(CFC's)
4. What are hydrochlorofluorocarbons. What are its advantages anddisadvantages.
5. Comment on the statement, Carbon Dioxide: An AlternativeSolvent
6. What are surfactants. Give suitableexamples.

PART C (8 Mark Questions)

1. Explain the classification of surfactants with suitableexamples.
2. Explain the Micelle Structure of aSurfactant
3. Describe about the Surfactant for Liquid or Supercritical FluidCO_2

4. What are the advantages and disadvantages in using supercritical carbon dioxide(sc-CO2) as an alternativesolvent.
5. WhatismeantbySupercriticalCO_2.Commentonitsadvantagesanddisadvantages.

DEPARTMENT OF CHEMISTRY

Online questions (Multiple choice questions)

GREEN METHODS IN CHEMISTRY (18CHU404A)

UNIT III

S.No	**Question**	**Option 1**	**Option 2**	**Option 3**	**Option 4**	**Answer**
1	Example of Organic volatile compounds used as a solvent	Benzoic acid	Acetic acid	Benzaldehyde	Xylene	Xylene
2	Example of Organic volatile Hydrocarbon used as a solvent	Benzoic acid	Acetic acid	Benzaldehyde	Toluene	Toluene
3	Example of Organic volatile hydrocarbon used as a solvent	Benzaldehyde	Acetic acid	Benzoic acid	Benzene	Benzene
4	Example of halogenated Organic compounds used as a solvent	Benzoic acid	Methylene dichloride	Benzaldehyde	Benzene	Methylene dichloride
5	Example of halogenated Organic compounds used as a solvent	Benzoic acid	Chloroform	Toluene	Benzene	Chloroform
6	Example of Organic volatile compounds used as a solvent	Benzoic acid	Acetic acid	Benzaldehyde	Isopropyl alcohol	Isopropyl alcohol
7	Decompose in the stratosphere under theinfluence of high energy UV radiation	Hydrochloro fluorocarbons	Chlorofluorocarbons	Aromatic hydrocarbons	Saturated aliphatic hydrocarbons	Chlorofluorocarbons

8	These decomposition products catalyze reactions thatdeplete the stratospheric ozone layer	Hydrochloro fluorocarbons	Chlorofluorocarbons	Aromatic hydrocarbons	Saturated aliphatic hydrocarbons	Chlorofluorocarbons
9	Vast majority of the molecules are destroyed inthe troposphere.	Hydrochloro fluorocarbons	Chlorofluorocarbons	Aromatic hydrocarbons	Saturated aliphatic hydrocarbons	Hydrochloro fluorocarbons
10	Significant increases in the intensity of harmful UVradiation reaching the surface of the earth results	Hydrochloro fluorocarbons	Chlorofluoromethane	Toluene	n-Hexane	Chlorofluoromethane
11	Widely used as refrigerants, propellants for aerosol, and blowing agents	Hydrochloro fluorocarbons	Chlorofluorocarbons	Aromatic hydrocarbons	Saturated aliphatic hydrocarbons	Chlorofluorocarbons
12	Nonflammable, nontoxic, and chemically unreactive compound	Carbon di oxide	Chlorofluoromethane	Toluene	n-Hexane	Carbon di oxide
13	Available as a cheaply recovered byproduct from the production of ammonia and from natural gas wells	Carbon di oxide	Chlorofluoromethane	Toluene	n-Hexane	Carbon di oxide
14	The used compound can easily be recovered, purified, and reused	Carbon di oxide	Chlorofluoromethane	Toluene	n-Hexane	Carbon di oxide
15	Carbon dioxide is a	non polar molecule since the dipoles of	Polar molecule since the dipoles of the two bonds do not cancel	Assymetric compound	Non-volatile compound	non polar molecule since the dipoles of the two bonds cancel one

		the two bonds cancel one another.	one another.			another.
16	Carbon dioxide will dissolve	smaller non polar molecules ¬ hydrocarbons having less than 20 carbon atoms	Grease	Proteins	Polar molecules	smaller non polar molecules ¬ hydrocarbons having less than 20 carbon atoms
17	Carbon dioxide will dissolve	organic molecules such as aldehydes, esters, and ketones	Grease	Proteins	Polar molecules	organic molecules such as aldehydes, esters, and ketones
18	Carbon di oxide will not dissolve	larger molecules such as oils, waxes, grease, polymers, and proteins, or polar molecules.	organic molecules such as aldehydes, esters, and ketones	hydrocarbons having less than 20 carbon atoms	Non polar molecules	larger molecules such as oils, waxes, grease, polymers, and proteins, or polar molecules.
19	Surfactant is a molecule that contains	A polar portion and a non polar portion.	A polar portion only	A non-polar portion only	Neutral portion and a non polar portion.	A polar portion and a non polar portion
20	Can interact with both polar and non polar molecules	Hydrochloro fluorocarbons	Chlorofluorocarbons	Aromatic hydrocarbons	Surfactants	Surfactants
21	The substance increases the solubility of the otherwise insoluble substances.	Hydrochloro fluorocarbons	Chlorofluorocarbons	Aromatic hydrocarbons	Surfactants	Surfactants
22	Micelles are	surfactant	Chlorofluorocarbons in	Aromatic	Grease in oil	surfactant molecules in

		molecules in water tend to cluster into a spherical geometry	the atmosphere	hydrocarbons as a solvent		water tend to cluster into a spherical geometry
23	In water, surfactant molecules tend to cluster into a spherical geometry to form Micelles which are	non polar ends of the surfactant lie on the inside of the sphere	non polar ends of the surfactant lie on the inside of the sphere ¬ polar ends on the outside	polar ends of the surfactant lie on the inside of the sphere ¬ non-polar ends on the outside	Non-polar ends of the surfactant lie on the inside of the sphere	non polar ends of the surfactant lie on the inside of the sphere ¬ polar ends on the outside
24	A Surfactant for Liquid or Supercritical Fluid CO_2must have	both CO_2 -philic(CO_2 loving) and CO_2 -phobic functionality	Sufficient to have CO_2 -philic (CO_2 loving) functionality	Only CO_2 -phobic functionality	A repellencytendency	both CO_2 -philic(CO_2 loving) and CO_2 -phobic functionality
25	The application on supercritical carbon dioxide (sc-CO2) as an alternative solvent to traditional organic ones, despite of its several desirable characteristics, is often hindered because CO2 is	non-polar, and only dissolves small and apolar molecules.	polar, and dissolves small polar molecules.	non-polar, and only dissolves larger polar molecules.	Zwitterionicand only dissolves small and apolar molecules.	Non-polar, and only dissolves small and apolar molecules.
26	The sc-CO2-suitable surfactants are molecules composed of a CO2-philic part	generally containing a perfluorocarbon chain	capable of solubilizing polar compounds	Generally containing apolar molecules	Generally containing dipolar ions	generally containing a perfluorocarbon chain
27	The sc-CO2-suitable surfactants are molecules composed of a CO2-	generally containing a perfluorocarbon	capable of solubilizing polar compounds	Generally containing apolar	Generally containing dipolar ions	capable of solubilizing polar compounds

	phobic part	chain		molecules		
28	The compound which is the main cause of climate change	perfluorocarbon	Carbon di oxide	Sulphurdi oxide	Chlorofluoro hydrocarbons	Carbon di oxide
29	The surface-active portion of the surfactant bears a negative charge, it is called	Cationic surfactant	Zwitterionic surfactant	Anionic surfactant	Non-ionic surfactant	Anionic surfactant
30	The surface-active portion of the surfactant bears a positive charge, it is called	Cationic surfactant	Zwitterionic surfactant	Anionic surfactant	Non-ionic surfactant	Cationic surfactant
31	The surface-active portion of the surfactant bears both charges	Cationic surfactant	Zwitterionic surfactant	Anionic surfactant	Non-ionic surfactant	Zwitterionic surfactant
32	An example for anionic surfactant	Alkane carboxylic salts (soap)	Amine salts	Long-chain amino acid salts	Long chain ethers	Alkane carboxylic salts (soap)
33	The surface-active portion of the surfactant bears no charges	Cationic surfactant	Zwitterionic surfactant	Anionic surfactant	Non-ionic surfactant	Non-ionic surfactant
34	An example for anionic surfactant	Alkane sulphonic salts (detergents)	Amine salts	Long-chain amino acid salts	Long chain ethers	Alkane sulphonic salts (detergents)
35	An example for anionic surfactant	Alkyl-aromatic sulfonic salts	Amine salts	Long-chain amino acid salts	Long chain ethers	Alkyl-aromatic sulfonic salts
36	An example for anionic surfactant	Phosphates, phosphoric salts	Amine salts	Long-chain amino acid salts	Long chain ethers	Phosphates, phosphoric salts
37	An example for cationic surfactant	Phosphates, phosphoric salts	Amine salts	Long-chain amino acid salts	Long chain ethers	Amine salts
38	An example for cationic surfactant	Phosphates, phosphoric salts	Quarternary ammonium salts	Long-chain amino acid salts	Long chain ethers	Quarternary ammonium salts
39	An example for zwitterionic surfactant	Alkyl-aromatic sulfonic salts	Amine salts	Long-chain amino acid salts	Long chain ethers	Long-chain amino acid salts
40	An example for zwitterionicsurfactant	Alkyl-aromatic sulfonic salts	Amine salts	Betains	Long chain ethers	Betains

41	An example for non-ionic surfactant	Alkyl-aromatic sulfonic salts	Amine salts	Betains	Long chain ethers	Long chain ethers
42	An example for non-ionic surfactant	Alkyl-aromatic sulfonic salts	Amine salts	Betains	Long chain esters	Long chain esters
43	Alkane carboxylic salts (soap) is an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Anionic surfactant
44	Alkane sulphonic salts (detergents) is an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Anionic surfactant
45	Alkyl-aromatic sulfonic saltsis an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Anionic surfactant
46	Phosphates, phosphoric saltsis an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Anionic surfactant
47	Amine saltsis an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Cationic surfactant
48	Quarternary ammonium saltsis an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Cationic surfactant
49	Long-chain amino acid saltsis an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Zwitterionic surfactant
50	Betainsis an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Zwitterionic surfactant
51	Long chain ethersis an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Non-ionic surfactant
52	Long chain estersis an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Non-ionic surfactant
53	Surfactants are	Hydrophilic in nature	Hydrophobic in nature	Amphiphilic in nature	Electrophilic in nature	Amphiphilic in nature
54	Sodium stearate is an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Anionic surfactant
55	Cetyltrimethylammonium bromide is an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Cationic surfactant
56	Polyoxyethylene alcohol is	Anionic	Cationic surfactant	Zwitterionic	Non-ionic surfactant	Non-ionic surfactant

	an example for	surfactant		surfactant		
57	Dodecyl betaine is an example for	Anionic surfactant	Cationic surfactant	Zwitterionic surfactant	Non-ionic surfactant	Zwitterionic surfactant
58	Example for anionic surfactant	Sodium stearate	Cetyltrimethylammonium bromide	Polyoxyethylene alcohol	Dodecyl betaine	Sodium stearate
59	Example for cationic surfactant	Sodium stearate	Cetyltrimethylammonium bromide	Polyoxyethylene alcohol	Dodecyl betaine	Cetyltrimethylammonium bromide
60	Example for non-ionic surfactant	Sodium stearate	Cetyltrimethylammonium bromide	Polyoxyethylene alcohol	Dodecyl betaine	Polyoxyethylene alcohol

UNIT IV

SYLLABUS

Designing of environmentally safe marine antifoulant. Rightfit pigment: Synthetic azo pigments to replace toxic organic and inorganic pigments.

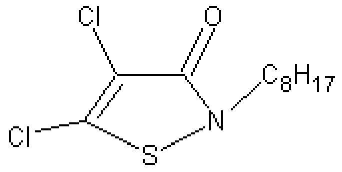
Designing of environmentally safe marine antifoulant.

During the past 10-15 years efforts have been underway to develop antifoulants which are less harmful to the environment but with the same efficacy as organotins.

Ideally these compounds should:

1. Rapidly degrade in the environment and rapidly partition to thesediment, resulting Innon hazardous environmental concentrations with limitedbioavailability
2.At environmental concentrations be toxic only to targetorganisms
1. Result in minimum bioconcentration

One of the most significant advancements in the area of antifoulants has been made by the Rohm and Haas Company with the development of SEA-NINE 211. The environmental significance of Rohm and Haas's discovery of Sea-Nine 211 was recognized with aPresidential Green Chemistry Challenge Award in 1996. Sea-Nine 211 won a prestigious Presidential Green Chemistry Challenge award in the category "the design of chemicals which are less toxic than current alternatives." The active ingredient in Sea-Nine 211, 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOI), is a member of the the isothiazolone family ofantifoulants.



4,5-dichloro-2-n-octyl-4-isothiazolin-3-one

DCOI

Designing an Environmentally Safe Marine Antifoulant

Innovation and Benefits:

Rohm and Haas developed Sea-Nine, a novel antifoulant to control the growth of plants and animals on the hulls of ships. In 1995, fouling cost the shipping industry approximately $3 billion a year in increased fuel consumption. Sea-Nine replaces environmentally persistent and toxic tin-containing antifoulants.

Summary of Technology:

Fouling, the unwanted growth of plants and animals on a ship's surface, costs the shipping industry approximately $3 billion a year, largely due to increased fuel consumption to overcome hydrodynamic drag. Increased fuel consumption contributes to pollution, global warming, and acid rain.The main compounds used worldwide to control fouling are the organotinantifoulants, such as tributyltin oxide (TBTO).

While effective, they persist in the environment and cause toxic effects, including acute toxicity, bioaccumulation, decreased reproductive viability, and increased shell thickness in shellfish.

These harmful effects led to an EPA special review and to the OrganotinAntifoulant Paint Control Act of 1988. This act mandated restrictions on the use of tin in the United States, and charged the EPA and the U.S. Navy with conducting research on alternatives to organotins. Rohm and Haas Company searched for an environmentally safe alternative to organotin compounds.

Compounds from the 3-isothiazolone class were chosen as likely candidates and over 140 were screened for antifouling activity. The 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (Sea-Nine antifoulant) was chosen as the candidate for commercial development.

Extensive environmental testing compared Sea-Nine antifoulant to TBTO, the current industrystandard.

1. Sea-Nine antifoulant degraded extremely rapidly with a half-life of one day in seawater and one hour insediment.

2. Tin had bioaccumulation factors as high as 10,000-fold, whereas Sea-Nine antifoulant's bioaccumulation was essentiallyzero.

3. Both TBTO and Sea-Nine were acutely toxic to marine organisms, but TBTO had widespread chronic toxicity, whereas Sea-Nine antifoulant showed no chronic toxicity. Thus, the maximum allowable environmental concentration (MAEC) for Sea-Nine antifoulantwas 0.63 parts per billion (ppb) whereas the MAEC for TBTO was 0.002 ppb.

Hundreds of ships have been painted with coatings containing Sea- Nine worldwide. Rohm and Haas Company obtained EPA registration for the use of Sea-Nine antifoulant, the first new antifoulant registration in over a decade.

Rightfit pigments

Innovation and Benefits:

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

Summary of Technology:

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

(1) Their higher cost often acts as a deterrent toreformulation;
(2) Their production uses large volumes of organicsolvents;
(3) Some require large quantities of polyphosphoric acid, resulting in phosphates inthe effluent;and
(4) Some are based on dichlorobenzidine or polychlorinatedphenyls.

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

In 2002, Engelhard produced only 1.2 million pounds of heavy-metal pigments; they expect to phase them out completely in2004.

1. Rightfit pigments eliminate the risk to human health and the environment from exposure to heavy metals such as cadmium, chromium(VI), and lead used in the manufacture of cadmium and chrome yellowpigments.
2. They are expected to have very low potential toxicity based on toxicitystudies, physical properties, and structural similarities to many widely used foodcolorants.
3. Because they have low potential toxicity and very low migration, most of the Rightfit pigments have been approved both by the U.S. Food andDrug

Administration (FDA) and the Canadian Health Protection Branch (HPB) for indirect food contact applications.

4. In addition, these pigments are manufactured in aqueous medium, eliminating exposure to the polychlorinated intermediates and organic solvents associated with the manufacture of traditional high-performancepigments.

Rightfit pigments have additional benefits, such as

1. Good dispersibility,
2. Improved dimensionalstability,
3. Improved heat stability,and
4. Improved colorstrength.
5. Their higher color strength achieves the same color values using lesspigment.
6. Rightfit pigments also cover a wide color range from purple to green-shade yellow color.
7. Being closely related chemically, these pigments are mutually compatible, so two or more can combine to achieve any desired intermediate colorshade.

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

Achievements by Engelhard Corporation

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

Environmental Achievements

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

Presidential Green Chemistry Challenge Awards

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

Key Issues

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

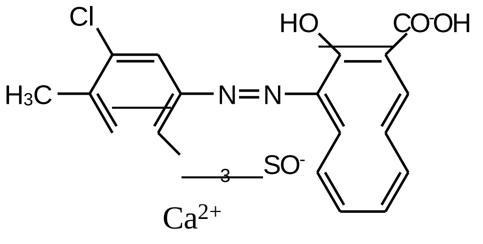
Rightfit Pigments: Environmental Impact

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

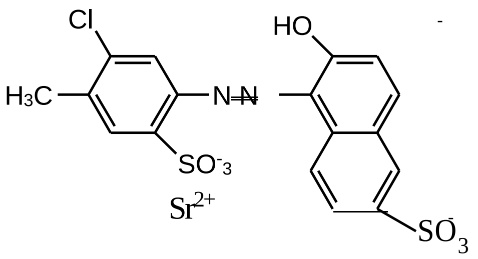
Key Technologies Applied

- Modification of ChemicalStructure
- Mixed CrystalFormation
- Selection of Appropriate LakingMetal
- SelectiveMetallization
- Generation of Desired CrystalForm
- Appropriate SurfaceTreatment

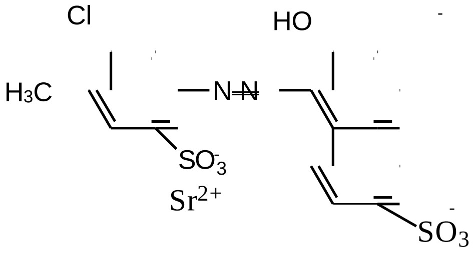
Technology- Modification of Chemical Structure



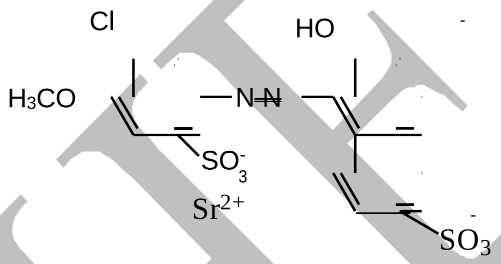
Pigment Red; Heatstability238°C



Redfit Scarlet; Heat stability289°C

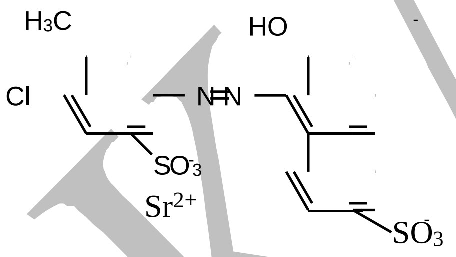


Yellow shade red; Heatstability289°C

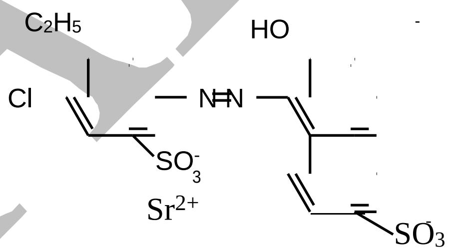


Blue shade red; Heat stability315°C

Technology- Mixed Crystal Formation



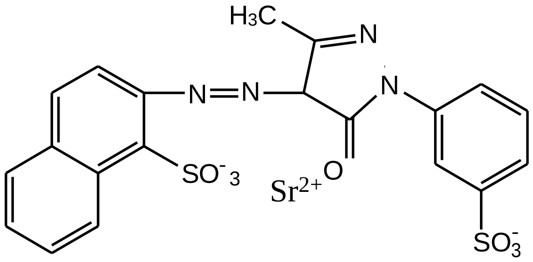
Hueangle31.7



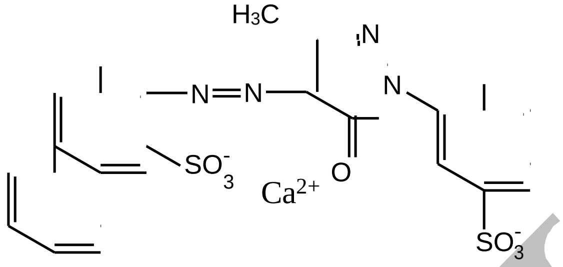
Hue angle23.3

Mixed crystal 1:1; Hue angle 25.8

Technology-Selection of Appropriate Laking Metal

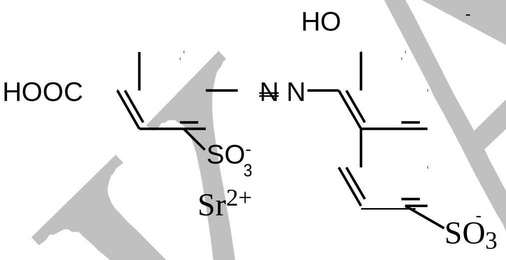


Reddish Yellow; Hue amgle 69.5

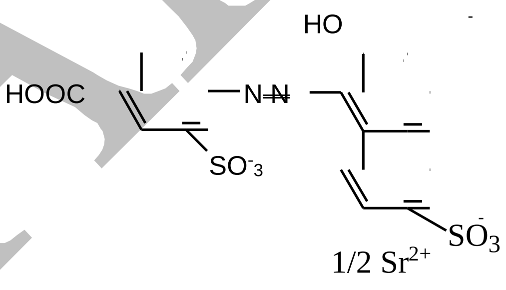


Very Reddish Yellow; Hue amgle 63.5

Technology-Selective Laking

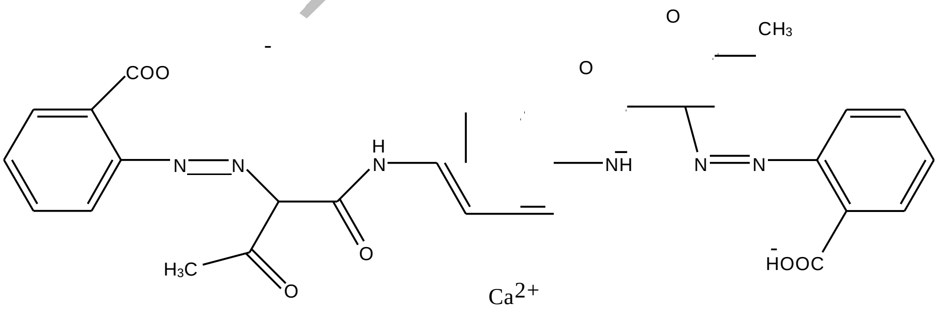


Medium red



Brillant orange

Technology-Generation of Desired Crystal Form



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

Technology-Appropriate Surface Treatment

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

Intelluctual property rights

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

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

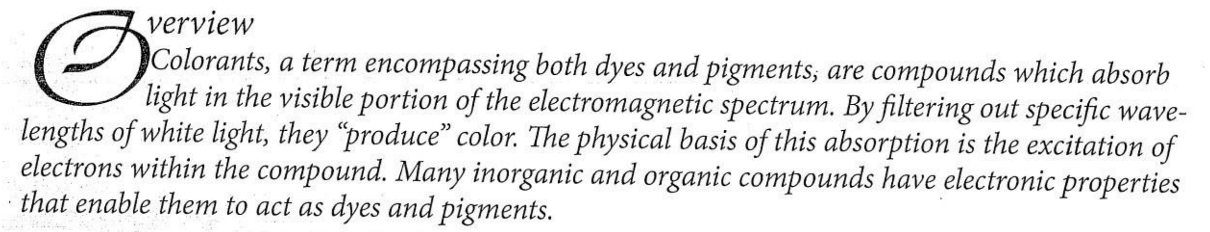
When EPA began regulating heavy metals in the 1970s, color formulators started turning to organic pigments such as dichlorobenzidines, isoindolinones, and quinacridones. Although these organic pigments meet performance requirements, they are relatively expensive and their manufacture requires large volumes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

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

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

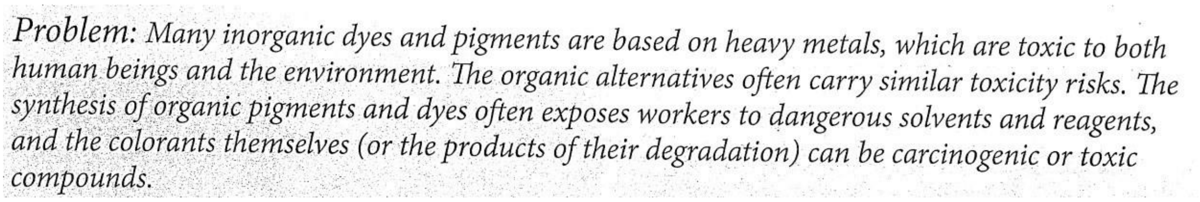
Because of their solubility, azo dyes undergo N=N cleavage, resulting in generation of aromatic amines that in some cases are toxic, Bindra noted. The azo pigments, on the other hand, are virtually insoluble and are unlikely to undergo N=N cleavage. Therefore, they have a lower demonstrated toxicity,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

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

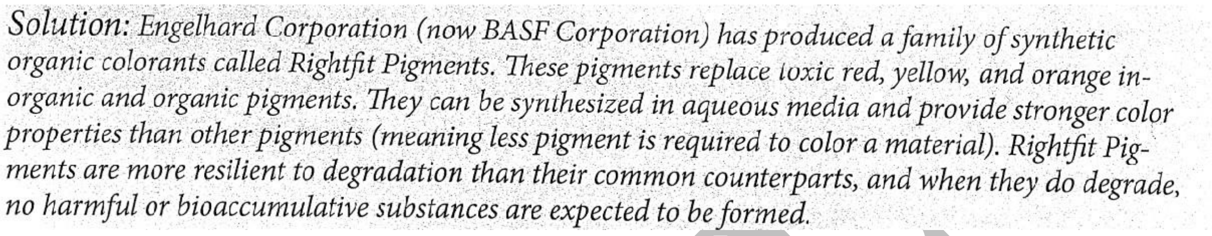


Overview

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



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



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

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

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

95% of the pigments available worldwide contain heavy metls.

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

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

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

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

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

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

POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What are the requirements for an ideal greenerantifoulants.
2. What is the chemical name and structure active ingredient in Sea-Nine211.
3. What is the innovatin and benefit of *Designing an Environmentally SafeMarine Antifoulant by* Rohm and Haas's discovery of Sea-Nine211.
4. What are the innovations and benefits of the Rightfitpigments.

5. Summarise the benefits of the rightfit pigments.
6. What are the key environmental issues lyeing behind the usage of conventionalclours and pigments.
7. Explain the environmental impact of the Rightfitpigments.

PART C (8 Mark Questions)

1. The environmental significance of Rohm and Haas's discovery of Sea-Nine 211 was recognized with a Presidential Green Chemistry Challenge Award in 1996. Look up the three focus areas for this award and determine which focus area this case best fits into.
2. List out any two of the twelve principles of green chemistrythat are addressed by the green chemistry developed by Rohm and Haas's discovery of Sea-Nine211.
3. Explain the summary of the technology developed by Rohm and Haas's discoveryof Sea-Nine211.
4. Summarise the technology developed by the Right fit pigments in developingtheir materials.
5. Explain with suitable examples the key technologies followed by Rightfitpigments.

DEPARTMENT OF CHEMISTRY

Online questions (Multiple choice questions)

GREEN METHODS IN CHEMISTRY (18CHU404A)

UNIT IV

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	A substance (such as paint for use on the bottom of a boat) designed to prevent, reduce, or eliminate fouling	Antifoulants	Anticorrosive agents	Antimicrobial substances	Antifungal substances	Antifoulants
2.	Antifoulants are	Prevent corrosion	Prevents bacterial growth	A substance which prevents fouling	Prevents the growth of fungi	A substance which prevents fouling
3	Accumulation of microorganisms on wetted surfaces is called	corrosion	Biofouling	Eutrophication	bactericidal	Biofouling
4	Biofouling on marine vessels poses	hydrodynamic friction, leading to increased drag	Only bad smell	Beautufucation problem	Friction problem	hydrodynamic friction, leading to increased drag
5	Microfouling means	attachment of larger organisms to ships	attachment of larger organisms to the medical equipments	attachment of larger organisms to our houses	biofilm formation and bacterial adhesion	biofilm formation and bacterial adhesion
6	Macrofouling means	attachment of larger organisms to ships	attachment of larger organisms to the medical equipments	Due to biofilm formation	Due to bacterial adhesion	attachment of larger organisms to ships
7	Examples for hard fouling organisms	seaweed,	hydroids	algae	molluscs	molluscs
8	Examples for hard fouling organisms	seaweed	hydroids	algae	tube worms	tube worms

9	Examples for soft fouling organisms	molluscs	tube worms	barnacles	algae	algae
10	Examples for soft fouling organisms	molluscs	tube worms	barnacles	seaweed	seaweed
11	Initial step for marine fouling	biofilm formation	Attachment of macrofoulers	bacterial adhesion	colonization	biofilm formation
12	The last step for marine fouling	biofilm formation	Attachment of macrofoulers	bacterial adhesion	colonization	Attachment of macrofoulers
13	The biofilm formation in biofouling is due to	Formation of covalent bonds	Van der waals interaction	Formation of ionic interactions	Metallic bonds	Van der waals interaction
14	The antifoulantSEA-NINE 211 was manufactured by	M/s Dupont	Rohm and Haas Company	Rightfit company	Relaince industries	Rohm and Haas Company
15	Rohm and Haas Company produces	antifoulantSEA-NINE 211	Organic pigments	refrigerants	Green manures	antifoulantSEA-NINE 211
16	Presidential Green Chemistry Challenge Award in 1996 was awarded to	M/s Dupont	Rohm and Haas Company	Rightfit company	Relaince industries	Rohm and Haas Company
17	Presidential Green Chemistry Challenge Award in 1996 was awarded for the production ofantifoulantSEA-NINE 211 for the reason	Prevention of waste	Using green solvents	the design of chemicals which are less toxic than current alternatives	Using green catalysts	the design of chemicals which are less toxic than current alternatives
18	The active ingredient in Sea-Nine 211 is	4,5-dibromo-2-*n*-octyl-4-isothiazolin-3-one	4,5-dichloro-2-*n*-octyl-4-thiadiazole	4,5-dichloro-2-*n*-octyl-4-pyrazole	4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one	4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one
19	The active ingredient in Sea-Nine 211 belongs to	Thiadiazole group	Triazole group	Rhodanine group	isothiazolone family	isothiazolone family
20	The antifoulantSEA-NINE 211	Controls cancer cells	control the growth of plants and animals on the hulls of ships	Cures diabetes	Contrls blood pressure	control the growth of plants and animals on the hulls of ships
21	Organotinantifoulants is	4,5-dichloro-2-*n*-	isothiazolone	tributyltin oxide	Thiadiazole group	tributyltin oxide

		octyl-4-isothiazolin-3-one	family			
22	The antifoulantSEA-NINE 211 is preferred to Organotin because	It is environmentally free	It causes cause toxic effects	It causes bioaccumulation	they persist in the environment	It is environmentally free
23	The half life period of Sea-Nine antifoulant	One day in sea water	One week in sea water	One month in sea water	One year in sea water	One day in sea water
24	Sea-Nine antifoulant degraded extremely rapidly with a half-life of	One hour in sediment	One day in sediment	One month in sea water	One year in sediment	One hour in sediment
25	Sea-Nine antifoulant had bioaccumulation factors	Of zero	10 fold than organotin	100 fold than organotin	1000 fold than organotin	Of zero
26	Sea-Nine antifoulant showed	chronic toxicity	no chronic toxicity	Widespread chronic toxicity	Acute toxicity	no chronic toxicity
27	Rightfit azo pigments contain	calcium	Lead	chromium	cadmium	calcium
28	Rightfit azo pigments contain	Barium	Lead	chromium	cadmium	Barium
29	Rightfit azo pigments contain	Strontium	Lead	chromium	cadmium	Strontium
30	Conventional pigments contain	Lead	Calcium	Barium	Strontium	Lead
31	Conventional pigments contain	Chromium	Calcium	Barium	Strontium	Chromium
32	Conventional pigments contain	cadmium	Calcium	Barium	Strontium	cadmium
33	The drawback of high-performance pigments to conventional pigments is	meet performance requirements	Their higher cost often acts as a deterrent to reformulation	Their production uses low volumes of organic solvents	Some require lesser quantities of polyphosphoric acid	Their higher cost often acts as a deterrent to reformulation
34	The drawback of high-performance pigments to conventional pigments is	meet performance requirements	Their lower cost often acts as a deterrent to reformulation	Their production uses high volumes of organic solvents	Some require lesser quantities of polyphosphoric acid	Their production uses high volumes of organic solvents
35	The drawback of high-	meet performance	Their low cost	Their production	Some require	Some require

	performance pigments to conventional pigments is	requirements	often acts as a deterrent to reformulation	uses low volumes of organic solvents	higher quantities of polyphosphoric acid	higher quantities of polyphosphoric acid
36	Rightfit pigments have	right environmental impact	Their higher cost often acts as a deterrent to reformulation	Their production uses high volumes of organic solvents	Some require higher quantities of polyphosphoricacid	right environmental impact
37	Rightfit pigments have	right colour space	Their higher cost often acts as a deterrent to reformulation	Their production uses high volumes of organic solvents	Some require higher quantities of polyphosphoric acid	right colour space
38	Rightfit pigments have	right performance characteristics	Their higher cost often acts as a deterrent to reformulation	Their production uses high volumes of organic solvents	Some require higher quantities of polyphosphoric acid	right performance characteristics
39	Rightfit pigments have	right cost-to-performance value	Their higher cost often acts as a deterrent to reformulation	Their production uses high volumes of organic solvents	Some require higher quantities of polyphosphoric acid	right cost-to-performance value
40	The pigments produced by RightFit Pigments	eliminate the risk to human health and the environment from exposure to heavy metals	to have very high potential toxicity	very high migration	are manufactured in polychlorinated intermediates and organic solvents	eliminate the risk to human health and the environment from exposure to heavy metals
41	The pigments produced by RightFit Pigments	Do not eliminate the risk to human health and the environment from exposure to heavy metals	to have very low potential toxicity	very high migration	are manufactured in polychlorinated intermediates and organic solvents	to have very low potential toxicity
42	The pigments produced by	Do not eliminate	to have very high	very low migration	are manufactured	very low migration

	RightFit Pigments	the risk to human health and the environment from exposure to heavy metals	potential toxicity		in polychlorinated intermediates and organic solvents	
43	The pigments produced by RightFit Pigments	Do not eliminate the risk to human health and the environment from exposure to heavy metals	to have very highpotential toxicity	very highmigration	are manufactured in aqueous media	are manufactured in aqueous media
44	Good dispersibility of pigments was observed in	Conventional pigments	High performance heavy metal pigments	RightFit pigments	Alkali metal pigments	RightFit pigments
45	Improved dimensional stability of pigments was observed in	Conventional pigments	High performance heavy metal pigments	Pigments produced by Right Fit pigments	Alkali metal pigments	Pigments produced by Right Fit pigments
46	Improved heat stability of pigments was observed in	Conventional pigments	High performance heavy metal pigments	RightFit pigments	Alkali metal pigments	RightFit pigments
47	Improved color strength of pigments was observed in	Conventional pigments	High performance heavy metal pigments	Pigments produced by Right Fit pigments	Alkali metal pigments	Pigments produced by Right Fit pigments
48	Their higher color strength achieves the same color values using less pigment	Conventional pigments	High performance heavy metal pigments	Pigments synthesised by Right Fit pigments	Alkali metal pigments	Pigments synthesised by Right Fit pigments
49	The pigments which cover a wide color range from purple to green-shade yellow color	Conventional pigments	High performance heavy metal pigments	Pigments synthesised by Right Fit pigments	Alkali metal pigments	Pigments synthesised by Right Fit pigments
50	Polychlorinated intermediates and organic solvents are used in the manufacture of	Conventional pigments	High performance heavy metal pigments	Pigments synthesised by Right Fit pigments	Alkali metal pigments	High performance heavy metal pigments

51	The key technology used by Rightfit pigments	Modification of Chemical Structure	Single crystal formation	No Surface treatement	Random metallisation	Modification of chemical structure
52	The key technology used by Rightfit pigments	No Modification of Chemical Structure	Mixed crystal formation	No Surface treatement	Random metallisation	Mixed crystal formation
53	The key technology used by Rightfit pigments	No Modification of Chemical Structure	Single crystal formation	Appropriate Surface treatement	Random metallisation	Appropriate Surface treatement
54	The key technology used by Rightfit pigments	No Modification of Chemical Structure	Single crystal formation	No Surface treatement	Selective metallisation	Selective metallisation
55	The key technology used by Rightfit pigments	No Modification of Chemical Structure	Single crystal formation	No Surface treatement	Selection of Appropriate Laking Metal	Selection of Appropriate Laking Metal
56	The key technology used by Rightfit pigments	No Modification of Chemical Structure	Single crystal formation	No Surface treatement	Generation of desired crystal form	Generation of desired crystal form
57	The Rightfit pigment for technology used- Modification of Chemical Structure	Redfit Scarlet	Pigment Red	Blue shade red	Reddish Yellow	Redfit Scarlet
58	The Rightfit pigment for technology used- Selection of Appropriate Laking Metal	Redfit Scarlet	Pigment Red	Blue shade red	Medium Red	Medium Red
59	Example for organic pigments	dichlorobenzidines	Pigment Red	Blue shade red	Medium Red	dichlorobenzidines

60	The Rightfit pigment for technology used- Selection of Appropriate Laking Metal	Redfit Scarlet	Pigment Red	Blue shade red	Brilliant orange	Brilliant Orange

UNIT V
SYLLABUS

An efficient, green synthesis of a compostable and widely applicable plastic (poly lactic acid) made from corn.

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

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

Advantages of petrochemical-based polymers, which encouraged industries to use them are:
(a) low cost and high-speedproduction;
(b) high mechanicalperformance;
(c) good barrier properties;and
(d) good heatsealability.

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

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

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

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

(a) Extracteddirectlyfromnaturalrawmaterials, suchaspolysaccharideslikestarchand cellulose; proteins like gelatin, casein, and silk; and marineprokaryotes;

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

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

(d) Producedfromcrudeoillikealiphaticandaromaticpolyesters,polyvinylalcohol,and modifiedpolyolefins, which are sensitive to temperature andlight.

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

This being the situation what problem we face

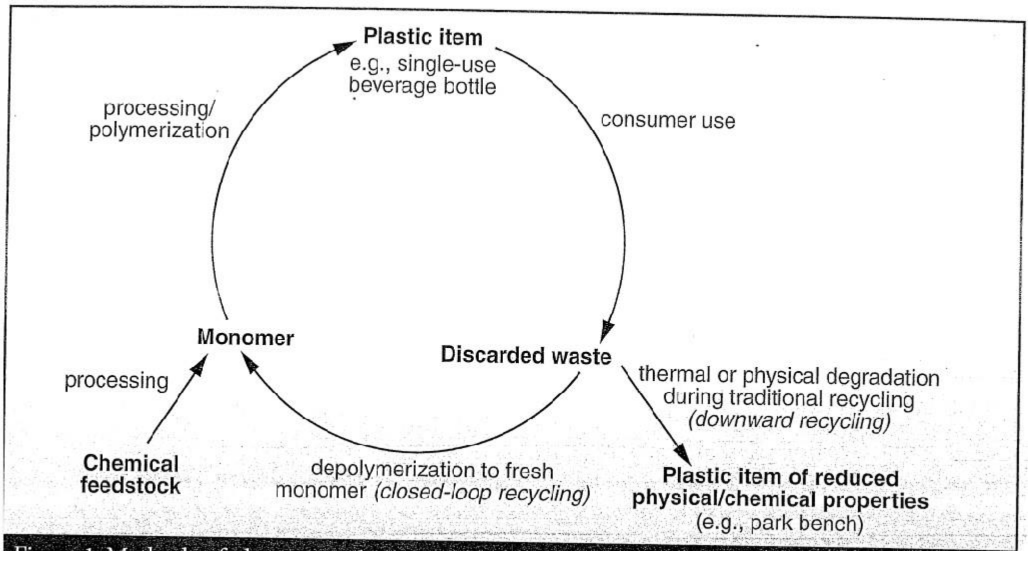
Almost all plastic products made today are made from crude oil which is a non-renewable source that is quickly being depleted. Eventhough some people encourage us to reuse and recycle plastic commodities, these practice will not permanently solve the problem generated by plastic waste. Many plastic items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

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

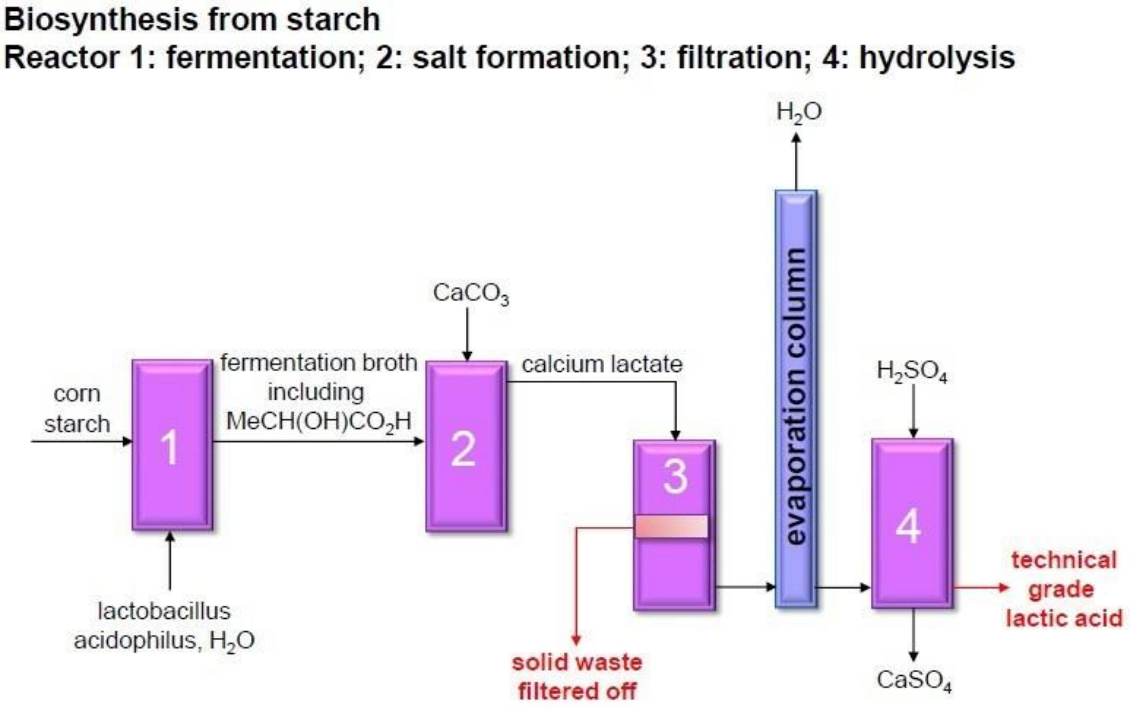
Because of such issues as contamination and thermal degradation, most plastic products are downward recycled into a product with inferior quality. For example a plastic drink bottle that is recycled does not return to a consumer as a fresh drink bottle, but rather as an item such as plastic chair or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

So what will the solution

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



Methods of recycling.

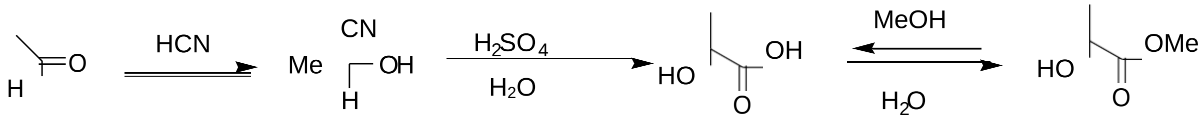


Biosynthesis from starch
Reactor 1: fermentation; 2: salt formation; 3: filtration; 4: hydrolysis

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

Chemical synthesis of lactic acid

Lactic acid can also be synthesised from acetaldehyde.



The advantages of this synthetic method is that

1. all the reactions involved are fast and high yieldingreactions

2. MeOH generated in final step isrecycled
3. Produces high purity lactic acid(99%)

The disadvantages are

1. HCN is highly toxic; acetaldehyde and MeOH are alsotoxic
2. Waste stream of Ammonium sulphate is produced(but can be used asa fertilizer)
3. Several energy intensive distillationsrequired.

Biochemical Process

The advantages are 1.Renewablefeedstock 2. Uses non-hazardous materials

The disadvantagesare

1. Slow process (every cycle takes 4-6days)
2. Quantity of product per reactor volume islow
3. Evaporation is required (due to low saltconcentration)
4. Technical grade lactic acid(85 % purity) produced. In order to produce high purity product, the material has to undergo the methanol transesterificationprocess.
5. Waste stream of $CaSO_4$ produced and very large quantities of wastewater.

PLA Production

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

1. Limited capacity due to the dependency on a by-product of anotherprocess,
2. Inability to make only the desirable L-lactic acid stereoisomer,and

3. High manufacturingcosts.

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

- a. Using species of the *Lactobacillus* genus such as *Lactobacillus delbrueckii, L.amylophilus, L. bulgaricus, and L.leichmanii*,
- b. pH range of 5.4 to6.4,
- c. Temperature range of 38 to 42 °C,and
- d. Low oxygenconcentration.

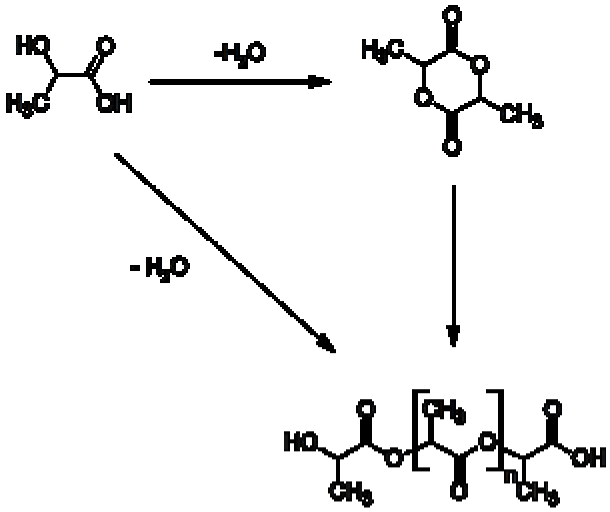
Generally, pure L-lactic acid is used for PLA production.

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

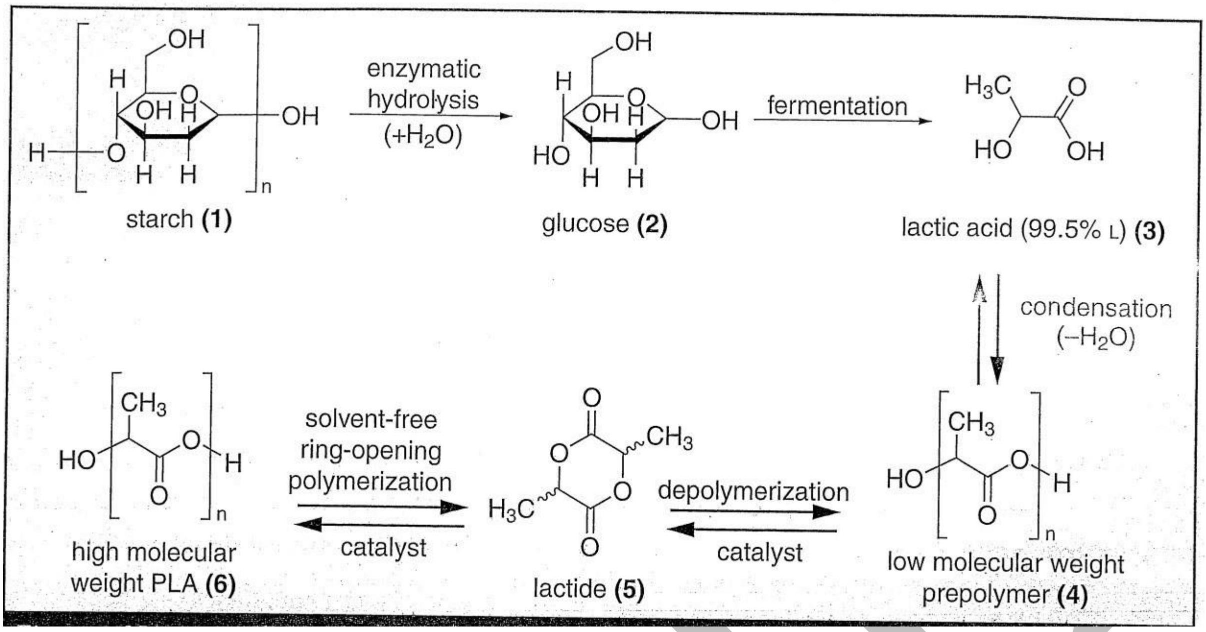
Another route to PLA is the direct condensation of lactic acid monomers. This process needs to be carried out at less than 200 °C; above that temperature, the entropically favoured lactide monomer is generated.

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

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



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



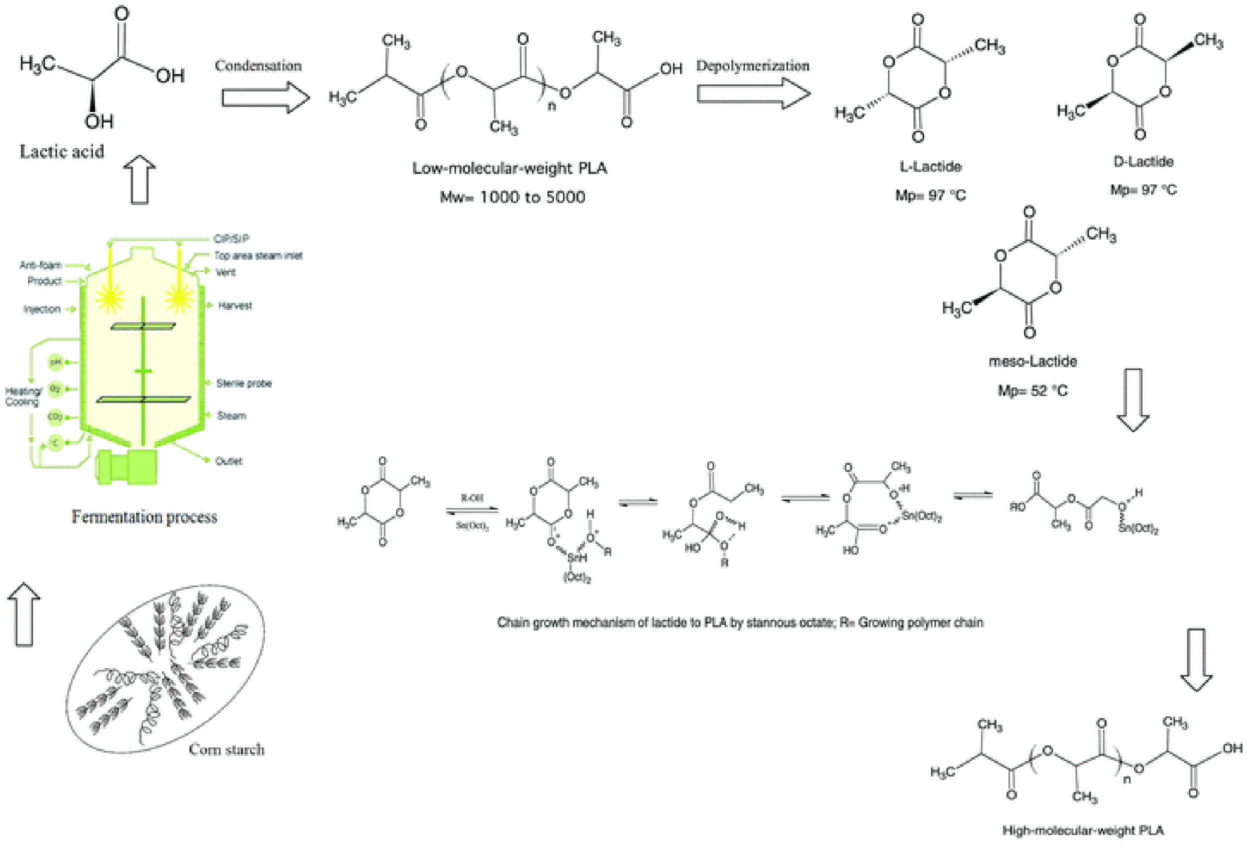
Production of PLA from starch

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

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

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

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



Current production steps for PLA.

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

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

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

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

PLA or poly-lactide was discovered in 1932 by Carothers (at DuPont). He was only able to produce a low molecular weight PLA by heating lactic acid under vacuum while removing the condensed water. The problem at that time was to increase the molecular weight of the products; and, finally, by ring-opening polymerization of the lactide, high-molecular weight PLA was synthesized. PLA was 1st used in combination with polyglycolic acid (PGA) as suture material and sold under the name Vicryl in the U.S.A. in1974.

In comparison to other biopolymers, the production of PLA has numerous advantages including:

(a) production of the lactide monomer from lactic acid, which is produced by fermentationof a renewable agricultural sourcecorn;

(b) fixation of significant quantities of carbon dioxide via corn (maize) production by the cornplant;

(c) significant energysavings;

(d) the ability to recycle back to lactic acid by hydrolysis oralcoholysis;

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

(f) reduction of landfillvolumes;

(g) improvement of the agricultural economy;and

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

Briefly, PLA is based on agricultural (crop growing), biological (fermentation), andchemical (polymerization) sciences andtechnologies.

PLA Processing Technologies

The methods of manufacture for biopolymers are all established polymer-manufacturing techniques, but the control and application of these methods must be varied to cope with certain factors associated with exploiting the advantages of biopolymers. The manufacturing routes all show certain fundamental similarities, with the major differences depending on whether a thermoset or thermoplastic biopolymer is to be processed.

The conditions in biopolymer processes such as injection molding are least damaging to polymer melts, and most problematic in continuous processes like extrusion, particularly in processes where the extrudate is stretched, such as film blowing. The limiting factors for processing conditions for biopolymers are the same as for petrochemical-based ones: degradation at the upper limits of temperature and shear, and lack of homogeneity at the lower limits. However, these limits are somewhat more tightly drawn at the upper limits for biopolymers. The results of exceeding these upper limits are degradation of the polymer, resulting in molding defects such as weld lines, discoloration, or a strong odor in the final product.

Commercial PLA resins are packaged in crystalline and amorphous pellet forms. Crystalline and amorphous pellets look significantly different. Semicrystalline pellets are opaque and amorphous pellets are transparent. Different types of PLA resins with different application ranges are being produced and each customer should specify packaging demands. In Table 2, available commercial PLA resins for food packaging applications are characterized.

Table 2 Commercial PLA resins adapted by NatureWorks

Product code	Applications	Usages
2002D	Extrusion, thermoforming	Dairy containers, food serviceware, transparent food containers, blister packaging, cold drink cups

Product code	**Applications**	**Usages**
3001D 3051D	Injection molding for applications with heat deflection temperatures lower than 55 °C (130 °F)	Cutlery, cups, plates, and saucers, and outdoor novelties
3251D	Injection molding, having higher melt flow capability than other PLA resins for easier molding of thin-walled parts	Injection molding applications, both clear andopaque, requiring high gloss, UV resistance, andstiffness
4032D	Biaxially oriented films with use temperatures up to 150 °C (300 °F), barrier to flavor and grease, and oil resistance	Laminations, printed films with higher curing temperatures, other packaging applications
4042D	Biaxially oriented films with use temperatures up to 130 °C (265 °F), barrier to flavor and grease, and superior oil resistance	Candy twist-wrap, salad, and vegetable bags, window envelope film, lidding film, label film, other packaging applications
4060D	Heat sealant with a seal initiation temperature of 80 °C	Can be coextruded with other PLA resin to form a sealant layer for biaxially- oriented PLA film
7000D	Injection stretch blow molding, for 1:2 stage operations	Fresh dairy, edible oils, fresh water
7032D	Injection stretch blow molding, for 1:2 stage operation	Fruit juices, sports drinks, jams, and jellies

The processing technologies for producing different packaging applications with PLA resins are mentioned here.

PLA production is a popular idea as it represents the fulfillment of the dream of cost-efficient, non-petroleum plastic production. The huge benefit of PLA as a bioplastic is its versatility and the fact that it naturally degrades when exposed to the environment. For example, a PLA bottle left in the ocean would typically degrade in six to 24months.

Compared to conventional plastics (which in the same environment can take several hundred to a thousand years to degrade) this is truly phenomenal. Accordingly, there is a high potential for PLA to be very useful in short lifespan applications where biodegradability is highly beneficial (e.g. as a plastic water bottle or as a container for fruit and vegetables). Of note, despite its ability to degrade when exposed to the elements over a long time, PLA is extremely robust in any normal application (e.g. as a plastic electronicspart).

Chemical and physical properties

Due to the chiral nature of lactic acid, several distinct forms of polylactide exist: poly-L-lactide (**PLLA**) is the product resulting from polymerization of L,L-lactide (also known as L-lactide).

PLLA has a crystallinityof around 37%, a glass transition temperature 60–65 °C, a meltingtemperature 173–178 °C and a tensile modulus 2.7–16 GPa. Heat-resistant PLA can withstand temperatures of 110 °C. PLA is soluble in chlorinated solvents, hot benzene, tetrahydrofuran, anddioxane.

Polylactic acid can be processed like most thermoplastics into fiber (for example, using conventional melt spinning processes) and film. PLA has similar mechanical properties to PETE polymer, but has a significantly lower maximum continuous use temperature. The tensile strength for 3-D printed PLA was previouslydetermined.

The melting temperature of PLLA can be increased by 40–50 °C and its heat deflection temperature can be increased from approximately 60 °C to up to 190 °C by physically blending the polymer with PDLA (poly-D-lactide). PDLA and PLLA form a highly regular stereocomplex with increased crystallinity. The temperature stability is maximised when a 1:1 blend is used, but even at lower concentrations of 3–10% of PDLA, there is still a substantial improvement. In the later case, PDLA acts as a nucleating agent, thereby increasing the crystallization rate. Biodegradation of PDLA is slower than for PLA due to the higher crystallinity ofPDLA.

There is also poly(L-lactide-*co*-D,L-lactide) (PLDLLA) – used as PLDLLA/TCP scaffolds for boneengineering.

What is PLA, and what is it used for?

Polylactic Acid (PLA) is different than most thermoplastic polymers in that it is derived from renewable resources like corn starch or sugar cane. Most plastics, by contrast, are derived from the distillation and polymerization of nonrenewable petroleum reserves. Plastics that are derived from biomass (e.g. PLA) are known as "bioplastics."

Polylactic Acid is biodegradable and has characteristics similar to polypropylene (PP), polyethylene (PE), or polystyrene (PS). It can be produced from already existing manufacturing equipment (those designed and originally used for petrochemical industry plastics). This makes it relatively cost efficient to produce. Accordingly, PLA has the second largest production volume of any bioplastic (the most common typically cited as thermoplasticstarch).

There are a vast array of applications for Polylactic Acid. Some of the most common uses include plastic films, bottles, and biodegradable medical devices (e.g. screws, pins, rods, and plates that are expected to biodegrade within 6-12 months). PLA constricts under heat and is thereby suitable for use as a shrink wrap material.

What Are The Different Types of Polylactic Acid and Why is it Used so Often?

There are several different types of Polylactic Acid to include Racemic PLLA (Poly-L-lactic Acid), Regular PLLA (Poly-L-lactic Acid), PDLA (Poly-D-lactic Acid), and PDLLA (Poly-DL-lactic Acid). They each have slightly different characteristics but are similar in that they are produced from a renewable resource (lactic acid: $C_3H_6O_3$) as opposed to traditional plastics which are derived from nonrenewable petroleum.

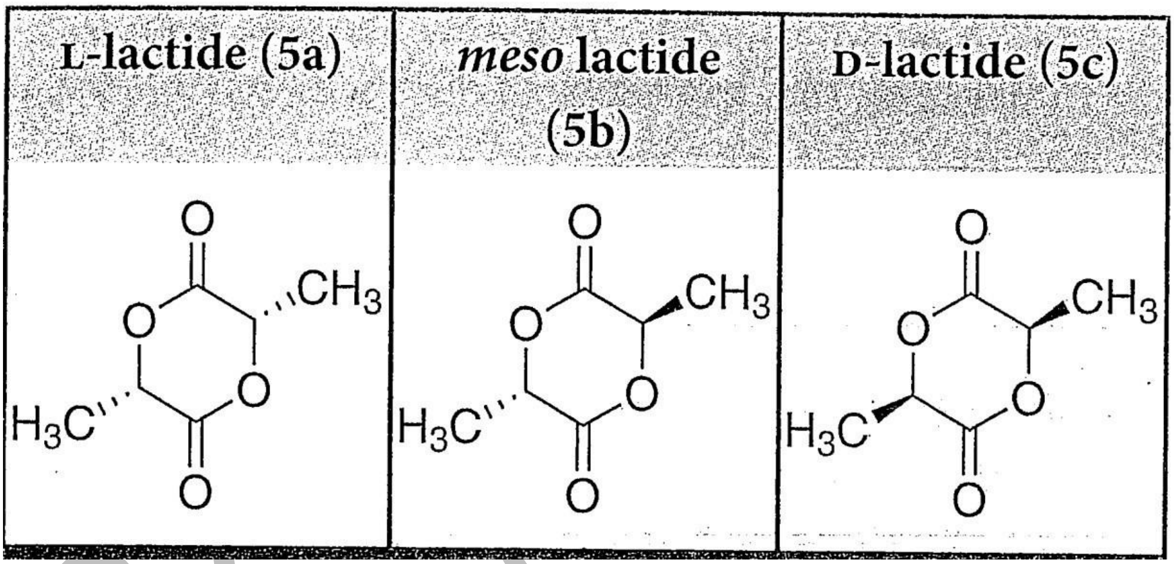
Is PLA toxic?

In solid form, no. In fact, Polylactic Acid (PLA) is biodegradable. It is often used in food handling and medical implants that biodegrade within the body over time. Like most plastics, it has the potential to be toxic if inhaled and/or absorbed into the skin or eyes as a vapor or liquid (i.e. during manufacturing processes). Be careful and closely follow handling instructions for molten polymer in particular.

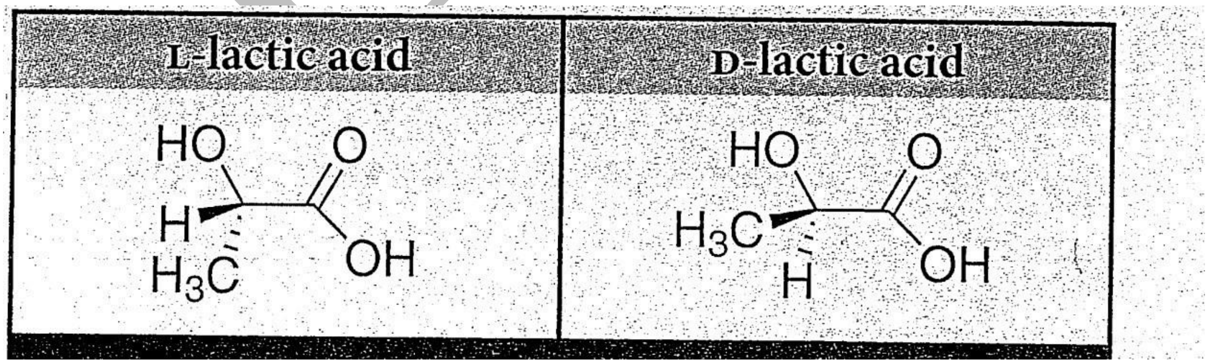
What are the Disadvantages of Polylactic Acid?

PLA has a relatively low glass transition temperature (typically between 111 and 145 °F). This makes it fairly unsuitable for high temperature applications. Even things like a hot car in the summer could cause parts to soften and deform.

Polylactic Acid is a little bit more brittle than ABS for 3D prototyping but it has some advantages as well. For a full comparison of the two plastics as they relate to 3D printing read here.



Isomers of Lactide



Isomers of lactic acid

Due to its biocompatibility, the medical community has used PLA for many years for making bone screws, sutures, surgical staples and tissue scaffolding.

PLA's physical properties like high gloss, clarity, printability, heat sealability, oil and grease resistance and its ability to act as a flavour and odour barrier, are comparable or superior than that of polystyrene and polyethylene terephthalate(PET).

The process of producing PLA designed by Nature works received a presidential Green chemistry Challenge award in the year 2002. Unlike most other polymer synthesis that use crude oil as a chemical feedstock, Nature Work process uses starch harvested from corn. Besides the obvious advantage of using renewable source, the use of corn as the feed stock provides the economic benefit of not having a market price directly linked to the rising cost of the crude oil. Starch is a biopolymer produced in plants by the linking of glucose molecules. Glucose is the product of photosynthesis, and therefore one might consider carbon di oxide and water as the required feedstock for the preparation ofPLA.

The Nature works process begins by reactingwater enzymatically with the corn derived starch, which cleaved the starch glycosidic linkage to form glucose, the monomer of starch. The glucose is then converted into lactic acid via fermentation. This process involves the generation of pyruvate (as in glycolysis) which is then converted into lactic acid (99.5% L-lactic acid). Lactic acid is then polymerised in to an oligomeric 'pre- polymer' in a mild solventless condensation polymerization. We should recognise the reaction between the lactic acid carboxylic acid functionality with hydroxyl functionality as esterification. The low molecular weight prepolymer that is formed is then catalytically broken down into a cyclic dimer (two linked monomers) of lactic acid called lactide with three possible stereochemical isomers which undergoes actualpolymerization.

1. The development of Nature works PLA won the presenditial Green Chemistry award. Look up the three focus areas for this award and determine which focus area this case best fitsinto.

2. List out any two of the twelve principles of green chemistry that are addressed by the green chemistry developed by Nature WorksPLA.

3. What are some other starch rich plant that could be used to producePLA

4. Nature Works market the product as "compositable" and not as "Biodegradable". What is the difference between these twoterms.

5. What is the stereochemical relationship between the two forms of lactic acid andthree forms ofLactide.

6. What compounds would you expect PLA to degrade to in theenvironment.

7. Propose a mechanism for the formation of PLA "pre-polymer" from lactic acid inaqueous acidic environment. Why is this reaction referred tocondensation.

8. When composted, PLA releases carbon di oxide into the atmosphere. Does this carbon di oxide add to the global greenhouse effect. Why or whynot

POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What Advantages of petrochemical-based polymers, which encouraged industries to usethem
2. What arethedisadvantages of petrochemical-based polymers, which discouraged industries to usethem
3. Mention any three alternative ways for plastics wastemanagement.
4. Neither reusing or recycling of plastic is always beneficial as we are led to believe. Comment on thestatement.
5. Explain the method of recycling of a plastic material.
6. How lactic acid is synthesized in the laboratory. What are its advantages and disadvantages.
7. Suggest some New ideas for decreasing PLA final price and making production processes more eco-friendly, in comparison to earlier productionprocess.
8. In comparison to other biopolymers, the production of PLA has numerousadvantages. Justify thestatement.
9. What is PLA, and what is it usedfor?
10. Is PLA toxic. Comment on the statement.
11. What are the disadvantages fPLA.
12. What are starch rich plants that could be used to producePLA
13. Nature Works market the product as "compositable" and not as"Biodegradable". What is the difference between these twoterms.
14. What compounds would you expect PLA to degrade to in theenvironment.

PART C (8 Mark Questions)

1. What Are The Different Types of Polylactic Acid and Why is it Used soOften?
2. What are the possible monomers of prepearing PLA. Draw theirstructres.
3. The development of Nature works PLA won the presenditial Green Chemistry award. Look up the three focus areas for this award and determine which focus area this case best fitsinto.
4. List out any two of the twelve principles of green chemistry that are addressed by the green chemistry developed by Nature WorksPLA.

5. What is the stereochemical relationship between the two forms of lactic acid andthree forms ofLactide.
6. Propose a mechanism for the formation of PLA "pre-polymer" from lactic acidin aqueous acidic environment. Why is this reaction referred tocondensation.
7. When composted, PLA releases carbon di oxide into the atmosphere. Does thiscarbon di oxide add to the global greenhouse effect. Why or whynot.
8. What are bio-polymers. How many different types of biopolymers wererecognized fromnature.
9. What is polylactic acid. Explain its biosynthesis fromstarch.
10. Explain the biochemical process of preparing lactic acid. What are its advantages and disadvantages.
11. Explain the manufacturing process of PLA from corn. What are theadvantages.

DEPARTMENT OF CHEMISTRY

Online questions (Multiple choice questions)

GREEN METHODS IN CHEMISTRY (18CHU404A)

UNIT V

S.No	Question	Option 1	Option 2	Option 3	Option 4	Answer
1	One of the advantage of petrochemical-based polymers, which encouraged industries to use them	low cost and high-speed production	declining oil and gas resources	increasing oil and gas prices during recent decades	uneconomical costs and cross-contaminations in their recycling	low cost and high-speed production
2	An advantage of petrochemical-based polymers, which encouraged industries to use them	declining oil and gas resources	high mechanical performance	increasing oil and gas prices during recent decades	uneconomical costs and cross-contaminations in their recycling	high mechanical performance
3	Among the following an advantage of petrochemical-based polymers, which encouraged industries to use them	consumer toxicity risks about their monomers or oligomers migrating to edible materials	uneconomical costs and cross-contaminations in their recycling	good barrier properties	environmental concerns for their degradation or incineration and global warming	good barrier properties
4	One of the advantage of petrochemical-based polymers, which encouraged industries to use them	declining oil and gas resources	increasing oil and gas prices during recent decades	uneconomical costs and cross-contaminations in their recycling	good heat sealability	good heat sealability
5	One of the disadvantage of petrochemical-based polymers, which encouraged industries to use them	declining oil and gas resources	good heat sealability	high mechanical performance	low cost and high-speed production	declining oil and gas resources

6	Among the following a disadvantage of petrochemical-based polymers, which encouraged industries to use them	good heat sealability	increasing oil and gas prices during recent decades	high mechanical performance	low cost and high-speed production	increasing oil and gas prices during recent decades
7	Adisadvantage of petrochemical-based polymers, which encouraged industries to use them	high mechanical performance	low cost and high-speed production	uneconomical costs and cross-contaminations in their recycling	good heat sealability	uneconomical costs and cross-contaminations in their recycling
8	Adisadvantage of petrochemical-based polymers, which encouraged industries to use them	high mechanical performance	low cost and high-speed production	consumer toxicity risks about their monomers or oligomers migrating to edible materials	good heat sealability	consumer toxicity risks about their monomers or oligomers migrating to edible materials
9	One of the way for plastics waste management	Burying the plastic in the soil	Converting them in to vapour	Dissolving them in water and mix with sea water	Mechanical recycling of the plastic	Mechanical recycling of the plastic
10	One of the way for plastics waste management	Burying the plastic in the soil	Converting them in to vapour	biological recycling	Dissolving them in water and mix with sea water	biological recycling
11	One of the way for plastics waste management	Burying the plastic in the soil	energy recovery	Converting them in to vapour	Dissolving them in water and mix with sea water	energy recovery
12	polysaccharides like starch and cellulose are	Extracted directly from natural raw materials	Produced by chemical synthesis from bio-derived monomers	Produced by microorganisms or genetically modified bacteria	Produced from crude oil	Extracted directly from natural raw materials
13	Biopolymer Extracted directly from natural raw materials	poly-lactic acid	Cellulose and starch	polyhydroxybutyrate (PHB)	polyvinyl alcohol	Cellulose and starch
14	Biopolymers like poly-lactic acid	Extracted directly from natural raw materials	Produced by chemical synthesis from bio-derived	Produced by microorganisms or genetically modified	Produced from crude oil	Produced by chemical synthesis from bio-derived

			monomers	bacteria		monomers
15	Biopolymers Produced by chemical synthesis from bio-derived monomers	poly-lactic acid	Cellulose and starch	polyhydroxybutyrate (PHB)	polyvinyl alcohol	Poly lactic acid
16	Biopolymers like polyhydroxybutyrate (PHB)	Extracted directly from natural raw materials	Produced by chemical synthesis from bio-derived monomers	Produced by microorganisms or genetically modified bacteria	Produced from crude oil	Produced by microorganisms or genetically modified bacteria
17	Biopolymers Produced by microorganisms or genetically modified bacteria	poly-lactic acid	Cellulose and starch	polyhydroxybutyrate (PHB)	polyvinyl alcohol	polyhydroxybutyrate (PHB)
18	Biopolymers like poly-vinyl alcohol	Extracted directly from natural raw materials	Produced by chemical synthesis from bio-derived monomers	Produced by microorganisms or genetically modified bacteria	Produced from crude oil	Produced from crude oil
19	Example for a biopolymer produced from crude oil	poly-lactic acid	Cellulose and starch	polyhydroxybutyrate (PHB)	polyvinyl alcohol	Polyvinyl alcohol
20	Example for a biodegradable polymer	poly-lactic acid	Bakelite	polystyrene	Nylon	poly-lactic acid
21	Polylactic acid is prepared from	corn	wheat	onion	tomato	corn
22	Polylactic acid is prepared from	Starch	wheat	onion	tomato	Starch
23	The monomer of poly lactic acid is	Lactic acid	Acetic acid	Linoleic acid	Linolinic acid	Lactic acid
24	The monomer of poly lactic acid is	cyclic di-ester, lactide	Acetic acid	Linoleic acid	Linolinic acid	cyclic di-ester, lactide
25	Lactic acid is prepared from	benzaldehyde	acetone	acetaldehyde	acetophenone	acetaldehyde
26	The advantage of the synthetic method for the preparation of lactic acid is	HCN is highly toxic	all the reactions involved are fast and high yielding reactions	Several energy intensive distillations required.	Waste stream of ammonium sulphate is produced.	all the reactions involved are fast and high yielding reactions
27	The advantage of the synthetic	HCN is highly	Produces high	Several energy	Waste stream of	Produces high

	method for the preparation of lactic acid is	toxic	purity lactic acid	intensive distillations required.	ammonium sulphate is produced.	purity lactic acid
28	The advantage of the synthetic method for the preparation of lactic acid is	HCN is highly toxic	Methanol generated in final step is recycled	Several energy intensive distillations required.	Waste stream of ammonium sulphate is produced.	Methanol generated in final step is recycled
29	The advantage of preparing poly lactic acid by biochemical process is	It is from a Renewable feedstock	It is a Slow process	Quantity of product per reactor volume is low	Technical grade lactic acid(85 % purity) produced	It is from a Renewable feedstock
30	The advantage of preparing poly lactic acid by biochemical process is	Uses non-hazardous materials	It is a Slow process	Quantity of product per reactor volume is low	Technical grade lactic acid(85 % purity) produced	Uses non-hazardous materials
31	The disadvantage of preparing poly lactic acid by biochemical process is	Uses non-hazardous materials	It is from a Renewable feedstock	The process is faster	It is a Slow process	It is a Slow process
32	The disadvantage of preparing poly lactic acid by biochemical process is	Uses non-hazardous materials	It is from a Renewable feedstock	The process is faster	Quantity of product per reactor volume is low	Quantity of product per reactor volume is low
33	The drawback of preparing poly lactic acid by biochemical process is	Uses non-hazardous materials	It is from a Renewable feedstock	The process is faster	Technical grade lactic acid(85 % purity) produced	Technical grade lactic acid(85 % purity) produced
34	The setback of preparing poly lactic acid by biochemical process is	Uses non-hazardous materials	It is from a Renewable feedstock	The process is faster	Evaporation is required (due to low salt	Evaporation is required (due to low salt

					concentration	concentration
35	The setback of preparing poly lactic acid by biochemical process is	Uses non-hazardous materials	It is from a Renewable feedstock	The process is faster	Waste stream of $CaSO_4$ produced and very large quantities of waste water	Waste stream of $CaSO_4$ produced and very large quantities of waste water
36	Lactic acid is	2-hydroxy propionic acid	2-amino propionic acid	2-hydroxy acetic acid	2-aminoacetic acid	2-hydroxy propionic acid
37	An optically active compound is	Butanoic acid	2-hydroxy propionic acid	2-hydroxy acetic acid	2-aminoacetic acid	2-hydroxy propionic acid
38	The limitations of synthetic method of prepearing lactic acid is	Limited capacity due to the dependency on a by-product of another process	Uses non-hazardous materials	It is from a Renewable feedstock	The process is faster	Limited capacity due to the dependency on a by-product of another process
39	The method which is preferably used for industrial production of lactic acid is	Heterofermentative method	Homofermentative method	Synthetic method	Chemical synthesis	Homofermentative method
40	The homofermentative method is preferably used for industrial production of lactic acid. The optimum PH is	1.0 to 2.0	5.4 to 6.4	Neutral PH	10.5 to 12.5	5.4 to 6.4
41	The homofermentative method is preferably used for industrial production of lactic acid. The optimum temperature is	-5 to -10 °C	20 to 30 °C	38 to 42 °C	80 to 100 °C	38 to 42 °C
42	The homofermentative method is preferably used for industrial production of lactic acid. The optimum oxygen content should be	Very high concentration	High oxygen concentration	Oxygen is not required	Low oxygen concentration	Low oxygen concentration
43	The lactic acid used for PLA	L-lactic acid	d-lactic acid	ld-lactic acid	Meso lactic acid	L-lactic acid

	production					
44	NatureWorks exclusively usesWhich substance for the production of PLA	Carbohydrates	Proteins	Fats	Vitamins	Carbohydrates
45	Lactide purification is accomplished by	vacuum-distillation of high temperatures	vacuum-distillation of low temperatures	sublimation	Crystillasation	vacuum-distillation of high temperatures
46	The most considered active initiator for the L-lactide ring-opening polymerization	Cobaltoctoate	stannous octoate	stannous acetate	Iron carbonyl	stannous octoate
47	The most considered active initiator for the L-lactide ring-opening polymerization is stannous octoate which causes	a high degree of racemization at high temperature	a low degree of racemization at low temperature	a low degree of racemization at high temperature	a high degree of racemization at low temperature	a low degree of racemization at high temperature
48	(bis 2-ethyl hexanoate, $SnOct_2$) is	Cobaltoctoate	stannous octoate	stannous acetate	Iron carbonyl	stannous octoate
49	stannous octoate is the initiator used for the synthesis of PLA, it is	Highly toxic	Low toxic	poisonous	volatile	Low toxic
50	New idea for decreasing PLA final price and making production processes more eco-friendly	Using proteins instead of carbohydrates	Using sugarcane instead of corn	Substituting some part of electricity energy by wind power energy	Using fatty acids	Substituting some part of electricity energy by wind power energy
51	One of the most positive points of PLA production in comparison with the other hydrocarbon-based polymers	decrease of CO_2 emission	Increase of CO_2 emission	Less CO production	High green house gas formation	decrease of CO_2 emission
52	PLA was produced by	The Nature Works	Right Fit pigments	M/s Dupont	Rohm and Haas Company	The Nature Works
53	Before the preparation of lactic acid from Corn, initially corn is converted into	Sucrose	Pentose	Glucose	Fructose	Glucose

54	Lactide is formed from Lactic acid by	Reduction	Oxidation	Esterification	Hydroxylation	Esterification
55	The precursor of lactic acid during the conversion of corn into lactic acid is	Pyruvate	xylose	galactose	Mannose	Pyruvate
56	The required feedstock for the preparation of PLA	Carbondioxide and water	Xylose	Corn	Starch	Carbondioxide and water
57	A a cyclic dimer of lactic acid called lactide which undergoes actual polymerization to form PLA consists of .	three possible stereochemical isomers	two possible stereochemical isomers	four possible stereochemical isomers	Five possible stereochemical isomers	three possible stereochemical isomers
58	The presidential Green chemistry Challenge award in the year 2002 was awarded for the production of PLA	The Nature Works	Right Fit pigments	M/s Dupont	Rohm and Haas Company	The Nature Works
59	The presidential Green chemistry Challenge award in the year 2002 was awarded to The Nature Works	For the production of PLA	For the production of Inorganic pigments	For the production of organic pigments	For the production of antifouling agents	For the production of PLA
60	Starch is a biopolymer produced in plants by the linking of	Fructose	Xylose	Glucose	Mannose	Glucose