GREEN CHEMISTRY

Fundamentals and Applications

Editors
Suresh C. Ameta
Rakshit Ameta

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CONTENTS

List of Contributors .... *ix*
List of Abbreviations .... *xiii*
Preface .... *xvii*

1. Introduction 1
Rakshit Ameta

2. Benign Starting Materials 9
Sanyogita Sharma, Neelam Kunwar, Sangeeta Kalal, and P. B. Punjabi

3. Eco-Friendly Products 43
Neelu Chouhan, Anil Kumar, Ajay Sharma, and Rameshwar Ameta

4. Green Catalysts 87
Shikha Panchal, Yuvraj Jhala, Anuradha Soni, and Suresh C. Ameta

5. Ionic Liquids: Promising Solvents 109
Arpit Pathak, Nirmala Jangid, Rakshit Ameta, and P. B. Punjabi

6. Supercritical Fluids 137
Abhilasha Jain, Shikha Panchal, Shweta Sharma, and Ramashwar Ameta

7. Other Green Solvents 161
Abhilasha Jain, Ritu Vyas, Aarti Ameta, and P. B. Punjabi

8. Photocatalysis: An Emerging Technology 199
Indu Bhati, Paras Tak, H. S. Sharma, and Rakshit Ameta

9. Photo-Fenton Reactions: A Green Chemical Route 225
Surbhi Benjamin, Noopur Ameta, P. B. Punjabi, and Suresh C. Ameta

10. Sonochemistry: A Pollution Free Pathway 255
Garima Ameta, Surbhi Benjamin, Vikas Sharma, and Shipra Bhardwaj

11. Microwave Assisted Organic Synthesis: A Need of the Day 283
Chetna Ameta, K. L. Ameta, B. K. Sharma, and Rajat Ameta

12. Green Composites 317
Yasmin, N. P. S. Chauhan, and Rohit Ameta

13. Green Manufacturing Processes 353
Jitendra Vardia, Dipti Soni, and Rakshit Ameta

14. Present Scenario and Future Trends.. 367
Suresh C. Ameta

Index 371

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LIST OF ABBREVIATIONS

2,4-D	2,4-dichlorophenoxyacetic acid
2-MeTHF	2-Methyl tetrahydrofuran
ABS	Acrylonitrile-butadiene-styrene
ACCN	1,1′-Azobis(cyclohexanecarbonitrile)
AIBN	Azo-bis-isobutyronitrile
AL	Alkaline liquid
AMBI	5-amino-6-methyl-2-benzimidazolone
AOPs	Advanced oxidation processes
Ap–CVD	Atmospheric chemical vapor decomposition
BDO	1,4-Butanediol
bmimBr	1-Butyl-3-methylimidazolium bromide
BVMOs	Baeyer–Villiger monooxygenases
Bzf	3-Furfuryl-8-methoxy-3,4-dihydro-2*H*-1,3- benzoxazine
Bzs	3-Octadecyl-8-methoxy-3,4-dihydro-2*H*-1,3-benzoxazine
C2C	Cradle-to-cradle
CaLB	Candida antarctica lipase B
CAN	Ceric ammonium nitrate
CCL	Candida cylindracea lipase
CHP	Combined heat and power
CNHs	Carbon nanohorns
CNTs	Carbon nanotubes
CO_2	Carbon dioxide
CPC	Cetylpyridinium chloride
CPME	Cyclopentyl methyl ether
CRs	Carbon dioxide reactors
CVD	Chemical vapor deposition
DBS	Dodocylbenzene sulphonic acid, sodium salt
DCP	2,4-dichlorophenol
DMF	N, N-dimethylformamide
DMPU	N, N-Dimethylpropyleneurea

DMS	Dimethyl sulphide
DPPH	2,2-Diphenyl-1-picrylhydrazyl
Ee	Enantiomeric excess
emimCl	1-Ethyl-3-methylimidazolium chloride
EPA	Environmental protection agency
EPS	Exopolysaccharide
FA	Fly ash
FAME	Fatty acid methyl esters
FBS	Fluorous biphasic system
FeO_x	Ferrioxalate complex
F-SPE	Fluorous solid-phase extractions
Hb	Hemoglobin
HMF	5-Hydroxymethylfurfural
HOMO	Highest occupied molecular orbital
IPA	Isopropanol
LAS	Linear alkyl sulfonate
LCA	Life cycle assessment
LDA	Lithium diisopropylamide
LOI	Limiting oxygen index
LTMP	2,2,6,6-Tetramethylpiperidide
LUMO	Lowest unoccupied molecular orbital
MA	Maleic anhydride
MAOS	Microwave assisted organic synthesis
MCL	Medium-chain length
MM	Micro fibrillated materials
MPG	Monopropylene glycol
M-S-H	Magnesium silicate hydrates
MSNs	Mesoporous silica nanoparticles
MW	Microwave
NBTPT	1-benzyl-2,4,6-triphenylpyridinium tetrafluoroborate
NCW	Near critical water
NGOs	Non government organizations
NTA	Nitrilotriacetate
NTO	5-Nitro-1,2,4-triazol-3-one
nZVI	Nanoscale zero-valent iron
P_a	Acoustic pressure

PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PE	Polythene
PEG	Polyethylene glycol
PHA	Polyhydroxy alkanoates
PHAs	Polyhydroxyalkanoates
PHB	Poly-3-hydroxybutyrate
PHB	Polyhydroxy butyrate
PHE	Phenanthrene
PHH	Polyhydroxyhexanoate
PHV	Polyhydroxyvalerate
PICs	Products of incomplete combustion
PLA	Polylactic acid
p-NTS	p-nitrotoluene-ortho-sulphonic acid
PPA	Polyphosphoric acid
PPCP	Pharmaceuticals and personal care products
PPD	p-Phenylenediamine
PPG	Procaine penicillin-G
PS	Polystyrene
PTC	Phase transfer catalyst
PTT	Polytrimethylene terephthalate
PVC	Poly vinyl chloride
RB-5	Reactive black-5
RME	Reaction mass efficiency
ROL	Rhizopus oryzae lipase
SA	Sand aggregates
SAIER	Strongly acidic ion exchange resin
$ScCO_2$	Supercritical carbon dioxide
SCFs	Supercritical fluids
ScH_2O	Supercritical water
SCL	Short-chain length
SCMs	Supplementary cementitious materials
SCW	Supercritical water
SCWO	Supercritical water oxidation
SFC	Supercritical fluid chromatography
SLS	SODIUM lauryl sulphate

SOFC	Solid oxide fuel cells
SP	Super plasticizer
SPB	Sodium perbonate
SSF	Simultaneous saccharification and fermentation
SSRIs	Selective serotonin reuptake inhibitors
TBH	Tebuthiuron
TBPH	Tetrabutyl phosphonium hydroxide
TBTO	Tributyltin oxide
TCE	Trichloroethylene
THF	Tetrahydrofuran
TMAA	Tetramethyladipic acid
TMG	1,1,3,3-Tetramethylguanidinium
TNT	Trinitrotoluene
TOA	Trioctylamine
TX-100	Triton X-100
UASB	Upflow anaerobic sludge blanket
VOCs	Volatile organic compounds
WWTP	Waste water treatment plants
Xan	Xanthan

PREFACE

The role of chemistry in the advancement of human civilization is very significant, but this achievement has come at the cost of human health and the global environment. Many chemicals find their way up to the food chain and get circulated in the ecosystem. This book is a step to promote a strategy towards sustainable development and with an aim to create a 'Greener World.'

The utilization of green chemistry principles in different industries can therefore be viewed as both an obligation and a significant opportunity to enhance our positive impact on the global community. Green chemistry can be defined as the invention, design and application of chemical products and processes to reduce or eliminate the generation of hazardous substances. Green chemistry is not a new branch of chemistry; rather it is a thought process on existing and new tools and knowledge of chemistry in a way that it continues to contribute to the society while protecting the environment also. Nowadays, green chemistry has been established as a pathway/route for a safer world, and its crucial role in the sustenance of the environment has been reviewed in this book.

This book addresses different topics under the domain of green chemistry, such as introduction, green reactants, green catalysts, green products, green solvents, different AOPs, and the use of green processes on the industrial scale. The book also deals with the current and future impact of green chemistry and its education in order to maximize atom economy.

The authors have aimed to enlighten readers regarding the green routes that are both environment friendly and beneficial on the industrial scale as well. The basic need is to put the theories into practice, and readers are requested to read, understand, and also give suggestions, if any.

— Suresh C. Ameta and Rakshit Ameta

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CHAPTER 1

INTRODUCTION

RAKSHIT AMETA

CONTENTS

Keywords 7
References 7

The entire world is in the cancerous grip of rapidly increasing environmental pollution in its various facets like water pollution, air pollution, soil pollution, and so on. This problem is further supported by global warming and energy crisis. Environmental pollution makes life miserable on this beautiful planet, “The Earth”. This is all because of use of gray chemistry to fulfill different demands of materials with varied applications, such as metallurgy, synthesis of pharmaceuticals and other chemicals, use of volatile organic solvents, polymers, dry cleaning, agriculture, use of detergents, and so on, which creates different kind of pollutions. Men cannot survive without using many of these toxic chemicals to make their life more comfortable even at the cost of their health. Therefore, there is a pressing demand all over the globe to either reduce the use of more toxic materials or to replace them with less toxic or less harmful alternates.

This can be achieved by transforming from gray chemistry to green chemistry. The term green chemistry was used first by Paul T. Anastas in the beginning of last decade of 20th century. The field of green chemistry has been excellently presented by several workers (Tundo and Anastas, 2000; Anastas et al., 2000; Ameta, 2002; Lancaster, 2002; Ameta et al., 2004; Matlack, 2008; Ameta et al., 2012).The green chemistry is in no way different from gray chemistry except the approach toward a chemical process, may be manufacture, design, and applications. Green chemistry is totally different from environmental chemistry. In environmental chemistry, one takes care of the kind of pollution, extent of pollution, and methods to combat against this pollution whereas green chemistry takes care of all these factors in advance. It is something like diagnosis of any disease and its treatment is environmental chemistry while prevention from that disease is green chemistry. There is a well-known proverb that “Precaution is better than Cure”. Prevention is a green chemical pathway while cure is an environmental pathway.

Apart from the existing forms of pollutions, we are going to face and even we are facing these emerging faces of pollution today also that is, polymer and detergent pollutions. Almost all materials like metal, wood, textile, and so on, are slowly being replaced by one or other kind of polymers, which has resulted into accumulation of this polymeric material into the dumping yards. The disposal of this dumped material or its recycling is a burning problem of the day.

Soap is biodegradable but as it does not work in hard water, therefore, it is rapidly being substituted by detergent. We have almost forgotten the use of washing soap leaving aside bathing soap. These detergents are not biodegradable and, therefore, remain for years together in nearby water resources; thus, making this water unfit for its use as portable water. It is utmost necessary to find out either some substitute for these detergents or to develop methods for degrading the accumulated detergents in water.

Pharmaceutical industries are facing a problem, which is like a double headed arrow. The drugs should be toxic to bacteria or fungi but it should not be harmful to human beings, animals, plants, and so on. If an effort is being made to increase the efficacy of a drug, insecticides, weedicides, and so on, it may also increase its toxicity, which is undesirable. To keep the toxicity low and increasing the efficiency is a challenging task for a chemist because one is working to achieve two totally opposing objectives. However, green chemistry may provide some feasible solutions to this problem.

According to Anastas, green chemistry utilizes a set of 12 principles that either reduces or eliminates the use or generation of any hazardous substance in designing, manufacture and application of chemicals. This is as approach, which is based on reducing the amount of waste generated at source rather than treating this waste after it has been formed. We as the chemists are normally blamed for creating pollution, but the green chemical approach not only solve the problem of pollution but it will also provide the methods to synthesize or utilize substances in an eco-friendly manner. Green chemical approach is holistic in nature and encompasses almost all the major branches of chemical science, such as organic or inorganic synthesis, catalysis, drug discovery, material science, polymer, nanochemistry, supramolecular chemistry, treatment of waste water, and so on.

Green chemistry is also known synonymously as:

1. Clean Chemistry
2. Atom Economy
3. Benign by Design Chemistry
4. Eco-Friendly Chemistry
5. Environmentally Benign Chemistry
6. Sustainable Chemistry and also
7. E-Chemistry

To achieve green chemical pathway at laboratory as well as industrial level still exists as a challenge for chemists. Collaborative efforts are urgently needed from government, industries, academics, and non government organizations (NGOs) to face this challenge.

In a presidential address to Indian Chemical Society, Ameta (2002) has very rightly given the slogan:

Green Chemistry: Green Earth

Clean Chemistry: Clean Earth

There may be a confusion that green chemical pathway is almost benign, but it is not a perfectly true statement because there cannot be any chemical, which is perfectly benign and therefore, green chemistry diverts use of chemicals from malign to benign manner. Common salt is necessary for life, but it may develop hypertension, if taken in excess; so it is the case with carbohydrates (sugar), which are required for providing energy for daily routine life but if given in excess, it may be harmful to humans. Therefore, shifting from less benign (more malign) to more benign (less malign) process may be considered as a green chemical approach. Someone has well said that "A matter may act as poison if given in large amount, and a poison if given in very small amount may act as a nectar". This is the basic concept of homoeopathy, which deals with very small concentrations of toxic chemicals and surprisingly enough, it may cure many dreadful diseases. The efficiency of these homoeopathic medicines increases on dilutions.

The green chemical approach is governed by 12 principles given by Anastas (Anastas and Warner, 1998).These principles are important in combating against environmental pollution and for the betterment of human health. These principles are:

(i) ***Prevention***: It is better to prevent waste rather than treating or cleaning up waste after it is produced.

(ii) ***Atom economy***: Syntheses should be so designed wherever possible, to maximize the incorporation of all materials used in the process into their final products.

(iii) ***Less hazardous chemical syntheses***: Wherever practicable, synthetic methods should be designed so as to use and generate substances possessing little or no toxicity to human health and the environment.

(iv) ***Designing safer chemicals*****:** Chemical products should be designed to affect their desired function while minimizing their toxicity.

(v) ***Safer solvents and auxiliaries***: The use of auxiliary substances (e.g., solvents, separating agents, etc.) should be made unnecessary, wherever possible and innocuous, when used.

(vi) ***Design for energy efficiency***: Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

(vii) ***Use of renewable feed stocks***: A raw material or feedstock should be renewable rather than depleting, whenever technically and economically practicable or feasible.

(viii) ***Unnecessary derivatization***: Blocking group, protection or deprotection, and temporary modification of physical or chemical processes should be avoided whenever possible.

(ix) ***Catalysis***: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

(x) ***Design for degradation***: Chemical products should be designed so that at the end of their function, they break down into innocuous or harmless degradation products and do not persist in the environment.

(xi) ***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.

(x) ***Inherently safer chemistry for accident prevention***: Substances and the form of a substance used in chemical process should be chosen to minimize the potential for chemical accidents, including releases of chemicals, explosions and fires.

Atom economy is an important concept in philosophy of green chemistry (Trost, 1995; Sheldon, 2000). It is important to utilize maximum number of atoms of the reactant to minimize the generation of waste products. It is defined as atom economy in green chemistry, meaning by one has to be economic in use of atoms. The atom economy is defined as:

$$\%\,\text{Atom Economy} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weight of all reac tan ts}} \times 100\%$$

Addition reactions and rearrangements are normally follow atom economy but the chemistry is not complete with only these reactions, hence, some substitution and elimination reactions are also required; thus, generation of wastes is bound to be there but the efforts of the chemists should be to produce minimum byproducts.

"Gray" process can be made "Green" by making a judicious selection of green substrate, green solvents, green reagents, green catalysts, green conditions, and so on, to synthesize a green product.

Principles of green chemistry are beautifully condensed by Tang et al. (2008) as PRODUCTIVELY:

Principles of Green Chemistry:

P – Prevent wastes

R – Renewable materials

O – Omit derivatization steps

D – Degradable chemical products

C – Catalytic reagents

T – Temperature and pressure ambient

I – In-process monitoring

V – Very few auxiliary substances

E – E-factor, maximize feed in product

L – Low toxicity of chemical products

Y – Yes, it's safe

Efforts are being made to fulfill all the 12 conditions to make a chemical process perfectly green, but it is not always practicable to satisfy all the requirement of 12 principles of green chemistry. Therefore, a chemical process is better defined as greener than the other chemical processes, which fulfills more conditions and further researches may make it still greener and this process will go on.

KEYWORDS

- **Environment**
- **Eco-friendly chemistry**
- **Green chemistry**
- **Pollution**

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CHAPTER 2

BENIGN STARTING MATERIALS

SANYOGITA SHARMA, NEELAM KUNWAR, SANGEETA KALAL, and P. B. PUNJABI

CONTENTS

2.1 Introduction ... 10
2.2 Material and Methods ... 11
    2.2.1 Sustainability ... 11
    2.2.2 Sustainable Materials ... 14
    2.2.3 Choice of Starting Materials ... 16
Keywords ... 38
References ... 38

2.1 INTRODUCTION

Our environment is composed of atmosphere, earth, water, and space. Under normal circumstances, it remains clean and therefore, enjoyable. However, with increasing world population and with limited natural resources, the composition and complex nature of our environment has changed. Our world is beautiful, but the increasing use and improper disposal of the effluents from various industries is creating pollution of the environment.

The time is approaching for natural gas and petroleum production to peak, plateau, and then decline. Prices are also increased substantially in the last few decades contributing to the almost uncertainty. These trends and the uncertain future inevitably influence industrial nations. As our fossil raw materials are irreversibly decreasing supported by pollution pressure on our environment, the progressive changeover of chemical industry to renewable feedstocks for their raw materials has become an inevitable necessity (Okkerse and Bekkum, 1999).

It will have to proceed increasingly to the renewable raw material basis before natural gas, oil, and all other sources are exhausted. The over reliance of chemical industry on fossil raw material has its limits as these are depleting at a rapid pace and are not renewable. Now there is a question, when will fossil fuels be exhausted? Or when will fossil raw materials become so expensive that biofeedstocks become economically competitive alternative? Experts opine the end of cheap oil for 2040 at the latest (Umbach, 1996; Klass, 1998). This is a development that one can witness by the fact that chemical industries are now combating the increasing costs of natural oil and gas (Campbell and Laherrere, 1998).

The future is quite promising. Scientists and technologists following the trends on sustainability and natural resources are persuading industries either to use alternative resources or to develop some new approaches toward more efficient chemical processes. Thus, there is a pressing demand for the transition to a more bio-based production system, but this is hampered by different obstacles. Fossil based raw materials are relatively more economic at present and the process technology for their conversion into organic chemicals is well developed. It is basically different form that is required for transforming carbohydrates into products with industrial applications.

2.2 MATERIAL AND METHODS

2.2.1 SUSTAINABILITY

The most commonly used definition for sustainable development comes from a report by the World Commission on Environment and Development that is, "To meet the needs of the present without compromising the ability of future generations to meet their own needs." Green chemistry and green engineering are striving hard to develop new methodologies for sustainable development. Their proposals focus on:

(i) **Renewable feedstocks and raw materials:** (Dewulf and Lagenhove, 2006; Benaglia, 2009) Green chemistry needs to change starting materials into renewable feedstocks. The most desired property of basic starting material is its lower toxicity and environmental impact. Health and safety protection of workers involved and the environment is on top priority. Green chemistry is just proposing change of direction from fossil-based feedstocks into biological raw materials. There are many problems in using these materials, but in the last few years, there are some encouraging new results for large scale production and use of alternative renewable materials. The terrestrial biomass is quite complex containing high molecular weight products like sugars, hydroxy and amino acids, lipids and biopolymers (cellulose, hemicellulose, chitin, starch, and lignin), and proteins. The most important class of biomolecules produced is carbohydrates (~75% of the annually renewable biomass approximately 200 billion tons). A minor fraction (4%) of this is used by man, while the rest decays or recycles along natural pathways. The bulk of this annually renewable feedstocks (carbohydrate biomass) is polysaccharides, and their non food utilization is limited to textile, paper, and coating industries.

(ii) Oleochemistry: Oleochemicals like fats and oils (from plants and animals) as raw materials is becoming a new source of chemical feedstocks (Hill, 2000; Gutsche et al., 2008). A series of new raw materials exist in the market with variety of applications like cosmetics, polymers, lubricating oils, and so on.

(iii) Photochemistry: Green chemistry also puts a lot of emphasis on some photochemical reactions in chemical processes (Albini and Fagnoni, 2004; Ravelli et al., 2009). Light (in ultraviolet and visible region) can catalyze many reactions. Photochemistry has a great potential and quite a few interesting research findings, which were introduced in the last few years including some applications Ultraviolet as well as visible light from Sun is considered as renewable energy sources and thus, photochemistry can contribute to some of the green synthetic chemistry applications.

(iv) Biocatalysis and biotransformations: Biocatalysis is particularly a green technology with many applications, which are considered benign for the environment and energy efficient (Ran et al, 2008; Whittall and Sutton, 2009; Cheng and Gross, 2011; Tao and Kazlauskas, 2011). Enzymes have been used for many synthetic chemical routes with great advantage in the food and pharmaceutical industries. Biocatalysis is in the interface of fermentation techniques (food and alcoholic drink industries) with some other industrial processes, where enzymes are used for higher yields and low energy consumption. Biotransformations can be achieved through biocatalysis and these are considered good green techniques for a series of chemical industries and a variety of chemical products. An ecofriendly and economic biocatalytic route with lipase extracted from *Aspergillus niger* as an efficient biocatalyst has been suggested for the glycerol carbonate synthesis (Tudorache et al., 2012).

(v) **Capture or sequestration of carbon dioxide:** Green chemistry is involved in carbon dioxide reduction in chemical industries. Climate change and phenomenon of greenhouse effects due to CO_2 emission is considered a very important environmental problem by green chemists. Any effort to reduce CO_2 emissions during the industrial process is an important goal from green chemistry point of view. Also, any design in chemical processes, which sequester or capture or can use CO_2 is worthy from the aims of green chemistry (Holtz, 2003; Hester, 2009; Allen and Brent, 2010; Leimkuhler, 2010).

(vi) **Waste biomass as chemical feedstock, biomaterials and biofuel:** The advances in last decade were to use biomass for the production of various materials and these were quite impressive. It was known for decades that biomass from agricultural processes goes almost as waste. Biomass is considered a solution of very important problem of sustainability with increasing fossil fuel prices. In recent years, many new technologies showed the use of biomass as biofuel, raw material for the production of biomaterials, polymers and various other applications (Ravindranath and Hall, 1995; Ragauskas et al., 2006; Soetaert and Vendamme, 2009). Selective hydrogenation of alternative oils is a useful tool for the production of biofuels. Highly selective hydrogenation of non food oils like flax over non toxic heterogeneous catalyst can be used to make them suitable for biodiesel formulation (Zaccheria et al., 2009). A renewable gasoline was prepared directly from aqueous phase hydrodeoxygenation of aqueous sugar solution in a two-bed reactor (Li et al., 2011). Catalytic upgrading of bio-oil using 1-octene and 1-butanol over sulfonic acid catalysts was done by Zhang et al. (2011). It is an atom economic route for upgrading bio-oil to oxygenated fuels by simultaneous acid catalyzed reactions with olefins and alcohols. A route to liquid hydrocarbon fuels has been suggested by Case et al., (2012) by pyrolyzing mixtures of levulinic acid and formic acid salts. This one step process is operated at atmospheric pressure without catalyst or hydrogen addition.

(vii) **Biodegradation of biomass to biogas and biodiesel:** Biomass is well known for its use for biofuel, especially from organic wastes in landfills. Biomass can be used for the production of biodiesel through some chemical and physical processes. Akbar et al. (2009) prepared Na doped SiO_2 solid catalyst by sol-gel method for the production of biodiesel from jatropha oil. The biodiesel was produced by transesterification of jatropha oil over solid catalyst, Na/SiO_2, form fatty acid methyl ester with very high yield under mild conditions of operation. Biodiesel was also produced by palladium catalyzed decarboxylation of higher aliphatic esters (Han et al., 2010). It is an effective and highly selective decarboxylation approach to convert higher aliphatic esters into diesel like paraffins. The methodology of this process provides a new protocol to utilization of biomass-based resources, especially to the second generation biodiesel production. Biomass offered an opportunity for the production of 19% of energy on a global scale. Now, it is estimated that 4% of all fuel products in cars is produced from biomass. Dicyclohexylguanidine group covalently attached on silica gel is an efficient basic heterogeneous catalyst for the production of biodiesel in a continuous flow reactor (Balbino et al., 2011). Crude glycerol obtained from biodiesel waste was found suitable for the production of intracellular non-reducing sugar trehalose and relatively pure propionic acid simultaneously (Ruhal et al., 2011).

2.2.2 SUSTAINABLE MATERIALS

Materials produced and used in modern society are quite diverse and evolving. There are approximately 75,000 chemicals used commercially. As not a single formulation has a unique sustainability, it is useful to provide an operational definition. A sustainable material is that, which fits within the constraints of a sustainable material system. In order to be sustainable, a material must be appropriate for the system and vice versa.

Two strategies have been identified to support a sustainable materials economy. (i) Dematerialization, which involves developing ways to use less material to provide the same service in order to satisfy human needs and (ii) Detoxification of materials used in products and industrial processes.

Chemistry plays a pivotal role in production of food, materials supply for clothing and shelter, preventing disease, and providing health care products. Organic chemicals are some of the important starting materials for a large number of major chemical industries. The production of organic chemicals as raw materials or reagents for other applications is a major sector of manufacturing polymers, pharmaceuticals, pesticides, paints, artificial fibers, food additives, and so on. Organic synthesis on a large scale as compared to the laboratory scale, involves the use of energy and basic chemical ingredients from the petrochemical sector, catalysts and after the end of the reaction, separation, purification, storage, packaging, distribution, and so on. During these processes, there are many problems of health and safety for workers in addition to the environmental problems caused by their use and disposal as waste.

For a long time, the most important goal of a chemist was to prepare a compound in suitable amounts and desirable high purity from available starting materials. In a world with a continuously increasing population and limited resources, the idea of a sustainable development is of major importance for the future in the 21st century.

In the last two decades, much more attention has been paid to the effect of chemical production on the environment. It is clear that it is much better, less difficult and less expensive to develop processes and compounds that are sustainable from scratch than to change an existing chemical process or to remove a toxic chemical from the environment to reduce its potential hazard and pollution created by it. In order to do so, chemists, biochemists, engineers, and pharmacists working together in drug development or constructing new materials must think always about sustainability when they transform their ideas into any products and processes.

They must learn to judge the suitability of a chemical transformation or the use of a chemical compound within a limit of different parameters. It is not only the yield of the reaction, which counts but also which starting materials are required or used? Whether one can make these from renewable resources? Do these generate toxic by-products and how these by-products can be avoided? How much waste material is generated by this process and whether it is an energy efficient process? Asking such questions at the beginning of any chemical compound, process and technology development will lead to a proper, more efficient, and sustainable use of chemistry.

Chemistry is the science of material and its transformation, which plays a key role in the process and acts as the bridge between physics, material sciences, and life sciences. Only those chemical processes, which have reached (after careful optimization) maximum efficiency, will lead to more sustainable compounds and process. The awareness, creativity, and progressive attitude of a scientist is necessary to bring these reactions and chemical processes to maximum efficiency. The term "Green Chemistry" has been coined for all such efforts achieving this goal. Therefore, attempts have been made by them to design synthesis and manufacturing processes in such a way that the waste products are minimized so that they have no or negligible effect on the environment and their disposal is also convenient.

It is therefore necessary that the starting materials, solvent, and catalyst should be carefully chosen for carrying out reactions for example, use of benzene as solvent must be avoided at any cost since it is carcinogenic in nature. If possible, it is better to carry out reactions in the aqueous phase.

2.2.3 CHOICE OF STARTING MATERIALS

It is very important to make a proper selection of the appropriate starting materials. Till now, most of the organic synthesis makes use of petrochemicals and other hazardous or toxic chemicals, which affect the workers handling these starting materials. Petrochemicals are non renewable and these also require considerable amounts of energy and therefore, it is important to reduce the use of such petrochemicals by using alternative starting materials of agricultural or biological origin.

Feedstock selection largely dictates the reactions and conditions that will be employed in a chemical synthesis and it should come from renewable sources rather than depletable resources, as far as if possible ideal feedstock must be:

- Renewable
- Poses no hazards
- Converted to the desired product using few steps
- 100% yield
- 100% atom economy

CHEMICAL SUBSTITUTES AND REPLACEMENTS

Methylene chloride, benzene, and xylenes are among the top 20 starting materials produced in 1990 (Relsch, 1991). These are still used because economic losses are associated in phasing out these chemicals, but the chemical industries are introducing alternates at a rapid pace. N-Methyl-2-pyrrolidone has been commercialized as a promising replacement for methylene chloride.

Many a times, simple substitutes cannot replace these chemicals, which are unique precursors for the synthesis of secondary derivatives and materials. Formaldehyde and vinyl chloride have unique properties and tremendous industrial value, but these are also hazardous to humans. Such chemicals do not bioaccumulate, but have well known harmful threshold levels for humans. These are controlled by some regulations for their storage, transport, handling, and work place exposure. Therefore, some of the major initiatives have focused to replace them by utilizing some other renewable and environmentally benign starting materials, which are obtained from agricultural, animal and microbial resources.

RENEWABLE FEEDSTOCK FROM AGRICULTURE (BIOMASS)

Some major benefits of using biomass are

- It provides renewable feedstock
- It does not contributes to net CO_2 to the atmosphere
- It conserves fossil fuel leading to a secure domestic supply
- It provides a platform for making use of chemical products, which is otherwise considered waste.

(i) **Chemicals from fermentation processes (Glucose fermentation):** Glucose can be obtained from various carbohydrates like starch, cellulose, sucrose, and lactose. On a large scale, glucose is produced from starch by enzymatic hydrolysis. Corn is the main source of glucose. Another important source of producing glucose is woody biomass. Improvement in processes for harvesting and processing wood cellulose could result in an alternate source of glucose, which is relatively much less expensive than corn.

Mesoporous silica nanoparticles (MSNs) with different pore size were synthesized and used as hosts to physically adsorb or chemically link cellulose for its conversion to glucose. The results show that chemically linked cellulose onto large pore MSNs exhibits a glucose yield of more than 80% with excellent stability (Chang et al. 2011).

(a) **Lactic acid:** Lactic acid (2-hydroxypropionic acid) can be produced either by chemical synthesis or by fermentation of different carbohydrates such as glucose (obtained from starch), maltose (produced by specific enzymatic starch conversion), sucrose (obtained from syrups, juices, and molasses), lactose (produced from whey), and so on (Ravindranath and Hall, 1995). Lactic acid is produced on industrial scale today mainly through the fermentation of glucose. An important step in the lactic acid production is the recovery from fermentation broth. The traditional process for the recovery of lactic acid is still far from ideal. Lactic acid exists in two optically active isomeric forms, L (+) and D (–). It is used in the food, chemical, pharmaceutical, and cosmetic industries. It is a bifunctional compound bearing a hydroxyl group and an acid group and is utilized for number of chemical conversions to useful products.

Nowadays, there is an increasing demand for biodegradable polymers that can replace conventional plastic materials and can also be used as new materials like controlled drug delivery devices or artificial prostheses. Thus, polylactic acid polymers could be an environment friendly substitute to such plastics derived from petrochemical materials.

It esterifies with itself to give two primary esterification products: the linear lactic acid lactate (2-lactyloxypropanoic acid) and cyclic lactide (3,6-dimethyl-1,4-dioxane-2,5-dione). This lactide is an important compound, because it is a monomer for the production of poly (lactic acid) or polylactide, and other copolymers. Effective conversion of D-glucose into lactic acid has been described using microwave irradiation in solventless condition with alumina potassium hydroxide.

Esters of lactic acid and different alcohols (particularly methanol, ethanol, and butanol) are non toxic and biodegradable. These are high boiling liquids and have excellent solvent properties and therefore, replace toxic and halogenated solvents for a large range of industrial uses. Lactate esters are also used as plasticizers in cellulose and vinyl resins and they enhance the detergent properties of ionic surfactants. Direct hydrogenation of lactic acid or lactates produces propylene glycol and it can be an alternative green route to the petroleum based process. Propylene glycol (1,2-propanediol) is a commodity chemical, which can be used as a solvent for the production of unsaturated polyester resins, drugs, cosmetics, and foods (Corma et al., 2007). Dehydration of lactic acid gives acrylic acid. This acid, its amide and ester derivatives are the primary building blocks in the manufacture of acrylate polymers, which find numerous applications in surface coatings, textiles, adhesives, paper treatment, leather, fibers, detergents, and so on.

Advances in fermentation and especially in separation technology have reduced the potential production cost of lactic acid. The production of lactic acid from waste sugarcane bagasse derived cellulose was reported by Mukund et al. (2007). It deals with the simultaneous saccharification and fermentation (SSF) of sugarcane bagasse cellulose to lactic acid using *Penicillium janthinellum* mutant EUI and cellobiose utilizing *Lactobacillus delbrueckii* mutant Uc3. Salt assisted organic acid catalyzed depolymerization of cellulose was carried out by Stein et al. (2010). Dicarboxylic acids combined with inorganic salts (NaCl or $CaCl_2$) afford the depolymerization of crystalline cellulose under mild conditions in water. The mechanical force and layered catalysts can efficiently depolymerize cellulosic materials (up to 84% conversion) as observerd by Hick et al. (2010). The most effective mechanocatalyst was aluminosilicates based on the kaolinite structure.

Catalytic upgrading of lactic acid to fuels and chemicals by dehydration and C–C coupling reactions was observed by Serrano-Ruiz and Dumesic (2009). They described a single reactor catalytic process to convert aqueous solution of lactic acid into a spontaneously separating organic phase that can serve as a source of valuable chemicals (propanoic acid and C_4–C_7 ketones) and can be used to produce high-energy density fuels. Simultaneous saccharification and fermentation (SSF) of cellulosic substrate to D-lactic acid using EUI cellulases and Lactobacillus lactic mutant RM2-24 was reported (Singhvi et al., 2010). The SSF was carried out in screw-cap flasks at 42°C with shaking at 150rpm.

(b) **Succinic acid:** Succinic acid is also produced in this way. Succinic acid reacts with alcohols in the presence of acid catalysts to form dialkyl succinates (Fumagalli, 1997). The esters of succinic acid with low molecular weight alcohols (methyl and ethyl succinates) find applications as solvents and synthetic intermediates for very many important compounds.

Direct hydrogenation of succinic acid, succinic anhydride, and succinates leads to the formation of the products like 1,4-butanediol (BDO), tetrahydrofuran (THF), and γ-butyrolactone (GBL) 1,4-Butanediol is a compound of quite common interest as a starting material for the production of some important polymers such as polyesters, polyurethanes, and polyethers (Weissermel, 2003). γ-Butyrolactone was synthesized highly selectively from biomass derived 1,4-butanediol by vapor-phase dehydrocyclization over novel copper-silica nanocomposite catalyst (Hwang et al., 2011). A wide variety of aldehydes and ketones can undergo the Stobbe condensation with succinic ester giving a variety of compounds. These products find applications in technical and medical field, biological activities (Moussa et al., 1982; Baghos et al., 1993).

(c) **3-Hydroxypropionic acid:** 1,3-Propanediol is a starting material for the production of polyesters. It is used together with terephthalic acid to produce polytrimethylene terephthalate (PTT), which is in turn used in the manufacture of some fibers and resins. 3-Hydroxypropionic acid on dehydration gives acrylic acid. Acrylic acid and its derivatives (esters, salts, or amides) are important compounds and used as monomers in the manufacture of some polymers and copolymers. These