SYNTHESIS OF NANOSTRUCTURED CARBONECOUS MATERIAL FROM WASTE TYRE: A STRATEGIC APPROACH TOWARDS "TRASH-TO-TREASURE"

A dissertation submitted in the partial fulfillment of
the requirement for the degree of
Bachelor of Science
in
Chemistry

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DECLARATION

I declare that the thesis entitled "**SYNTHESIS OF NANOSTRUCTURED CARBONECOUS MATERIAL FROM WASTE TYRE: A STRATEGIC APPROACH TOWARDS TRASH-TO-TREASURE** " has been prepared by me under the supervision of **Dr.Sravendra Rana and Dr.Trideb Sinha** from **Department of Chemistry, Applied Sciences Cluster,School of Engineering, University of Petroleum & Energy Studies, Dehradun, India.**

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CERTIFICATE

I certify that, **Shruti Mishra** has prepared his project entitled "**Synthesis Of Nanostructured Carbonecous Material From Waste Tyre:A Strategic Approach Towards Trash-to-Treasure " for** the award of **B.Sc. (Hons) Chemistry,** under my/our guidance. He has carried out the work at the **Department of Chemistry, School of Engineering, University of Petroleum & Energy Studies, Dehradun, India.**

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PLAGIARISM CERTIFICATE

I, **Shruti Mishra**, hereby certify that the research dissertation titled "**Synthesis Of Nanostructured Carbonecous Material From Waste Tyre:A Strategic Approach Towards Trash-to-treasure**" submitted for the partial fulfillment of a B.Sc. degree from University of Petroleum Energy & Studies, Dehradun, India is an original idea and has not been copied/taken verbatim from anyone or from any other sources.

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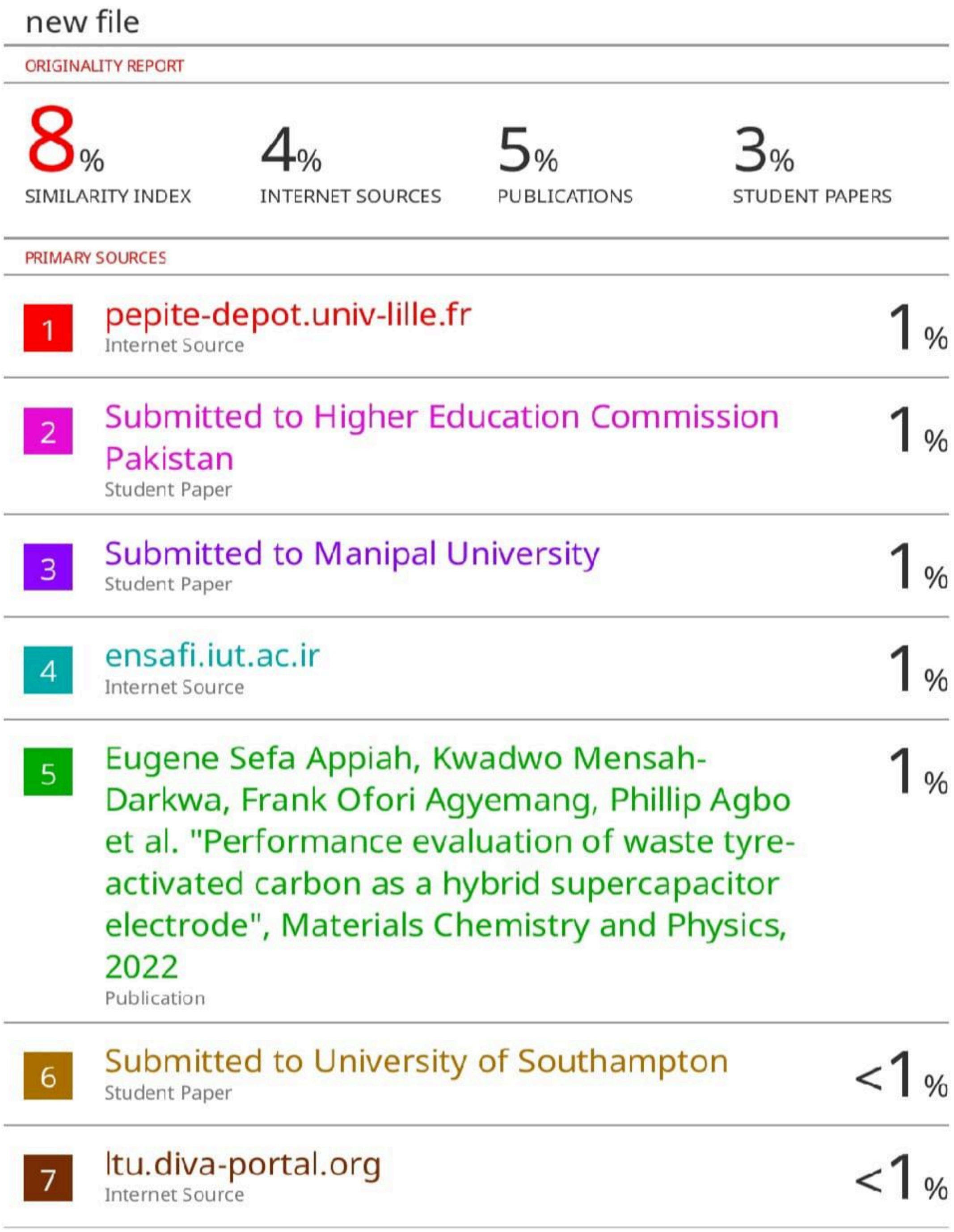

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Abstract

Waste tyres and other polymeric materials have been the most common type of waste dumped into the environment on a global scale. Waste tyres are a significant contributor to the European trash stream, with an estimated number of 3.3 million tons produced yearly and have a stockpile of 5.7 million tons in Europe with 10% of the total quantity being exported to Africa.

This chapter addresses the growing problem of waste tire generation and its associated environmental and public health concerns. It emphasizes the importance of proper waste tire management strategies that prioritize material recovery, energy generation, and the creation of valuable products.

The chapter explores the use of pyrolysis as a particularly promising method for waste tire management. Pyrolysis breaks down waste tires into valuable resources such as oil, char, steel, and gas, all with high commercial demand. This process contributes to a circular economy by minimizing waste and transforming end-of-life tires into reusable materials.

The chapter highlights the potential of pyrolysis to achieve sustainable waste tire management, minimizing environmental impact and maximizing economic benefits. It presents pyrolysis as the ideal solution for responsible tire end-of-life management.

KEYWORDS: DISCARDED TYRE, PYROLYSIS, TUBULAR FURNACE, FORMED-BY-PRODUCTS.

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CHAPTER 1

INTRODUCTION

1.1 Global Challenge of Waste Tires:

Waste tire disposal poses a significant global concern due to its negative aesthetic, environmental, and health impacts. The annual production of new tires (around 1.6 billion) is nearly matched by the generation of scrap tires (approximately 1.5 billion). These tires, being non-biodegradable, persist in the environment for extended periods, potentially harming both the environment and human health. Common problems associated with waste tire disposal include accidental fires, toxic chemicals leaching into the soil, breeding grounds for disease-carrying vectors, and the associated spread of epidemics, along with the inefficient use of valuable landfill space.

1.2 Alternative Solutions for Safe Disposal:

To safeguard the environment and public health, alternative approaches are crucial to replace traditional scrap tire disposal methods. Several waste tire management strategies have been adopted, including waste reduction, tire reuse, recycling (applications in civil engineering and thermochemical treatments like combustion, gasification, and pyrolysis), and landfilling as a last resort.

Global waste tire management practices are undergoing a significant shift. While historical data (2011) indicated a reliance on landfills (77%), minimal recycling (7%), and limited fuel use (11%), stricter environmental regulations and technological advancements are driving a more sustainable approach. Despite ongoing economic and non-economic challenges associated with the reduce-reuse-recycle (RRR) hierarchy, waste tire management is increasingly focused on:

- **Energy recovery:** Currently, the dominant method, utilizing 25-60% of waste tires.
- **Reuse:** Accounting for 5-23% of waste tires, with applications in various sectors.
- **Recycling:** Though representing only 3-15% currently, it remains the most recommended approach due to its potential for material recovery (civil engineering), energy generation (thermochemical treatments), and creation of valuable products (pyrolysis).

Within the realm of recycling, value-added product recovery emerges as the most promising strategy. These products, derived through pyrolysis, boast high commercial demand across various industries and societal applications. They promote a circular economy by minimizing waste while maximizing environmental and economic benefits.

This chapter delves into the challenges of waste tire disposal, explores the application of pyrolysis for waste tire management, and examines the utilization of products derived from this process.

1.3 CHARACTERIZATION OF DISCARDED TYRE

Effective scrap tire management begins with a thorough understanding of their composition and characteristics. Tires are a complex blend of materials, primarily consisting of natural rubber (NR), synthetic rubbers (SR) like butadiene rubber (BR) and styrene-butadiene rubber (SBR), carbon black, and various additives. The specific proportions of these components vary depending on the tire type. Typically, NR content ranges from 14-48%, SR from 10-27%, carbon black from 11-28%, steel from 14-25%, and fabric, fillers, and accelerators combined from 12-17% [3].

These materials are strategically incorporated to enhance specific tire properties. For instance, natural rubber improves resistance to cracking, while synthetic rubber enhances rolling resistance. Carbon black reinforces the tire against wear and tear, while steel improves handling and wear performance. Additionally, sulfur and zinc oxide play a crucial role in rubber vulcanization

Beyond the material composition, the elemental makeup of tires also varies based on the type. Common elements include carbon, hydrogen, nitrogen, sulfur, oxygen, and trace metals. Understanding both the material and elemental composition is essential for selecting the most appropriate scrap tire management strategies.

1.4 LITERATURE REVIEW:

In this chapter, the theory behind discarded tires is discussed. Previously reported research work on this technique is expounded on, compared to this research work.

Like Noor Najmi Bonnia et al.,2021 they synthesize Graphene Oxide from recycled Carbon of waste Tyre using Hummers Method.
The process involves strong oxidizing agents like potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4) to break down the tire's carbonaceous structure and introduce oxygen-containing functional groups (hydroxyl, carbonyl, and epoxide groups) onto the graphene sheets.
The oxidation process weakens the van der Waals forces holding the graphene layers together in the tire material. This allows for subsequent exfoliation using water or other solvents, separating the individual graphene sheets into graphene oxide flakes.
The resulting GO suspension requires purification to remove residual metal ions and unreacted starting materials.

Gaurav Tatrari et al.,2022, synthesis the bulk production of zinc doped reduced graphene oxide from waste tyre for supercapacitor application.
In this the zinc oxide used which acts as a catalyst and pyrolysis method has been done.
Joseph S.Gnanaraj et al.,2018 they develop Multifunctional Carbonaceous Nanomaterials from waste tires.In this synthesis, the Battery Grade Tyre- derived Carbon Material; as a potential anode material for Lithium Ion Batteries.

Ali A Ensafi et al.,2018 synthesis magnetic Fe2CuO4/rGO nanocomposite as an efficient recyclable catalyst to convert the waste tires into diesel fuel and as an effective mercury adsorbent from waste water.

Abhilash et.al.,2022, synthesis the graphene from waste carbon resources with the help of chemical processes through oxidation-reduction processes.

1.5 RESEARCH GAP

Development of Graphene using the Sustainable Disposal method still remains a challenge. Moreover, their applications in the field of electronics and composites can be explored.

Scalability and Cost-effectiveness: Current methods for synthesizing rGO from waste tires might be effective on a small scale, but research is needed to develop methods that are scalable and cost-effective for large-scale production. This could involve optimizing reaction conditions, finding alternative reagents, or developing continuous processes.

Control of rGO Properties: The properties of rGO, such as surface area, conductivity, and defect density, are crucial for its applications. More research is needed to understand how the waste tire pre-treatment and rGO synthesis process affect these properties. This would allow for targeted control of rGO properties for specific applications.

Environmental Impact: While converting waste tires to rGO is a form of recycling, the environmental impact of the synthesis process itself needs further investigation. Life cycle assessments should be conducted to compare the environmental footprint of rGO production from waste tires to other methods.

Integration with existing tire recycling processes: Many regions already have established methods for tire recycling. Research is needed to explore how rGO synthesis from waste tires can be integrated with existing recycling infrastructure to minimize disruption and maximize efficiency.

Safety of rGO from waste tires: There is limited knowledge on the potential presence of contaminants or harmful byproducts in rGO derived from waste tires. Safety assessments are needed to ensure the safe use of this material in various applications.

CHAPTER 2

EXPERIMENTAL DETAILS

2.1 METHOD AND MATERIAL

WASTE TYRE PYROLYSIS

Pyrolysis refers to the thermochemical breakdown of carbonaceous waste materials. This process occurs under controlled conditions, primarily in an oxygen-free environment, using high temperatures to convert waste into liquid, solid, and gaseous products. While the concept may seem simple, pyrolysis involves a complex interplay of simultaneous reactions.

The initial stage involves the evaporation of moisture present in the waste material. This is followed by devolatilization, where the organic components decompose and release volatile gases. The non-volatile fraction remains as a solid residue. The volatiles then undergo further breakdown into smaller molecules, influenced by the time they spend within the reactor (residence time). These lighter molecules can then condense into liquids, while the non-condensable components exit the system as gases.

The quality and quantity of the products obtained from pyrolysis depend heavily on several factors. Key parameters include temperature, residence time within the reactor, and pressure within the reaction vessel. Additionally, the composition and size of the feedstock material, the rate at which it's heated, and the flow rate of any introduced gas can also influence the final product distribution.

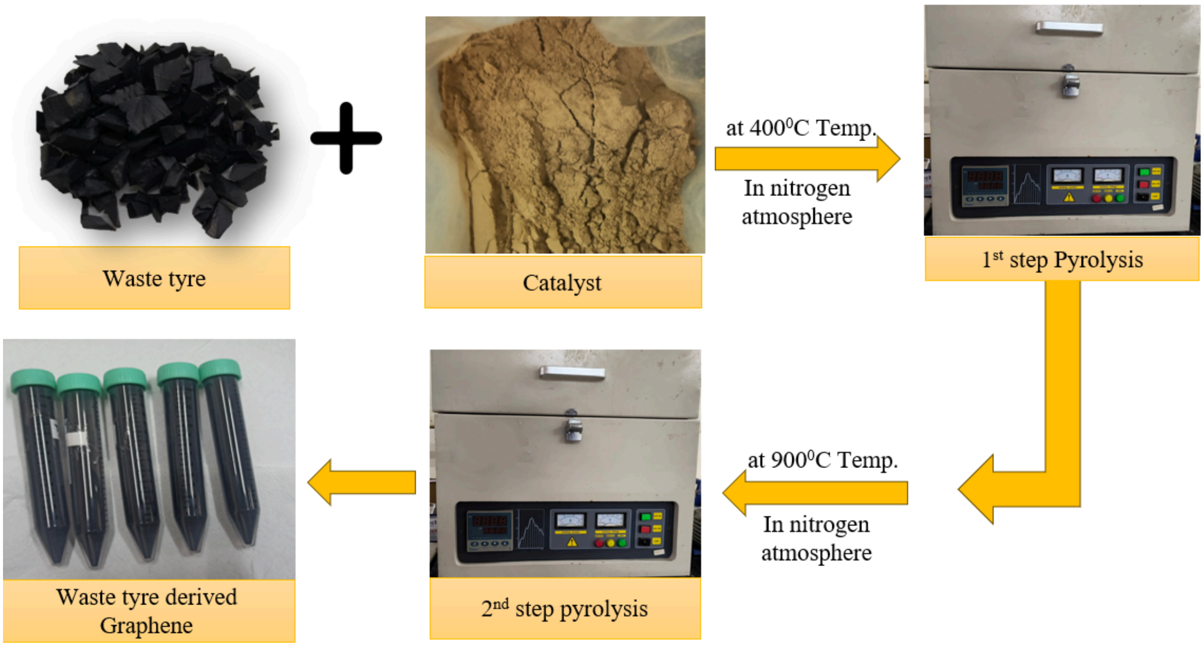


Fig1:*Synthesis of Reduced Graphene Oxide from Discarded Tyre*

In this pyrolysis method , take a discarded tyre. Cut the 5gram from that tyre and shred it into small pieces as maximum as possible. Wash the shredded pieces and dry it in the oven. Place the pieces in the Alumina Boat and put it in the Tubular Furnace.
Absence of Oxygen is necessary for the pyrolytic process of tyre.
It is a two step pyrolytic process, in the first step the maximum temperature reached at 450℃ after this cooling will take place.
On the next day, the maximum temperature reached 900℃ and again cooling will take place. finally the modified form of Graphene formed. It is washed with 5% concentrated Nitric acid and after this will neutralize its PH by washing it with water. So centrifuge it to remove all the impurities present in it.
Apart from the main product formed some byproducts are also formed and their amount depends on the temperature and the percentage of catalyst used.

The quality and quantity of products obtained from tire pyrolysis are primarily influenced by several operating conditions. These factors include:

- **Temperature:** Higher temperatures generally lead to increased gas yield and decreased char yield.
- **Residence Time:** Longer residence times for volatiles within the reactor can promote further breakdown into lighter gases, while shorter times favor liquid production. Carrier gas flow rate also impacts residence time and, consequently, product yield distribution.
- **Reactor Pressure:** Vacuum conditions within the reactor can enhance liquid yield at lower pyrolysis temperatures compared to atmospheric pressure.

Impact of Feedstock and Processing Parameters

Beyond these primary factors ,several other aspects influence product distribution:

- **Feedstock Composition:** The type of tire used (e.g., car, truck) can affect product yields even under identical operating conditions.
- **Feedstock Size:** Smaller particles experience faster heat transfer, resulting in higher gas yield. Conversely, larger particles lead to slower heat transfer and increased char production.
- **Heating Rate:** Faster heating rates accelerate the process, favoring the production of volatile fractions over slower heating rates.

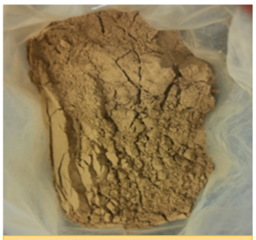
Reactor Design and Pyrolysis Technologies

1.The choice of reactor and pyrolysis technology significantly impacts product distribution. Common reactor types in tire pyrolysis include fixed bed, fluidized bed, moving bed, conical spouted bed, rotary kiln, and microwave reactors. Additionally, various technologies exist, such as thermal, catalytic, microwave, and vacuum pyrolysis. Each approach aims to optimize the process for desired product quality and quantity.

2.This revised version clarifies the key factors affecting product distribution and provides a more concise overview of the impact of feedstock, processing parameters, reactor design, and pyrolysis technologies.

Discarded Tyre

Fig.2

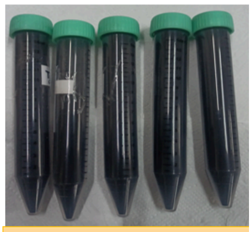


Nano-Clay

Fig.3

Alumina boat

Fig.4



R-GO samples

Fig.5

2.2 CHARACTERIZATION OF r-GO

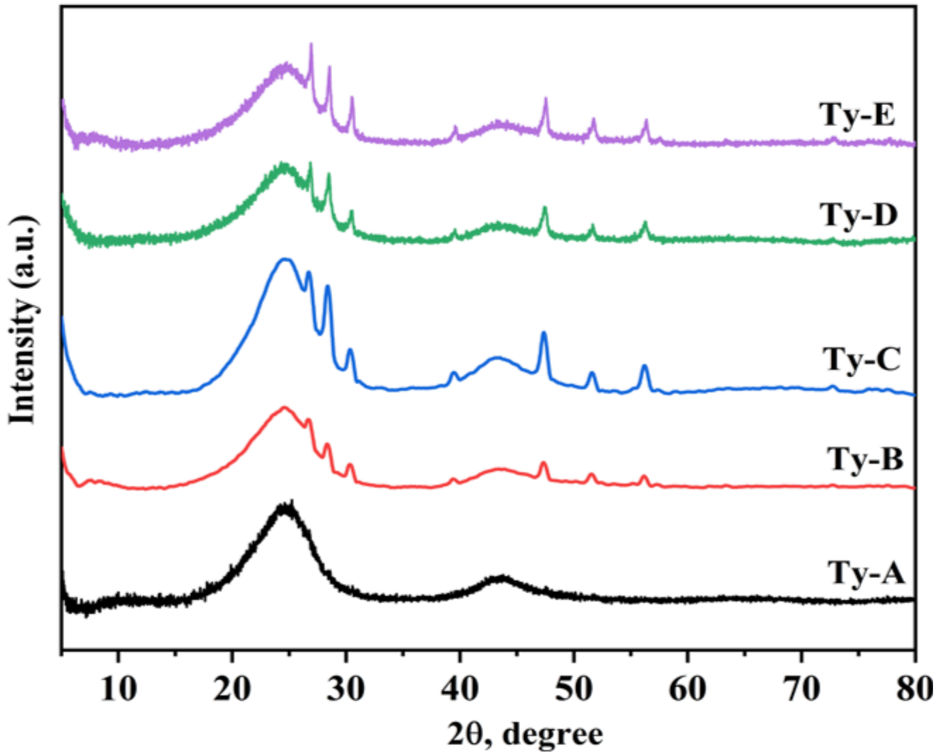


Fig.6 ***X-RAY DIFFRACTION***

X-ray diffraction (XRD) is a versatile non-destructive analytical technique used to analyze the crystallographic structure of materials.

XRD analysis provides information on a material's:

- Crystal structure: This includes the arrangement of atoms in the unit cell of the crystal.
- Phase identification: XRD can identify the different crystalline phases present in a material.
- Crystallite size: The size of the crystallites in a material can be determined from the width of the peaks in the XRD pattern.
- Lattice strain: The presence of strain in the crystal lattice can be detected by shifts in the peak positions in the XRD pattern.

XRD is a powerful tool for characterizing materials, and it has many applications in various fields. Here are some examples:

- In materials science, XRD is used to study the structure of new materials, investigate the effects of processing on material properties, and identify phases present in a material.
- In chemistry, XRD is used to identify unknown compounds, determine the purity of a sample, and study the structure of molecules.

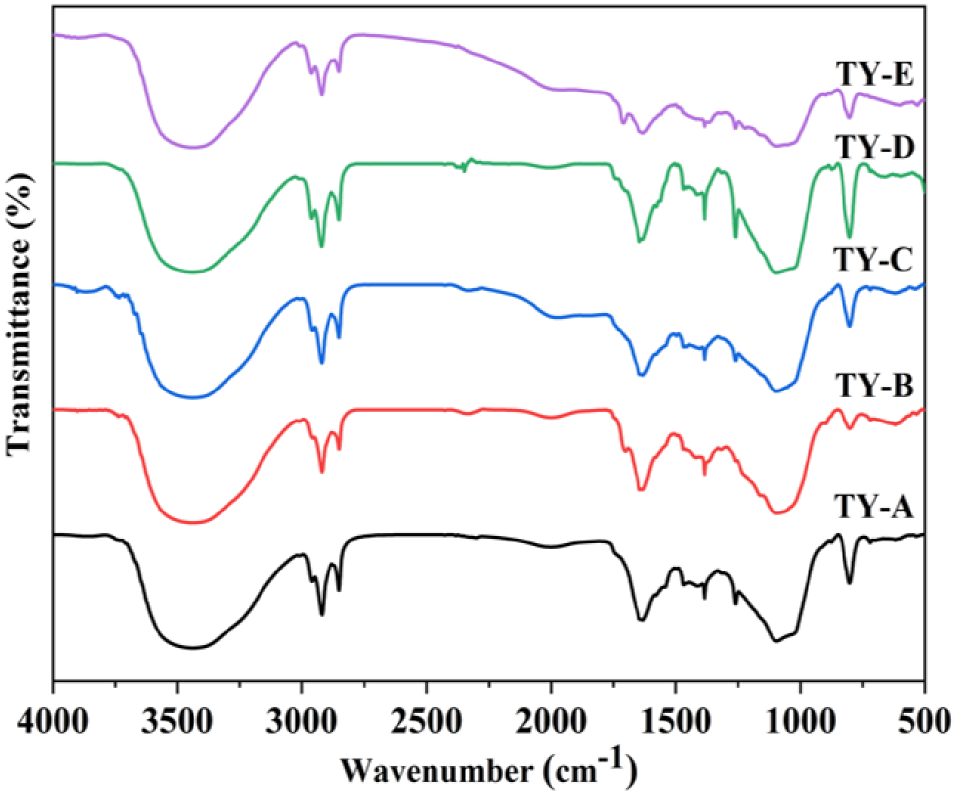


Fig.7 ***FOURIER TRANSFORM INFRARED SPECTROSCOPY***

FTIR stands for Fourier Transform Infrared Spectroscopy. It's a powerful analytical technique used to identify the chemical makeup of a material.

How it works:

1. **Infrared Light:** FTIR shines infrared radiation (light with a longer wavelength than visible light) on the sample.
2. **Absorption:** Certain frequencies of infrared light are absorbed by the sample, depending on the chemical bonds present.
3. **Interferometer:** A Michelson interferometer is used in the instrument. This creates a single beam with various infrared light frequencies and then analyzes how much of that light is absorbed by the sample. The raw data is collected as an interferogram.
4. **Fourier Transform:** A mathematical process (Fourier transform) is applied to the interferogram to convert it into a usable spectrum. This spectrum shows the intensity of light absorbed at different frequencies.
5. **Identification:** By comparing the spectrum with a library of reference spectra, the chemical makeup of the sample can be identified.

Applications of FTIR:

- Identifying unknown materials in research labs.
- Quality control in manufacturing industries (e.g., polymer analysis).
- Forensic analysis to identify materials involved in a crime.
- Analyzing biological samples for research purposes.

Fig.8 ***r-GO Synthesis***

THERMOGRAVIMETRIC SPECTROSCOPY

A TGA (thermogravimetric analysis) graph plots the weight of a sample on the y-axis as a function of temperature on the x-axis. In the case of rGO, the TGA graph typically shows a single major weight loss event. This weight loss is attributed to the decomposition of oxygen-containing functional groups (such as epoxides, carboxyls, and hydroxyls) that are present on the rGO surface due to the incomplete reduction of graphene oxide (GO).
Initial weight: The graph starts with a stable initial weight, representing the starting mass of the rGO sample.
Weight loss: As the temperature increases, the rGO begins to decompose. The oxygen-containing functional groups break down and are released as gaseous products (like CO, CO2, and H2O vapor). This decomposition leads to a decrease in the weight of the sample, reflected as a downward slope in the TGA graph.

Stable weight: After all the oxygen-containing functional groups have decomposed, the weight of the sample plateaus reaches a stable value. This final weight represents the mass of the remaining carbonaceous material, which is mostly graphene.

Degree of reduction: More reduced rGO will have a smaller weight loss compared to less reduced rGO because there are fewer oxygen-containing groups to decompose.
Heating rate: The rate at which the temperature is increased can affect the rate of decomposition and the temperature at which it occurs. A slower heating rate may result in a more gradual weight loss.

Sample size and composition: The size and composition of the rGO sample can also affect the shape of the TGA graph.

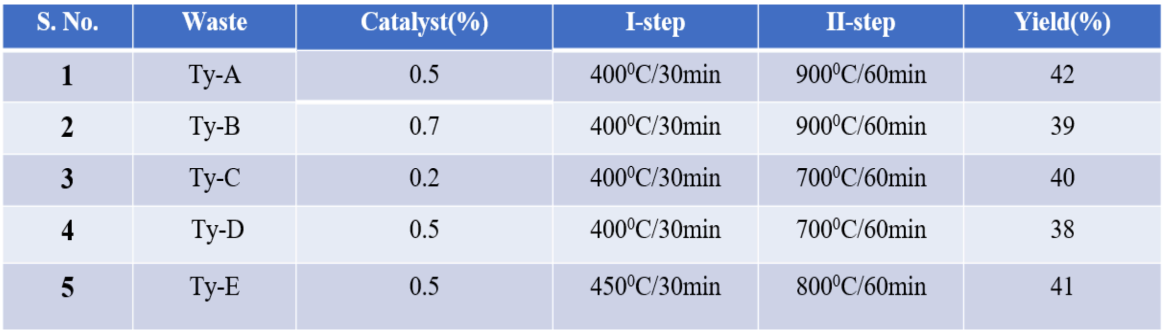
RAMAN SPECTROSCOPY

The x-axis of the graph shows the Raman shift in cm-1, which is a measure of the energy difference between the incident laser light and the scattered light. The y-axis shows the intensity of the Raman scattering in arbitrary units (a.u.).The Raman shift values correspond to the specific vibrational modes of the molecule, which involve the stretching, bending, and twisting motions of its atoms. Since different chemical bonds and functional groups within a molecule have distinct vibrational frequencies, the Raman spectrum reflects the unique molecular structure.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 RESULT AND CONCLUSION



S. No.	Waste	Catalyst(%)	I-step	II-step	Yield(%)
1	Ty-A	0.5	400^{0}C/30min	900^{0}C/60min	42
2	Ty-B	0.7	400^{0}C/30min	900^{0}C/60min	39
3	Ty-C	0.2	400^{0}C/30min	700^{0}C/60min	40
4	Ty-D	0.5	400^{0}C/30min	700^{0}C/60min	38
5	Ty-E	0.5	450^{0}C/30min	800^{0}C/60min	41

As the yield of the Ty-A sample is maximum at a maximum temperature 900℃.
And from XRD characterization the conclusion is that the peak of all the formed r-GO is at 24° which symbolizes that the formed product is r-GO.
Apart from this, in Ty-A there are no other extra peaks w.r.t. the other r-GO formed so it means that the by-products formed in Ty-A is minimal in amount.
So, the best formed product out of all is Ty-A.

3.2 SCOPE:

The produced Graphene would be used to develop the smart composite material consisting of self-healing as shape memory properties
Here are some examples of composites achievable through rGO synthesis:

- **Metal-rGO composites:** Combining rGO with metals like copper or titanium can result in composites with superior electrical and thermal conductivity, along with enhanced mechanical strength.

- **Polymer-rGO composites:** When incorporated into polymers, rGO can significantly improve their electrical conductivity, mechanical properties, and ability to act as a barrier.
- **Semiconductor-rGO composites:** Combining rGO with semiconductors can lead to composites with improved photocatalytic activity, making them highly efficient for applications in solar energy conversion and environmental cleanup.

A comparison study will be carried out with respect to commercial graphene to make a research article.

3.3 APPLICATIONS:

Reduced graphene oxide (rGO) boasts a range of exciting applications due to its unique properties that bridge the gap between graphene oxide (GO) and pristine graphene. Here's a glimpse into some of its promising applications:

Energy Storage:

- Supercapacitors: rGO's high surface area and conductivity make it a valuable electrode material for supercapacitors. This translates to faster charging and discharging cycles, enabling efficient energy storage for various applications.

- Lithium-ion Batteries: rGO can be incorporated into lithium-ion battery electrodes to improve their conductivity and cycling performance. This can lead to batteries with faster charging times and longer lifespans.

Electronics:

- Transparent Conductive Films: rGO, with its improved conductivity compared to GO, can be used to create transparent conductive films for touch screens, solar cells, and organic light-emitting diodes (OLEDs).

- Flexible Electronics: rGO's flexibility and conductivity make it suitable for developing flexible and wearable electronic devices.

Composites:

- Reinforcement Material: rGO can be integrated into polymers, ceramics, and metals to enhance their mechanical strength, thermal conductivity, and electrical conductivity. This finds applications in aerospace, automotive, and construction industries.

- Barrier Materials: rGO composites can act as effective barriers against gases and liquids due to the strong interfacial bonding between rGO and the matrix material.

Biomedical Applications:

- Drug Delivery: rGO's large surface area can be utilized to carry drugs and biomolecules for targeted drug delivery applications.

- Biosensors: rGO can be used in biosensors due to its ability to interact with biomolecules and its electrical conductivity. This allows for the detection of various biological markers for disease diagnosis.

- Tissue Engineering: rGO's biocompatibility and ability to promote cell growth hold promise for applications in tissue engineering, potentially aiding in tissue regeneration.

Environmental Applications:

- Water Purification: rGO can be used in water treatment membranes for efficient removal of contaminants like heavy metals and organic pollutants.

- Air Purification: rGO-based materials can be utilized for air filtration, capturing pollutants and improving air quality.

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