



**KARPAGAM ACADEMY OF HIGHER EDUCATION**  
(Deemed University Established Under Section 3 of UGC Act 1956)

**COIMBATORE-21**

**DEPARTMENT OF CHEMISTRY**

**SYLLABUS**

**B.Sc Chemistry**

**Semester-IV**

**2018-2019**

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**18CHU414A GREEN METHODS IN CHEMISTRY –PRACTICAL 3H 1C**

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**Instruction Hours/week:L:0 T:0 P:3**

**Marks: Internal:40 External: 60**

**Total:100**

**Course Objective**

1. To Understand the principles and the practical aspects of green chemistry

**Course Outcome**

1. This course enables the student to understand and apply the principles of green chemistry and the practical aspects of green chemistry

**Practical's**

1. Preparation and characterization of biodiesel from vegetable oil.
2. Extraction of D-limonene from orange peel using liquid CO<sub>2</sub> prepared from dry ice.
3. Mechano chemical solvent free synthesis of azomethine.
4. Solvent free, microwave assisted one pot synthesis of phthalocyanine complex of copper (II).

**Suggested Readings:**

**Text Books:**

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.

**Reference Books:**

1. Ryan, M.A. & Tinnes and, M. (2002). *Introduction to Green Chemistry*. American Chemical Society, Washington.
2. Lancaster, M. (2010). *Green Chemistry: An Introductory Text* (II Edition). RSC publishing.

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Coimbatore – 641 021.

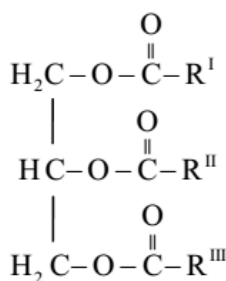
(For the candidates admitted from 2018 onwards)

**DEPARTMENT OF CHEMISTRY****SUBJECT NAME: GREEN METHODS IN CHEMISTRY –PRACTICAL****SUBJECT CODE: 17CHU414A****SEMESTER: IV****CLASS: II B.Sc CHEMISTRY****PREPARATION AND CHARACTERIZATION OF BIODIESEL FROM VEGETABLE OIL****Aim:**

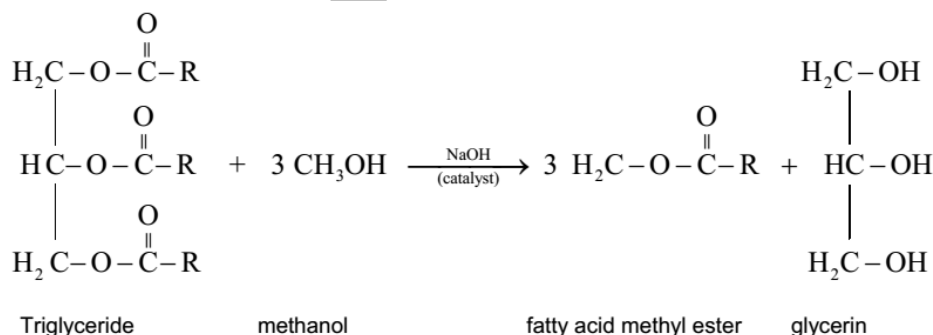
To prepare the biodiesel from vegetable oil and its characterization

In this experiment the biodiesel will be made from fresh vegetable oil to avoid the solids and a titration to determine the mass of sodium hydroxide needed to react with the whole oil molecules.

Vegetable oils are esters of glycerin, commonly called triglycerides, with different fatty acids with the structure:



Where RI, RII, and RIH can be the same or different fatty acids



The preparation of the biodiesel is a transesterification reaction where the triglycerides are converted into simpler methyl esters of the fatty acids (the biodiesel).

**Materials Required:**

Vegetable oil (cottonseed, coconut, or other oil of your choice)

Sodium hydroxide, NaOH, pellets

Methanol, CH<sub>3</sub>OH

**EXPERIMENTAL**

This experiment demonstrates the use of groundnut oil as an alternative. The reaction incorporates NaOH as a catalyst in order to achieve high yield and minimize waste. In addition, glycerol the by-product can be reused in order to make glycerin soap.

In this experiment we have synthesized biodiesel from a triester of glycerol (a triacylglycerol or triglyceride). This reaction is known as a transesterification reaction. Transesterification is the process of transforming one type of ester into another type of ester. This reaction incorporates the use of the strong base sodium methoxide. The overall mechanism is catalyzed by the presence of NaOH.

In the first step of the reaction, NaOH reacts with methanol in an acid-base reaction. The product of this reaction is the very strong base sodium methoxide and water.



In second step pure groundnut oil was warmed and poured into sodium methoxide solution with continuous stirring. At first the mixture was cloudy, and then two layers were separated. The contents were transferred into the separating funnel. The mixture was separated into two layers. The lower layer is of glycerol and the upper layer was of biodiesel. The system was allowed to settle down for an hour, and then biodiesel was separated with the help of separating funnel.

The same procedure was followed for the other vegetable oils such as sesame oil, mustard oil, coconut oil, jawas oil and soybean oil.

Confirmation of the biodiesel was done on FT-IR spectrometer. The IR value ranges from 1741 to 1745 cm<sup>-1</sup>, which clearly indicates carbonyl group of ester in biodiesel.

We performed some test for confirmation of glycerol:

(i) Glycerol + Conc.  $\text{H}_2\text{SO}_4$   $\longrightarrow$  No Colour

(ii) Glycerol + Conc.  $\text{H}_2\text{SO}_4$  + Heat  $\longrightarrow$  Yellow colour

**(iii) Dunstan's Test:** Aqueous solution of glycerol is added to borax phenolphthalein (few drops of alcoholic solution were added to very dilute solution of borax)  $\longrightarrow$  pink color disappears and reappears on warming.

**(iv) Determination of pH**

Add 5 drops of your biodiesel to 1 mL of distilled water and mix thoroughly. Using pH paper, estimate the aqueous pH of your biodiesel.

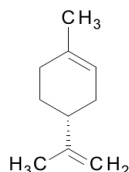
**Result:** All the above tests were positive, which confirms presence of glycerol.

## Extraction of D-limonene from orange peel using liquid CO<sub>2</sub> prepared from dry ice

### OBJECTIVE

To extract the essential oil limonene from orange peel using a green chemistry method.

**(D)-Limonene**  
**(4R)-isopropenyl-1-methylcyclohexene**



### Experimental Procedure

#### *Preparation of the Orange Rind*

1. Grate the outside of an orange peel (colored part) with the smallest grating surface of the grater.
2. Obtain 2.5 to 3.0 grams of orange rind.

#### *Preparation of the Extraction Vessel*

3. Record the mass of a 15 mL centrifuge tube by weighing it in a small tared beaker.
4. Slide a coiled copper wire into the tube. All wire should be inside the tube. Have the instructor cut off any extra wire. Record the mass of the tube and wire.
5. Add approximately 2.5 grams of grated orange rind to your tube.

**Note:** do not pack tightly. Calculate the exact mass of orange peel added to the tube.

#### *Preparation of the Extraction Environment*

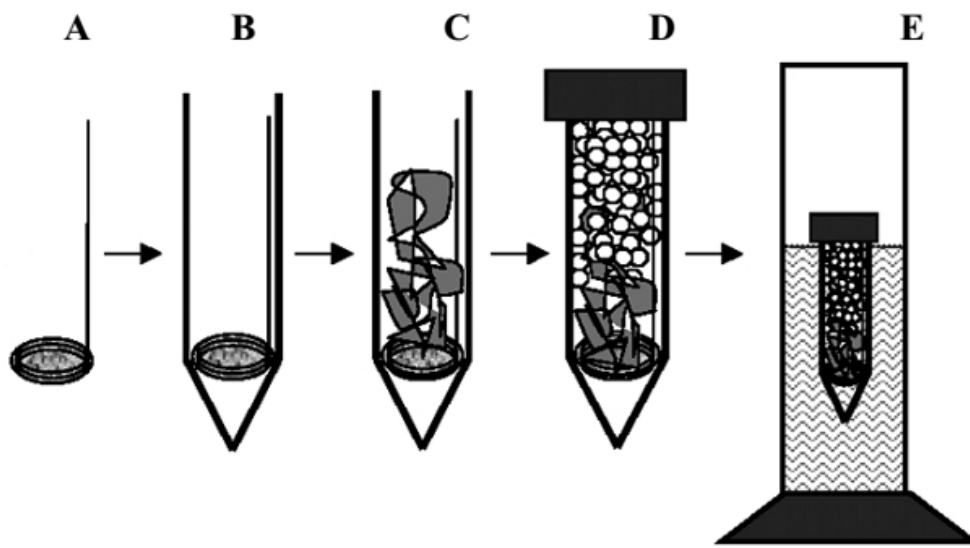
6. Fill a 250 mL plastic graduated cylinder one half to two thirds full of warm (40-50° C) tap water.

Note: Do not heat the water in the cylinder or add hot water later in the procedure. Any sudden increase in

temperature of surrounding water when the centrifuge tube is under pressure can cause the cap to blow off suddenly and violently.

Note: Move items that should not get wet away from the cylinder because splashing may occur if

the cap shoots off  
the tube.



#### *Extraction*

**NOTE: Due to the safety issues involved with the rapid increase of pressure during this procedure, it is important to read and understand the entire extraction procedure (#7-13) before beginning!**

7. Fill the rest of the centrifuge tube with crushed dry ice. **Remember to wear gloves!** Dry ice may be scooped up with the tube, added with a scoop, or poured into the tube from a beaker. Tap the tip of tube on the bench and add more dry ice until the tube is full. Twist cap on tightly until it stops turning. **If cap does not stop turning when tightened, remove the cap before proceeding.** Without a complete seal, the cap is likely to shoot off. Replace the cap with a new one before placing in water. If this does not provide a seal, replace the tube.

8. Immediately after capping, drop centrifuge tube, tapered end down, into the water in the cylinder (see Figure .E). Pressure will begin to build in the tube and gas will escape slowly from the region where the tube and the cap meet. **The plastic cylinder functions as a secondary container** and protects you from possible injury. If the tube shatters or the cap shoots off, any projectiles will be directed straight up. **Do not place anything (including your face) above the cylinder.** Watch the extraction from the side, not the top, of the cylinder.

9. After 15 seconds, liquid CO<sub>2</sub> should appear. If no liquid has appeared after *ca.* 1 minute, there is not a sufficient seal. Remove tube from cylinder, tighten cap, and put back in water. If repeated trials do not produce liquid, the cap or tube may need to be replaced. Liquid should boil and gas should escape for 2 – 3 minutes.

**NOTE:** During this time, it is sometimes helpful to slowly rotate the cylinder on its base to prevent the centrifuge tube from freezing to the side of the cylinder. **Never remove the tube from the plastic cylinder when the CO<sub>2</sub> is liquid.** Tubes may rupture due to pressure and therefore must always remain in secondary containment.

10. As the liquid boils, it should pass through the peel and move to the bottom of the tube. If it cannot reach the bottom of the tube, the oil will deposit in the region of the tube containing the orange peel. This does not allow for isolation of the product.

11. After the liquid has evaporated and gas is no longer escaping, remove the tube from the cylinder with tweezers and open the cap. **Open centrifuge tubes slowly and only after the gas has escaped.** Opening tubes that are under pressure could result in the ejection of the cap.

12. If necessary, rearrange the solid orange peel before the second extraction. A piece of wire can be used to break up the solid mass and create a channel to the bottom for liquid CO<sub>2</sub>. Repeat the extraction by refilling the tube with dry ice, resealing the cap, and putting the tube back in the water.

13. Product (approximately 0.1 mL pale yellow oil) should be in the tip of the tube when the extraction is complete. Carefully remove the solid and the trap by pulling the wire handle. Use tweezers if necessary. If any solid remains in the tube, remove it with a spatula or wire. **NOTE:** Keep tube upright to avoid product loss.

### ***Characterization and Verification of Purity***

14. Determine the mass of your product. Be sure to dry the outside of the tube with a paper towel.

15. Obtain an IR spectrum if possible and compare to known compounds.

## Mechano chemical solvent free synthesis of azomethine

### Aim:

### Principle

#### *Mechanochemical method*

The principle of this method is that the precursors under the conditions of the mechanical treatment undergo a chemical reaction resulting in the formation of the product. Given that the formation of the product takes place in the solid state, there is no need for filtration, which, in many cases proves to be quite difficult; there is no need for further treatments such as aging or hydrothermal treatment to increase the crystallinity of the product phases.

“Mechanochemistry is a branch of chemistry, which is concerned with chemical and physico-chemical changes of substances of all states of aggregation due to the influence of mechanical energy.” This definition is based on theoretical considerations of Ostwald concerning the relationship between chemical and mechanical energy. Despite the long history of mechanochemistry, the definition of a mechanochemical reaction was only recently incorporated into the chemical literature. The recent IUPAC Compendium of Chemical Terminology defines mechanochemical reaction as a “chemical reaction that is induced by mechanical energy”.

Unintentional chemical reactions accompany many forms of mechanical action, like grinding, sliding, or plastic deformation, while the deliberate application of mechanical energy, typically by means of high-energy ball milling, provides a method to prepare useful new materials and to improve the efficiency of complex processes. The chemical effects of mechanical action are different from the effects of heat, and realizing, explaining, and utilizing this fact is an important thread in the history of mechanochemistry.

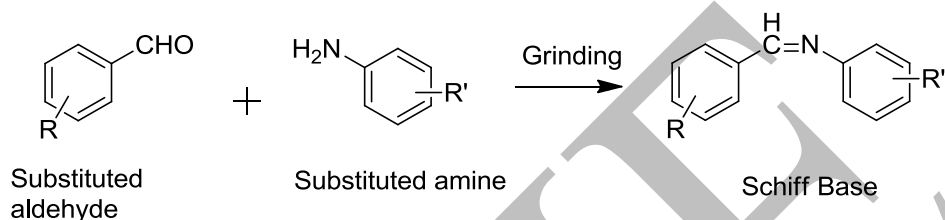
### Materials Required:

- Aldehyde
- Amine
- Mortar

### General procedure for the solvent-free synthesis of azo Schiff bases:

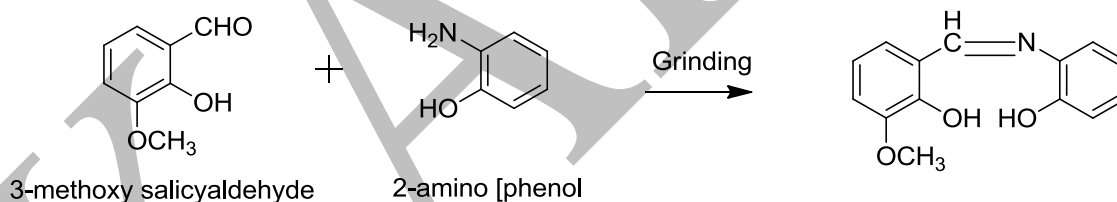


All solvent-free reactions were performed by grinding together 5.0 mmol of the pure amine with 5.0 mmol of the pure aldehyde in a mortar for one min and keeping the mixture at room temperature for 1.5 h in order to be formed quantitatively. The water produced in the reaction was removed at 70 °C under vacuum. The same procedure was used in the synthesis of Schiff bases with amine (5.0 mmol) and aldehyde (10.0 mmol).



*Synthesis of Schiff base:*

A mixture of 2-aminothiophenol (1 mmol), 3-methoxy salicylaldehyde (1 mmol) were ground together in a mortar with a pestle at 25 °C for the appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with water the solid thus obtained was filtered to get the desired product.



Result:

The yield of Schiff base compound:..... g

**MICROWAVE ASSISTED SYNTHESIS OF SCHIFF BASE****Aim:**

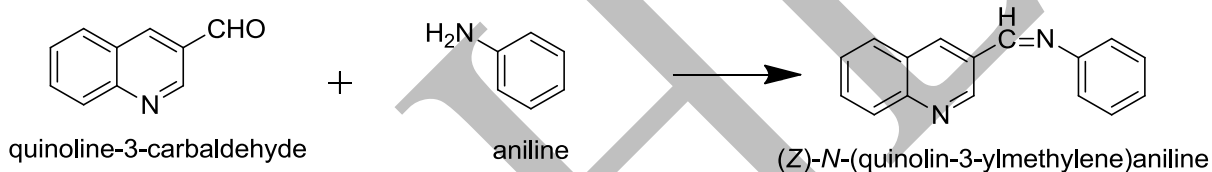
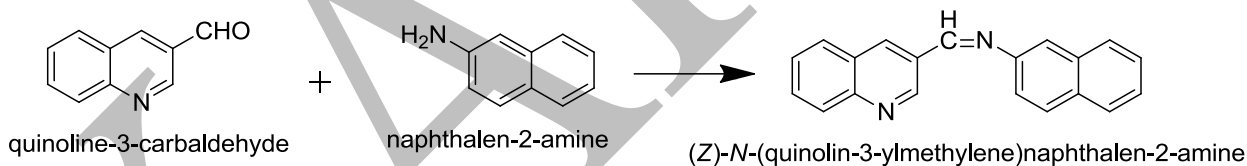
To synthesis the azomethine Schiff base compound by using microwave solvent free synthesis method.

**Materials Required:**

Substituted amine

Substituted aldehydes

Ethanol

**Synthesis of Schiff Base: (1)****Synthesis of Schiff Base: (2)****(i) GENERAL PROCEDURE FOR THE PREPARATION OF AZO SCHIFF BASES IN WATER:**

Solid starting materials were finely powdered before use. A mixture of aldehyde (2.5 mmol) and amine (2.5 mmol) was stirred in a small amount of water (5 ml) at room temperature for the mentioned time. In the case of Schiff bases 5.0 mmol aldehyde was used. The crystalline powder formed was collected by filtration, washed with water and dried in a desiccator to give azo Schiff bases.

**(ii) GENERAL PROCEDURE FOR SYNTHESIS OF SCHIFF'S BASE**

The Schiff base was prepared by reaction of equimolar (0.01 M) of amine and substituted aromatic aldehydes were transferred to a clean and dry Teflon vessel, and triturated to form uniform mixture, then addition a drops of ethanol. This mixture was

subjected to MW irradiation for 0.5-1 min at 400 watt power. After cooling, the formed crystals were filtered off, washed with several time of ethanol and recrystallized from ethanol.

**Result:**

The yield of Schiff base compound:.....g

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