## DISCIPLINE SPECIFIC ELECTIVE COURSE – 2 (DSE-2): Green Chemistry in Organic Synthesis

### CREDIT DISTRIBUTION, ELIGIBILITY AND PRE-REQUISITES OF THE COURSE

| Course title & Code | Credits | Credit distribution of the course | | | Eligibility criteria | Pre-requisite of the course (if any) |
|---|---|---|---|---|---|---|
| | | Lecture | Tutorial | Practical/ Practice | | |
| **Green Chemistry in Organic Synthesis (DSE-2)** | 04 | 03 | -- | 01 | Class 12th with Physics, Chemistry | Basic knowledge of organic reactions |

### Learning objectives

**The objectives of this course are as follows:**

- To create awareness about the chemistry that is not harmful for human health and the environment.
- To provide thorough knowledge of the green chemistry principles that can be used to develop chemistry in greener way.
- To familiarize students with new remediation technologies for the cleaning up of hazardous substances.
- To use green chemistry for boosting profits, increase productivity and ensure sustainability with absolute zero waste.
- To learn about innovations and applications of green chemistry in education that helps companies to gain environmental benefits as well as to achieve economic and societal goals also
- The objective of the practical component is to develop basic skills to be able to design, develop and run chemical processes in a sustainable way.

### Learning outcomes

**By studying this course, students will be able to:**

- List the twelve principles of green chemistry and build the basic understanding of toxicity, hazard and risk related to chemical substances.
- Calculate atom economy, E-factor and relate them in all organic synthesis
- State the uses of catalyst over stoichiometric reagents
- Debate and use green solvents, renewable feedstock, and renewable energy sources for carrying out safer chemistry
- Use green chemistry for problem solving, innovation and finding solutions to environmental problems.

- Design safer processes, chemicals, and products through understanding of inherently safer design (ISD)
- Discuss the success stories and use real-world cases to practice green chemistry

## SYLLABUS OF DSE-2

**UNIT – 1: Introduction (3 Hours**

Introduction to Green Chemistry, some important environmental laws, pollution prevention Act of 1990, emergence of green chemistry, need for Green Chemistry. Goals of Green Chemistry. Limitations/ Obstacles in the pursuit of the goals of Green Chemistry. Green chemistry in sustainable development.

**UNIT – 2: Application of Green Chemistry Principles (36 Hours**

Principles of Green Chemistry and designing a chemical synthesis
Concept familiarization and application of green chemistry principles using specific examples

1. Prevention of waste/ by products; waste or pollution prevention hierarchy
2. Green metrics to assess greenness of a reaction: Calculation of atom economy of the rearrangement, addition, substitution, and elimination reactions; calculation of E-factor for industrial processes
3. Prevention/ minimization of hazardous/ toxic products
4. Safer Solvent and Auxiliaries: Problems associated with conventional reaction media Some Common Green solvents: Introduction, application, advantages, and disadvantages of green solvents in organic synthesis (taking suitable examples). Special emphasis on the following:
   i. Super Critical Fluids (with special reference to carbon dioxide)
   ii. Water: Concept of In-water, and on-water reactions (with special reference to synthesis of terpinol and linalool in water, Benzoin condensation, Heck reaction)
   iii. Ionic Liquids: Physical properties and classification of Ionic Liquids (with special reference to Diels Alder reaction and Coumarin synthesis in ionic liquids)
   iv. Biomass derived Solvents: Physicochemical properties, Use of glycerol and its derivatives (Mizoroki–Heck reaction) and 2-methyltetrahydrofuran (Suzuki–Miyaura reaction).
5. Design for energy efficiency: Phenomenon of accelerating organic reactions by using the following Green Chemistry tools (taking suitable examples) and its advantages:
   i. Mechanochemistry
   ii. Ultrasound assisted reactions: Taking examples like Simmons Smith reaction, Diels–Alder reaction,
   iii. Microwave assisted reactions: Special emphasis on solvent-free synthesis- copper phthalocyanine and aspirin, In-water reactions-Hofmann Elimination, methyl benzoate to benzoic acid and Decarboxylation reaction;
   iv. Electrocatalysis: Taking examples like adiponitrile synthesis, synthesis of 3-bromothiophene.
   v. Visible light induced Reactions: with examples such as, syntheses of caprolactam and vitamin $D_3$, cis-trans isomerization of alkenes
6. Use of renewable starting materials: Illustrate with few examples such as biodiesel, bioethanol, polymers from renewable resources (PLA from corn), Synthesis and

properties of 2-Methyltetrahydrofuran, furfural and 5-Aminolevulinic acid (DALA) from levulinic acid

7. Avoidance of unnecessary derivatization – careful use of blocking/protecting groups (taking specific examples like selective oxidation of aldehydic group and synthesis of 6-Aminopenicillanic Acid (6-APA) from penicillin G
8. Catalysis and green chemistry
   Introduction to Catalysis (including concept of selectivity, turnover frequency and turnover number), Types of Catalysts: Heterogeneous catalysis and homogeneous catalysis (H-beta and zeolites in organic synthesis), General catalytic cycle for heterogeneous catalysis; Asymmetric catalysis (Monsanto route to L-dopa via asymmetric hydrogenation, synthesis of carbapenhem via Asymmetric reduction); Photocatalysis (with special reference to $TiO_2$); Biocatalysis (Synthesis of adipic acid/catechol using biocatalyst) and Nanocatalysis (oxazole synthesis using nanocatalyst)
9. Design for degradation: (Illustrate with the help of examples: soaps and detergents, pesticides, polymers)
10. Real Time monitoring of chemical processes using inline, offline, and online techniques
11. Inherently safer design/chemistry:
    Principle and subdivision of ISD, Bhopal Gas Tragedy (safer route to carbaryl) and Flixiborough accident (safer route to cyclohexanol, Asahi Process)

**UNIT – 3: Industrial Applications and Success Stories (6 Hours)**

- Vitamin C Synthesis using enzymes (Hoffman La Roche)
- Zoloft -Presidential Chemistry Award Winning Innovation (Pfizer)
- Methyl Methacrylate syngas process (Eastman Chemicals)
- Synthesis of herbicide disodium iminodiacetate
- Rightfit pigments azo dyes synthesis and their applications
- Healthier Fats and oils by Green Chemistry: Enzymatic Interesterification for production of No Trans-Fats and Oils.
- Synthesis of anti-tuberculosis drug Paramycin from waste water stream

## Practical component Credits:

**01 (Laboratory periods:15 classes of 2 hours each)**

**Note**: Characterization by melting point, UV-Visible spectroscopy, IR spectroscopy and any other specific method should be done (wherever applicable).

1. Preparation and characterization of nanoparticles of gold using tea leaves/silver nanoparticles using plant extracts.
2. Preparation of biodiesel from waste cooking oil and characterization (TLC, pH, solubility, combustion test, density, viscosity, gel formation at low temperature and IR can be provided).
3. Benzoin condensation using thiamine hydrochloride as a catalyst instead of cyanide.
4. Extraction of D-limonene from orange peel using liquid $CO_2$ prepared from dry ice.
5. Mechanochemical solvent free, solid-solid synthesis of azomethine using p-toluidine and o-vanillin/p-vanillin.
6. Microwave-assisted Knoevenagel reaction using anisaldehyde, ethylcyanoacetate and ammonium formate.

7. Photoreduction of benzophenone to benzopinacol in the presence of sunlight.
8. Photochemical conversion of dimethyl maleate to dimethyl fumarate (cis-trans isomerisation)
9. Benzil- Benzilic acid rearrangement: Preparation of benzilic acid in solid state under solvent-free condition.
10. Preparation of dibenzalacetone by cross aldol condensation reaction using base catalysed green method.

## Essential/recommended readings

### Theory:


1. Anastas, P.T., Warner, J.C. (2014), **Green Chemistry, Theory and Practice**, Oxford University Press.
2. Lancaster, M. (2016), **Green Chemistry: An Introductory Text**, 3rd Edition, RSC Publishing.
3. Cann, M. C., Connely, M.E. (2000), **Real-World cases in Green Chemistry, American Chemical Society**, Washington.
4. Matlack, A.S. (2010), **Introduction to Green Chemistry**, 2nd Edition, Boca Raton: CRC Press/Taylor & Francis Group publisher.
5. Alhuwalia,V.K., Kidwai, M.R. (2005), **New Trends in Green chemistry**, Anamalaya Publishers.
6. Sidhwani, I.T, Sharma, R.K. (2020), **An Introductory Text on Green Chemistry**, Wiley India Pvt Ltd.


### Practicals:


1. Kirchoff, M.; Ryan, M.A. (2002), **Greener approaches to undergraduate chemistry experiment**, American Chemical Society, Washington DC.
2. Sharma, R.K.; Sidhwani, I.T.; Chaudhari, M.K. (2013), **Green Chemistry Experiments: A monograph**, I.K. International Publishing House Pvt Ltd. New Delhi.
3. Pavia, D.L.; Lamponam, G.H.; Kriz, G.S.W. B. (2012), **Introduction to organic Laboratory Technique- A Microscale approach**, 4th Edition, Brooks-Cole Laboratory Series for Organic chemistry.
4. Sidhwani I.T. (2015), Wealth from Waste: A green method to produce biodiesel from waste cooking oil and generation of useful products from waste further generated. **DU Journal of Undergraduate Research and Innovation**, 1(1),131-151. ISSN: 2395-2334.
5. Sidhwani, I.T; Sharma, R.K. (2020), **An Introductory Text on Green Chemistry**, Wiley India Pvt Ltd.
6. **Monograph on Green Chemistry Laboratory Experiments**, Green Chemistry Task Force Committee, Department of Science and Technology, Government of India.
7. Pasricha, S., Chaudhary, A. (2021), **Practical Organic Chemistry: Volume–I**, I K International Publishing house Pvt. Ltd, New Delhi
8. Pasricha, S., Chaudhary, A. (2021), **Practical Organic Chemistry: Volume–II**, I K International Publishing house Pvt. Ltd, New Delhi