

**WASTE BIOMASS DERIVED HETEROGENEOUS CATALYSTS
AND THEIR APPLICATIONS IN ORGANIC
TRANSFORMATIONS**

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
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PHILOSOPHY**

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APPLICATIONS IN ORGANIC TRANSFORMATIONS**

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This Thesis is an original work of her research which has not been used previously and which has not been submitted to any other University for any purpose. She is duly permitted to submit her thesis for examination.

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LIST OF ABBREVIATIONS

BHET — Bis-(2 hydroxyethyl) terephthalate

BJH — Barrett–Joyner–Halenda (pore size analysis)

BLA — Bamboo Leaf Ash

CaO — Calcium oxide

DBU — 1,8-Diazabicyclo[5.4.0]undec-7-ene

DES — Deep Eutectic Solvent

DMT — Dimethyl terephthalate

DSC — Differential Scanning Calorimetry

EDX — Energy-Dispersive X-ray spectroscopy

EG — Ethylene glycol

FAME — Fatty Acid Methyl Esters

Fe₃O₄ — Magnetite (iron(II,III) oxide)

FFA — Free Fatty Acid

FTIR — Fourier Transform Infrared Spectroscopy

g — Gram

g-C₃N₄ — Graphitic carbon nitride

HEMT — 2-Hydroxyethyl methyl terephthalate

HPLC — High-Performance Liquid Chromatography

IL — Ionic Liquid

JCPDS — Joint Committee on Powder Diffraction Standards

LCA — Life Cycle Assessment

LDH — Layered Double Hydroxide

mg — Milligram wt% — Weight percent Temp — Temperature

min — Minutes h — Hour/hours

mL — Millilitre

MOF — Metal–Organic Framework

MWCNT — multi-walled carbon nanotube

NMR — Nuclear Magnetic Resonance

OPA — Orange Peel Ash

OPA@Fe₃O₄ — Orange-peel-extract-impregnated magnetic Fe₃O₄ nanocatalyst

PET — Poly(ethylene terephthalate)

POM — Polyoxometalate

SAED — Selected Area Electron Diffraction

SDG — Sustainable Development Goal(s)

SEM — Scanning Electron Microscopy

TEA — Techno-Economic Analysis

TEM — Transmission Electron Microscopy

TGA — Thermogravimetric Analysis

TPA — Terephthalic acid

UV–Vis — Ultraviolet–Visible spectroscopy

XPS — X-ray Photoelectron Spectroscopy

XRD — X-ray Diffraction

XRF — X-ray Fluorescence

CHAPTER 1

INTRODUCTION

1.1. Background

The trajectory of human development in the 21st century has been marked by dramatic demographic expansion, intensified industrialization, and mounting ecological strain. In November 2022, the global population reached an unprecedented milestone of 8 billion, as reported by the United Nations Department of Economic and Social Affairs (UN DESA, 2022). This represented not merely a numerical threshold, but a symbolic reflection of the accelerating demand humanity places upon planetary systems. The leap from 7 to 8 billion inhabitants in just over a decade illustrates not only the success of public health and agricultural advancements but also the urgent pressures these gains exert on natural resources, waste systems, and climate stability. Population growth, coupled with rising affluence and urbanization, has intensified the global appetite for energy, food, housing, and consumer goods. This heightened consumption is deeply intertwined with technological modernization and lifestyle transformation. Plastics, for instance, have become emblematic of contemporary convenience. Their lightweight, durable, and inexpensive properties have rendered them indispensable across sectors ranging from packaging and construction to transportation and medicine. Yet, this very convenience has precipitated a profound environmental crisis, one that is as much about consumption patterns as it is about material choice.

Simultaneously, the production and processing of agricultural and forest-based commodities have escalated in tandem with human needs, resulting in voluminous and diverse streams of organic residues. These biomass wastes, which include crop stubble, sugarcane bagasse, fruit peels, poultry litter, coconut husks, sawdust, shells, and spent grains, are generated in staggering quantities globally. The global annual production of biomass residues is approximately to be over 140 billion metric tons, making them one of the most abundant yet persistently undervalued renewable resources (FAO, 2023). Composed of cellulose, hemicellulose, lignin, and inorganics such as Ca, K, Mg, and Si, these materials possess immense latent potential for transformation into fuels, chemicals, and functional materials.

Despite this potential, a large proportion of biomass waste remains underutilized or improperly managed. Open-field burning and indiscriminate dumping are still prevalent in many regions, particularly in South and Southeast Asia, where mechanized agriculture outpaces sustainable waste infrastructure. Practices such as post-harvest stubble burning in northern India, for example, continue to contribute to severe air quality deterioration, seasonal haze, and respiratory diseases (Chanana et al., 2023). In addition to air pollution, the uncontrolled decomposition of organic residues in landfills emits methane, a potent greenhouse gas, and leaches nutrients and pathogens into groundwater systems. These inefficiencies highlight not only a technological shortfall but also a missed economic opportunity, where waste is not valorized but rather treated as a nuisance.

From a sustainability standpoint, reconfiguring biomass as a strategic feedstock rather than an environmental burden aligns with key global imperatives, particularly the United Nations Sustainable Development Goals (SDGs). Valorizing biomass supports SDG 7 (Affordable and Clean Energy), SDG 12 (Responsible Consumption and Production), and SDG 13 (Climate Action) by fostering cleaner energy systems, promoting circularity, and mitigating emissions (Desai, 2022). Over the past decade, advances in thermochemical and biochemical conversion technologies: such as pyrolysis, gasification, hydrothermal carbonization, and anaerobic digestion have demonstrated the feasibility of transforming diverse biomass into biochar, syngas, platform chemicals, and energy carriers (Kumar & Samadder, 2017; Singh et al., 2014b). At the heart of this evolution is the concept of the biorefinery: a holistic system designed to extract maximal value from biomass through a cascading series of conversions and separations, mimicking the petroleum refinery model but grounded in renewable carbon.

Among the myriad routes of biomass valorization, the synthesis of heterogeneous catalysts from biomass waste is particularly compelling. These catalysts, often derived via calcination or chemical activation of agro-residues, have emerged as green and cost-effective alternatives to conventional metal-based or homogeneous catalysts. Their widespread application in transesterification, esterification, aldol reactions, and polymer degradation positions them at the

intersection of waste management, green chemistry, and sustainable manufacturing. Importantly, such catalysts are not merely substitutes, they bring distinct advantages in terms of non-toxicity, reusability, structural tunability, and reduced lifecycle emissions.

In parallel, the modern plastic economy faces an existential challenge. The proliferation of synthetic polymers, while instrumental in enabling globalization and consumer convenience, has precipitated an ecological dilemma of planetary proportions. Of particular concern is polyethylene terephthalate (PET), a thermoplastic polyester that has found ubiquitous use in beverage bottles, food packaging, and textile fibers owing to its clarity, mechanical robustness, chemical inertness, and recyclability (Awaja & Pavel, 2005) (Seah et al., 2023). Global PET production surpassed 80 million metric tons in 2023 and continues to climb, propelled by growth in the fast-moving consumer goods (FMCG) and textile sectors.

Yet, PET's high performance comes at a significant environmental cost. Its resistance to microbial degradation means that once discarded, it persists in the environment for centuries, fragmenting into microplastics and infiltrating terrestrial and aquatic ecosystems. Marine plastic pollution, for instance, is now recognized as a global crisis, with PET constituting a major fraction of floating and submerged plastic debris (Jambeck et al., 2015). Despite the recyclability of PET in theory, in practice the global recycling rate remains under 30%, with most post-consumer PET either incinerated, thereby releasing greenhouse gases and toxins or consigned to landfills (OECD, 2022).

Conventional mechanical recycling, although widely adopted, suffers from limitations including polymer chain scission, thermal degradation, and contamination, resulting in downcycled products of lower quality. In contrast, chemical recycling offers a more promising and regenerative approach. By depolymerizing PET into its monomeric building blocks primarily ethylene glycol (EG) and terephthalic acid (TPA); chemical recycling enables the production of virgin-grade polymers, thereby supporting a truly circular plastics economy (Ragaert et al., 2017).

Among the various chemical recycling techniques, glycolysis and methanolysis have emerged as particularly promising for PET depolymerization under relatively mild conditions. However, these processes are often constrained by the need for efficient and environmentally acceptable catalysts. Traditional homogeneous catalysts such as zinc acetate or cobalt salts, while catalytically effective, are plagued by issues of separation, non-reusability, toxicity, and downstream contamination. To address these concerns, research has increasingly turned toward heterogeneous catalysts particularly those derived from renewable resources as a sustainable alternative.

In this context, biomass-derived solid catalysts offer a dual environmental advantage: they enable the valorization of agricultural and food waste while facilitating green catalytic processes such as PET chemical recycling. These materials, often produced via controlled calcination of biomass or doping with transition metals, exhibit basic or acidic surface functionalities that can catalyze transesterification reactions with high efficiency. The development of such catalysts thus integrates two major waste streams—organic residues and plastic waste into a single circular framework that aligns with principles of green chemistry, environmental remediation, and materials sustainability.

Accordingly, the present thesis seeks to integrate these threads: biomass waste management, PET recycling, and green catalysis, into a cohesive research narrative. By synthesizing heterogeneous catalysts from selected biomass residues and applying them in two domains (i) the chemical recycling of PET via glycolysis and methanolysis, and (ii) the solvent-free aldol condensation reaction, contributing to the broader discourse on sustainable materials design, circular waste valorization, and catalytic innovation.

1.2. Review of Literature

1.2.1. Chemical Recycling of PET via Glycolysis

Among the myriad chemical recycling approaches developed to tackle the environmental persistence of polyethylene terephthalate (PET), glycolysis has steadily emerged over the past three decades as a leading methodology, distinguished

by its operational simplicity, scalability, and ability to yield high-value intermediates. This depolymerization strategy facilitates the conversion of post-consumer PET waste into its monomeric constituents, chiefly bis(2-hydroxyethyl) terephthalate (BHET) and associated oligomeric fragments, through a transesterification reaction that involves the cleavage of the ester linkages in the polymer backbone by glycols, most commonly ethylene glycol (EG). Typically conducted under elevated thermal conditions ranging from 180 °C to 240 °C, this reaction transforms a chemically inert plastic into reusable building blocks suitable for the synthesis of virgin PET or specialty polyesters (Paszun & Szychaj, 1997; Xin et al., 2021).

Despite the straightforward chemical nature of this process, the reaction kinetics are notably sluggish under uncatalyzed conditions. The high activation energy required to break the ester bonds, compounded by the moderate nucleophilicity of EG, severely limits the conversion efficiency. Consequently, the deployment of a suitable catalyst becomes indispensable, not only to lower the energy barrier for bond cleavage but also to enhance the electrophilic activation of the PET carbonyl or the nucleophilic character of the glycol (Imran et al., 2013; Shukla & Harad, 2005).

Historically, homogeneous catalysts particularly metal acetates such as zinc acetate ($\text{Zn}(\text{OAc})_2$) have dominated early research efforts. Zinc acetate has garnered widespread recognition as a benchmark system, owing to its high catalytic activity and ability to facilitate BHET yields exceeding 90% within 60 to 90 minutes at reaction temperatures around 190 °C (Colomines et al., 2005; López-Fonseca et al., 2009; Xi et al., 2005a). However, homogeneous systems present several critical shortcomings. These include difficulties in catalyst-product separation, non-recyclability, and the risk of heavy metal leaching into the product stream, which not only complicates purification steps but also raises environmental and regulatory concerns. As such, these drawbacks severely constrain the industrial feasibility and environmental acceptability of homogeneous catalysis for large-scale PET recycling (H. Wang et al., 2009).

In response to these limitations, research attention has increasingly turned toward heterogeneous catalytic systems, which offer distinct advantages such as ease of separation, recyclability, and operational stability. Solid base catalysts like calcium oxide (CaO) and magnesium oxide (MgO), typically used at loadings around 10 wt%, have demonstrated competent catalytic performance, achieving BHET yields above 85% in 2–3 hours at approximately 200 °C (Shukla & Harad, 2005). Building on this, structurally advanced materials such as spinel-type oxides, exemplified by ZnMn_2O_4 , have shown even greater efficacy, delivering up to 92% BHET within just 60 minutes of reaction time (Imran et al., 2013). These catalysts benefit from a combination of surface basicity and thermal stability, although they remain susceptible to surface fouling, leaching, and sintering-induced deactivation, particularly under prolonged use or at elevated temperatures (Enache et al., 2024).

A parallel advancement in catalyst technology involves the use of nanoparticle-based systems. These nanocatalysts, including zero-valent metals (e.g., Ni, Co), metal oxides (ZnO , Fe_3O_4 , MnO_2), spinel ferrites (CoFe_2O_4 , ZnFe_2O_4), and carbonaceous hybrids (MWCNTs, g- C_3N_4 , graphene) offer transformative advantages over traditional macro- and micro-scale systems (Al-Sabagh, Yehia, Eshaq, et al., 2016; Du et al., 2020; Swapna et al., 2025; Yun et al., 2023). Their exceptionally high surface area-to-volume ratios, quantum confinement effects, and tailored surface chemistries significantly enhance PET glycolysis kinetics, often at lower energy inputs and under milder conditions.

Nickel and cobalt nanoparticles, due to their intrinsic redox activity, facilitate PET depolymerization by activating the carbonyl groups in ester linkages. Stabilized ultrasmall Co nanoparticles (~3 nm), for example, have shown nearly 96% depolymerization efficiency at 180 °C, producing BHET yields of up to 77% in less than one hour (Veregue et al., 2018a). However, particle aggregation and metal oxidation pose limitations that necessitate stabilizing agents or composite structures. To overcome these drawbacks, metal oxide nanocatalysts such as ZnO and MgO have been investigated. ZnO nanoparticles are particularly attractive due to their amphoteric nature and affordability. Alone, ZnO provides moderate activity, but its performance increases markedly in combination with Fe_3O_4 , forming dual-functional

ZnO–Fe₃O₄ composites that demonstrate synergistic acid–base interactions and magnetic separability. Such systems have delivered BHET yields exceeding 92% within 30 minutes at 190 °C (Yun et al., 2023).

Spinel ferrite nanoparticles, such as CoFe₂O₄, ZnFe₂O₄, and NiFe₂O₄ combine strong Lewis's acidity with thermal stability and magnetic recoverability. CoFe₂O₄, when modified with ionic liquids, achieved BHET yields of ~96% within 2.5 hours, demonstrating the role of surface modification in enhancing nanoparticle dispersibility and activity (T. Wang et al., 2021). Exfoliated manganese oxide nanosheets (2D MnO₂), owing to their high aspect ratios and abundant active edge sites, have achieved complete PET depolymerization at 200 °C in under 30 minutes, attaining 100% BHET yields (S. Bin Jin et al., 2021). Their activity surpasses many bulk oxides and remains stable across multiple reuse cycles.

Carbon-based nanomaterials have also garnered interest due to their electronic conductivity, large surface area, and tunable chemistry. MWCNTs decorated with Fe₃O₄ nanoparticles and g-C₃N₄ dispersed in EG have achieved BHET yields ranging from 80 to 100% under 30 to 60 minutes, with excellent thermal and catalytic (Al-Sabagh, Yehia, Eshaq, et al., 2016; Anbarasu et al., 2024). Nitrogen-doped silica composites with embedded γ -Fe₂O₃ further demonstrate improved PET degradation under milder conditions, outperforming γ -Fe₂O₃ alone (Casey et al., 2023).

In addition, advanced porous nanomaterials like MOFs and polyoxometalates (POMs) provide modular frameworks for catalytic design. 2D MOF nanosheets (e.g., ZIF-L) offer high-density surface sites and superior diffusion, while Keggin-type POMs substituted with transition metals (e.g., Ni, Co, Zn) catalyze glycolysis with high BHET selectivity and short residence times (N. Han et al., 2024; Nilwanna et al., 2024; Pham et al., 2024; Suo et al., 2017). These nanocatalyst systems represent the forefront of PET recycling catalysis. They excel in reaction rate, selectivity, reusability, and magnetic recoverability, a criteria essential for continuous, sustainable depolymerization. While concerns remain regarding synthesis cost, material toxicity, and large-scale deployment, ongoing research into greener

synthesis protocols and biomass-supported hybrids (e.g., biomass derived coated Fe_3O_4) (present work) offers a promising route to integrate nanotechnology with green catalysis.

In parallel, organocatalytic systems have gained traction as metal-free and environmentally benign alternatives. Superbases such as TBD and DBU have shown BHET yields near 90% under mild conditions (150 to 180 °C), operating via base-mediated activation and hydrogen bonding (Jehanno, Pérez-Madrigal, et al., 2018). Yet, their cost and stability remain barriers to scale-up. Furthermore, the integration of ionic liquids (ILs) and deep eutectic solvents (DESs) into PET glycolysis systems has introduced multifunctional catalytic environments, where the solvent system also actively participates in the depolymerization. For instance, imidazolium-based ILs such as [Bmim][OAc] and choline chloride-based DESs have facilitated efficient PET degradation at 180-200 °C, yielding 80-88% BHET and displaying noteworthy reusability over several cycles (Xin et al., 2021). However, challenges such as high viscosity, synthesis complexity, and post-reaction separation difficulties continue to hinder the widespread commercial viability of these systems.

Amid these evolving approaches, a sustainable and increasingly impactful alternative has emerged in the form of biomass-derived solid catalysts. Synthesized from natural and renewable feedstocks such as agricultural residues (e.g., eggshells, shells, bones, husks), these materials not only address the dual challenge of plastic and biomass waste but also offer a green catalytic route grounded in circular economy principles. Their preparation typically involves calcination, yielding CaO- rich or K_2O -based matrices with strong basic properties ideal for transesterification reactions. For instance, Yunita et al. (2019) demonstrated the catalytic efficacy of CaO derived from calcined ostrich eggshells, achieving high BHET yield at 192 °C within 2 hours using only 1 wt% catalyst (Yunita et al., 2019).

The sustainable appeal of biomass-derived catalysts extends beyond their renewable origin. Unlike conventional catalysts, these systems are often free of toxic metals, exhibit minimal leaching, and can be regenerated with relatively low energy input. However, their performance is closely tied to their structural and

compositional characteristics, which vary depending on the source biomass and preparation conditions. As such, optimizing these parameters through advanced characterization techniques: XRD, BET, SEM, XPS, and reaction modeling becomes critical for consistent catalytic behavior (Clark et al., 2012; Sheldon, 2016).

Altogether, the landscape of PET glycolysis catalysis is evolving toward greener, more sustainable alternatives. Glycolysis offers significant advantages over methanolysis and hydrolysis, including ambient pressure operation and minimal salt byproducts, while preserving polymer quality (Al-Sabagh, Yehia, Eshaq, et al., 2016; Awaja & Pavel, 2005). Yet, the continued reliance on homogeneous systems underscores the urgent need to adopt catalysts that are not only efficient but also aligned with environmental stewardship. Biomass-derived solid catalysts, by virtue of their availability, eco-compatibility, and catalytic potential, represent a transformative step forward (Sheldon, 2016). Their development not only addresses the need for low-cost, high-efficiency systems but also contributes meaningfully to global efforts in waste valorization and sustainable materials recovery.

1.2.2. Chemical Recycling of PET via Methanolysis

Among the established chemical depolymerization methods for polyethylene terephthalate (PET), methanolysis represents a classical yet evolving approach that continues to attract scholarly and industrial interest. Through a transesterification reaction with methanol, PET undergoes systematic cleavage of its ester linkages to generate dimethyl terephthalate (DMT) and ethylene glycol (EG) both of which are fundamental monomeric building blocks used in the synthesis of virgin PET and other polyester derivatives (Bartolome et al., 2013; Genta et al., 2007; M. Han, 2019; Jankauskaitė et al., 2008; Kang et al., 2020). By enabling the breakdown of high-molecular-weight polymers into recyclable monomers, methanolysis facilitates a closed-loop recycling paradigm, effectively aligning with circular economy principles (M. Han, 2019; Jankauskaitė et al., 2008).

Methanolysis is mechanistically akin to glycolysis in its transesterification pathway, but is differentiated by its stringent operational conditions. Typically, the reaction is conducted at elevated temperatures ranging from 180 to 250 °C, under

pressurized environments between 20 and 40 atm (Bartolome et al., 2013). Such high-pressure conditions are essential to maintain methanol in the liquid phase at elevated temperatures and to shift the thermodynamic equilibrium towards complete depolymerization. In the absence of continuous removal of reaction products, particularly DMT, the equilibrium can stagnate, necessitating careful process engineering to maximize conversion (Gurralla et al., 2024; J. Xie et al., 2025).

From a mechanistic standpoint, the depolymerization proceeds through a nucleophilic substitution reaction, wherein alcohol attacks the carbonyl carbon of the ester moieties in PET. This results in the formation of a tetrahedral intermediate, which subsequently collapses to expel ethylene glycol and form dialkyl terephthalate. The reaction is generally catalyzed by either acidic or basic species, which facilitate proton transfers or stabilize intermediates, thereby enhancing the overall reaction rate (Schlüter et al., 2024; Shirazimoghaddam et al., 2023).

In early studies and industrial implementations, homogeneous metal-based catalysts have dominated methanolysis research. Metal salts such as zinc acetate ($\text{Zn}(\text{OAc})_2$) and cobalt acetate ($\text{Co}(\text{OAc})_2$) have demonstrated high catalytic efficiency and rapid kinetics, often achieving near-complete PET depolymerization under optimized conditions (Mishra & Goje, 2003; Siddiqui et al., 2012). These systems function by activating the carbonyl carbon through coordination, thereby increasing its electrophilic susceptibility to methanol attack. However, their utility is marred by serious drawbacks, including difficulties in separation and recovery, non-recyclability, and risk of product contamination with residual metal ions. The latter is particularly problematic in food-grade or pharmaceutical applications of recycled PET monomers, where purity standards are stringent. Furthermore, the toxicity and environmental persistence of heavy metals pose additional barriers to the widespread adoption of these homogeneous systems, especially in jurisdictions with strict regulatory frameworks (Gurralla et al., 2024).

To mitigate these limitations, considerable research has shifted toward the development of greener and more sustainable catalytic systems, with a particular emphasis on metal-free organic base catalysts. Systems such as sodium methoxide

(NaOMe), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and triethylamine (TEA) have been explored as viable alternatives (*Catalysts for Pet Methanolysis*, 2020; Sanghavi et al., 2024; Tanaka et al., 2024; S. Xie et al., 2024). These catalysts offer several compelling advantages, including absence of metal contamination, lower corrosion risks, and easier downstream purification. Moreover, they have shown efficacy under comparatively milder thermal conditions (80-180 °C), which broadens their applicability for lower-energy recycling processes. Nevertheless, the performance of these systems is highly sensitive to reaction parameters, such as the methanol-to-PET molar ratio, catalyst loading, and residence time. Suboptimal conditions may lead to incomplete depolymerization, formation of side products such as dimethyl isophthalate or terephthalic acid derivatives, and process inefficiencies, thereby necessitating thorough optimization.

In parallel, ionic liquids (ILs) have emerged as a promising frontier in PET methanolysis due to their unique dual-functionality as solvents and catalysts (Jiang et al., 2022; Li et al., 2024; C. Liu et al., 2022; Ma et al., 2022; J. Xie et al., 2025). Compounds such as 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]) have exhibited excellent PET solvation ability, high thermal stability, and tunable acidity or basicity, which can be leveraged to promote transesterification. Methanolysis in IL media has yielded high monomeric conversions under relatively mild conditions (e.g., 200 °C for 2 h), with the additional benefit of catalyst recyclability over multiple cycles without significant loss in activity or selectivity (J. Xie et al., 2025). However, the widespread industrial application of ILs remains constrained by several factors: their complex synthesis routes, high material costs, potential environmental toxicity, and challenges in complete recovery and purification of the product stream, particularly when scaling beyond laboratory conditions.

In pursuit of more sustainable and efficient alternatives, nanocatalyst-based systems have rapidly gained momentum. Nanoparticles ranging from zero-valent metals and spinel ferrites to metal oxides and carbon-based composites offer exceptional catalytic performance due to their high surface area, quantum size effects, and tunable surface chemistry. These attributes facilitate rapid

transesterification, reduced activation energy barriers, and high monomer yields under comparatively milder conditions.

Among the earliest successful use, ultrasmall ZnO nanoparticles (~4 nm) dispersed in methanol were shown to act as pseudo-homogeneous catalysts. These colloidal systems offer the surface-accessibility of homogeneous catalysts with the recyclability of solids. Methanolysis reactions using ZnO nanodispersions achieved ~95% DMT yield within just 15 minutes at 170 °C, an order of magnitude faster than most conventional systems (Du et al., 2020). The activity, measured as 553 g PET per gram of ZnO per hour, substantially outperforms traditional catalysts and demonstrates the potential of nanoscale dispersion in overcoming mass-transfer limitations.

A parallel advancement in designing nanocatalysts is the use of multivalent cobalt nanoparticles supported on silica (Co/SiO₂) (Kumari et al., 2024). These heterogeneous systems leverage the dual oxidation states of cobalt to activate ester bonds in PET efficiently. Remarkably, near-complete PET conversion and high DMT yields were attained under relatively mild thermal conditions, all while allowing the catalyst to be filtered and reused without performance degradation. The heterogeneity of the system ensures that metallic residues do not contaminate the final product, a notable advantage over soluble metal salts.

Similarly, mesoporous MgO/NaY zeolite composites, incorporating basic MgO clusters into a high-surface-area support, have proven capable of driving methanolysis to completion within 30 minutes at 200 °C (Tang et al., 2022). The synergy between the strong basic sites of MgO and the enhanced diffusivity offered by the mesoporous support matrix ensures rapid and selective depolymerization, yielding over 90% DMT. The robustness of this system, coupled with its simplicity, highlights the practical utility of nanostructured basic catalysts in industrial applications.

A particularly compelling and environmentally aligned advancement has emerged in the form of biomass-derived nanocatalysts for PET methanolysis. These systems synthesize active materials, such as CaO, K₂O, and sulfonated carbon from

renewable waste biomass including fruit peels, shells, and animal bones, integrating waste valorization with high-performance catalysis. One such example is the OPA@Fe₃O₄ nanocatalyst (present work), wherein orange-peel ash (rich in basic oxides) is coated onto magnetic Fe₃O₄, offering both catalytic activity and facile magnetic recovery. This system delivered DMT substantial yield in only 1 hour at 200 °C and retained efficacy across multiple cycles, exemplifying the promise of biowaste-derived multifunctional catalysts (Lalmangaihzuola et al., 2023).

In addition to their comparative strengths, both biomass-derived catalysts and nanocatalysts are actively addressing several previously identified research gaps in sustainable catalysis. For instance, recent advancements in surface engineering, magnetic support incorporation, and hybrid designs are beginning to resolve limitations in catalyst recovery, structural integrity, and operational stability (Nilwanna et al., 2024; T. Wang et al., 2021).

Biomass-derived catalysts are now being increasingly standardized through controlled calcination, elemental analysis, and reactivity profiling, reducing the variability often associated with agro-waste feedstocks (Khangte et al., 2023; Y. Kim et al., 2022; Ponce et al., 2025; Yunita et al., 2019). Similarly, nanocatalysts are being developed with greener synthetic routes and bio-compatible supports, narrowing the gap between high performance and environmental acceptability (Al- Sabagh, Yehia, Eissa, Moustafa, Eshaq, Rabie, & Elmetwally, 2014b).

Moreover, novel platforms such as metal-organic frameworks (MOFs) and deep eutectic solvents (DES) are expanding the boundaries of what constitutes a nanocatalyst. For instance, UiO-66(Zr), though susceptible to structural rearrangement, was able to mediate PET deconstruction in a solvent-free setting (Li et al., 2024). DES systems, operating both as solvents and catalysts, have achieved near-complete PET conversion and DMT yields exceeding 95% at relatively low temperatures (130 °C), all without introducing metals into the system (Wu et al., 2022).

The application of both catalyst types in continuous-flow and scalable systems is also under exploration, with promising pilot studies indicating feasibility

for industrial use (Laldinpui et al., 2021). Moreover, hybrid bio-nano systems such as Fe₃O₄-supported biochar or sulfonated carbon-metal oxide composites show potential to bridge the gap between activity and sustainability (Bai et al., 2025; Song et al., 2024).

From a mechanistic standpoint, studies using advanced spectroscopy and computational modeling are beginning to elucidate the roles of embedded metals (K, Ca, Mg) and functional groups in biomass catalysts, providing a clearer framework for catalyst design (Amin et al., 2024; Dehkhoda, 2010). These advances not only address technical uncertainties but also strengthen the predictive capabilities necessary for wider adoption.

Finally, integration of life-cycle assessments (LCA), techno-economic analysis (TEA), and recyclability evaluations is gradually becoming standard in biomass catalyst research (Amin et al., 2024; Sharma et al., 2024). These methodologies are essential in affirming the long-term sustainability credentials of these systems compared to traditional homogeneous or synthetic nanocatalysts.

Together, these developments reflect an accelerating convergence of performance, scalability, and sustainability anchored primarily by the progress in biomass-derived catalyst systems, which have emerged as not only viable alternatives but as frontrunners in the effort to green chemical transformations. Their origin from abundant agricultural residues, ease of preparation, functional versatility, and alignment with environmental and economic objectives underscore their pivotal role in the transition to a circular, low-impact chemical economy. As the research community continues to address mechanistic ambiguities and standardization challenges, biomass-based solid catalysts stand well-positioned to redefine the benchmarks of sustainable catalysis.

1.2.3. Agro-Waste as Precursor to Greener PET Recycling Catalysts

As the global imperative shifts toward circular and low-carbon resource utilization, agro-waste valorization has emerged as a pivotal strategy for both mitigating biomass waste and developing sustainable catalysts for plastic depolymerization and organic transformations. This section explores the catalytic

potential of agro-waste-derived materials, specifically in PET glycolysis, methanolysis, and Aldol-type reactions by drawing from their well-documented performance in biodiesel transesterification and extending their relevance to emerging recycling platforms.

Building upon the intrinsic versatility, elemental diversity, and widespread geographic availability of biomass resources, agro-waste-derived solid catalysts have increasingly emerged as exceptionally promising candidates for facilitating a range of polymer depolymerization reactions most notably in the glycolysis and methanolysis of polyethylene terephthalate (PET) as well as for catalyzing transesterification reactions essential to biodiesel production. Agro-waste, broadly defined as the residual organic biomass resulting from agricultural practices and food processing operations, encompasses a wide spectrum of materials including fruit peels, nut shells, plant stalks, seed husks, and other lignocellulosic crop residues. These waste streams are typically enriched with catalytically active inorganic elements: such as calcium (Ca), potassium (K), magnesium (Mg), silicon (Si), and phosphorus (P), which, when subjected to suitable thermal activation or chemical modification, yield solid oxide frameworks capable of mediating both base- and acid-catalyzed transformations with high efficiency and specificity (Magdziarz et al., 2018; Odziejewicz et al., 2022; Vassilev et al., 2013).

Thermal calcination of calcium-rich agro-waste precursors particularly eggshells and animal bones transform the predominant calcium carbonate (CaCO_3) content into catalytically potent calcium oxide (CaO), a strong solid base. This CaO has demonstrated pronounced efficacy in driving the glycolytic depolymerization of PET. For instance, Yunita et al. (2019) reported that CaO derived from calcined ostrich eggshells was capable of catalyzing the depolymerization of PET at 192 °C within just 2 hours, using a mere 1 wt% of catalyst, and producing up to 76% BHET (Yunita et al., 2019). Such findings clearly illustrate the potential of agro-waste-derived catalysts to serve as environmentally sustainable and economically viable alternatives to conventional homogeneous metal-based catalysts, offering distinct advantages such as improved reusability, simplified separation, and reduced downstream contamination.

Among the catalytic applications most extensively studied using agro-waste-derived systems is the transesterification reaction, particularly in the context of biodiesel production (Khan et al., 2021; Odude et al., 2019). While these findings are derived from biodiesel systems, the catalytic behavior, especially base-promoted ester exchange and moisture tolerance, directly parallels the reactivity required for PET glycolysis and methanolysis, which also involve cleavage of ester bonds under thermal conditions. Banana peel ash, which contains a potassium oxide (K_2O) content exceeding 40%, has been shown to catalyze the transesterification of palm oil with methanol to fatty acid methyl esters (FAMES) with yields surpassing 95% under ambient temperature conditions and within a remarkably short reaction duration of 30 minutes (Pathak et al., 2018). Similarly, other agricultural residues such as cocoa pod husks and plantain peel ash have been successfully employed in the transformation of waste cooking oil into biodiesel, achieving conversion efficiencies above 90% under relatively mild thermal conditions (Etim et al., 2018; Olugbenga et al., 2013). Thereby highlighting the growing catalytic relevance of alkali-metal- enriched agricultural residues.

Calcium-laden biowaste materials including fish bones, bovine bones, and mollusk shells have also demonstrated high catalytic performance following calcination. These materials generate CaO-rich solids that are particularly well-suited for direct, one-pot transesterification of oils containing elevated free fatty acid (FFA) levels. Such catalysts obviate the need for a preliminary esterification step, thereby simplifying process integration and minimizing soap formation. These dual benefits ultimately contribute to improved biodiesel quality and reduced operational costs associated with post-reaction separation (Viriya-empikul et al., 2010; Wei et al., 2009).

Equally significant are acid-functionalized catalysts derived from agro-waste (X. Chen et al., 2022; Dulymahakamtorn et al., 2025; Konwar et al., 2014; Kumawat & Rokhum, 2022). The transesterification of triglycerides into fatty acid methyl esters (biodiesel) using biomass-derived heterogeneous catalysts proceeds through mechanistic pathways analogous to those observed in conventional base- and acid-catalyzed systems, with distinct roles played by the active sites present in the

catalyst. In the case of base-catalyzed transesterification, which is typical for catalysts derived from calcium- or potassium-rich biomass such as calcined eggshells, bones, or plant ashes, the reaction is initiated by the abstraction of a proton from methanol by basic surface sites, typically O^{2-} or OH^- groups (Pathak et al., 2018; Tobío-Pérez et al., 2022). This generates the reactive methoxide anion (CH_3O^-), which subsequently attacks the electrophilic carbonyl carbon of the triglyceride molecule. The resulting tetrahedral intermediate rearranges to release a molecule of methyl ester and a diglyceride, with the cycle repeating until three methyl ester molecules and one molecule of glycerol are formed. The high basicity and surface area of such bio-derived catalysts facilitate efficient alcohol activation and carbonyl polarization, enabling high conversion even at relatively low temperatures.

Conversely, acid-catalyzed mechanisms, commonly associated with sulfonated carbonaceous catalysts synthesized from cellulose, sugar, or lignocellulosic residues, follow a different route. Here, Brønsted acid sites (such as $-SO_3H$ groups) protonate the carbonyl oxygen of the triglyceride, enhancing its susceptibility to nucleophilic attack (Chandra Kishore et al., 2022; Kumawat & Rokhum, 2022). Methanol then attacks the activated carbonyl carbon, forming an intermediate that collapses to release a methyl ester and a diglyceride, much like in the base-catalyzed route. This pathway is particularly advantageous for oils with high free fatty acid (FFA) content, as the acidic sites can simultaneously catalyze the esterification of FFAs into methyl esters, thereby circumventing the soap formation that typically hampers base catalysis under such conditions (Tobío-Pérez et al., 2022).

In recent developments, bifunctional catalysts derived from biomass, combining both acidic and basic sites, or incorporating dual functional phases such as CaO supported on sulfonated carbon, have demonstrated the capacity to perform both esterification and transesterification in a single step (Dulymahakamtorn et al., 2025; Niju et al., 2016). These materials have also shown promise in C–C bond-forming reactions such as Aldol condensation, where synergistic acid-base interactions enhance enolate generation and product selectivity (Zhan et al., 2019). This integrated functionality is especially useful for processing low-grade or waste

feedstocks, including used cooking oil or sludge lipids, without necessitating separate pretreatment stages (Akhavue et al., 2020).

The efficiency of these catalysts is strongly influenced by their physicochemical properties, including surface area, porosity, and the strength and accessibility of active sites (Huber et al., 2006; Seah et al., 2023). To holistically evaluate and optimize biomass-derived heterogeneous catalysts for biodiesel production through esterification and transesterification, a multidimensional analytical approach is essential; one that integrates catalytic activity testing (via GC, NMR, or HPLC), structural and surface analysis (XRD, SEM/TEM, BET), acid–base profiling (FTIR), and stability assessments (TGA, XPS). This comprehensive methodology enables the correlation of catalytic performance with underlying structural and chemical characteristics across various reaction systems including PET glycolysis, methanolysis, and Aldol condensations thereby guiding the rational design of more efficient, durable, and environmentally sustainable catalyst systems. Calcination conditions, particularly temperature and duration, play a critical role in determining the phase composition and catalytic activity, for instance, ensuring complete conversion of CaCO_3 to reactive CaO without sintering. While leaching of active metal species such as K^+ or Ca^{2+} can enhance initial reaction rates by introducing a quasi-homogeneous component, it may also compromise catalyst reusability unless proper stabilization strategies are employed. Overall, the mechanistic pathways underpinning biomass-derived heterogeneous catalysis are well-established, yet highly tunable, offering a sustainable and adaptable platform for biodiesel synthesis through transesterification across a wide range of feedstocks (Chandra Kishore et al., 2022; Dehkhoda, 2010; Tobío-Pérez et al., 2022).

Despite the well-documented utility of agro-waste-derived catalysts in biodiesel synthesis and their expanding application in PET glycolysis, their role in the methanolysis of PET remains relatively underexplored. However, their distinct structural and compositional advantages including high intrinsic basicity, excellent thermal stability, and favorable surface morphology; suggest strong potential for alcoholysis depolymerization of PET involving transesterification. Particularly promising are CaO -based catalysts and sulfonated biochars, which together offer

bifunctional reactivity capable of facilitating both nucleophilic attack and ester activation. Their dual catalytic nature may prove advantageous in systems where mixed acid-base mechanisms dominate the reaction pathway.

Thus, agro-waste-derived catalysts represent a vital and underutilized resource for sustainable catalysis. Their demonstrated applicability in biodiesel transesterification and growing relevance in PET glycolysis highlight their broad catalytic flexibility. However, the largely untapped potential for PET methanolysis and carbon–carbon bond-forming Aldol reactions necessitates expanded investigation. By integrating these materials into circular processing strategies, researchers can advance waste-to-resource pathways that align with global sustainability targets, reduce dependency on critical raw materials, and promote decentralized chemical production platforms. Their proven performance in glycolysis and transesterification, coupled with their untapped potential in PET methanolysis, positions them as key enablers of green chemical technologies. By valorizing agricultural residues and diverting organic waste from disposal streams, these catalysts contribute meaningfully to the realization of a circular economy, environmentally responsible material life cycles, and the broader objectives of low- impact, resource-efficient chemical manufacturing.

1.2.4. Examples of Organic Transformations catalysed by Biomass-Derived Solid

Building upon the material insights outlined in **Section 1.2.3**, biomass- derived solid catalysts, particularly those obtained from fruit peels, crop residues, and other agro-waste hold increasing promise not only as sustainable alternatives to conventional catalysts, but as versatile catalytic platforms for a broad array of organic reactions. recent developments suggest that these materials are equally capable in mediating carbon–carbon bond-forming reactions, esterification, transesterification, and oxidation–reduction processes (J. Chen et al., 2008; Chimni & Mahajan, 2005; Khiangte et al., 2023; Ki et al., 2022; Patil et al., 2013).

The catalytic appeal of biomass-derived materials lies in their inherent structural tunability and diverse inorganic composition. When subjected to

calcination, hydrothermal treatment, or chemical modification, these wastes generate catalytically active solid phases with tunable Brønsted and Lewis acid–base functionalities. This makes them exceptionally versatile for mediating a wide range of organic transformations including esterification, transesterification, carbon–carbon bond formation, and oxidation–reduction reactions under relatively mild and environmentally benign conditions. Additionally, their porous structure, surface area, and compatibility with metal doping enable enhanced active site dispersion, improving both activity and reusability across multiple catalytic cycles.

Among the earliest and most studied applications of these catalysts are C–C bond-forming reactions. Chitosan-derived catalysts, for instance, exploit the nucleophilic nature of surface amine groups or embedded metal ions such as Cu(II) to efficiently mediate Henry and Knoevenagel condensations with excellent yields and selectivity (Goncalves et al., 2018; Kühbeck et al., 2012). Similarly, calcined agro-wastes like banana peel ash naturally rich in K_2CO_3 and CaO, have proven highly effective in solvent-free C–C coupling reactions, delivering high product yields and excellent reusability under green reaction conditions (Pathak et al., 2019; Patil et al., 2013). These findings provide mechanistic insights relevant to PET- derived monomer valorization, where such condensations may be applicable to the upcycling of BHET or DMT into functional materials.

The Suzuki-Miyaura cross-coupling, a cornerstone of pharmaceutical and fine chemical synthesis, has also benefitted from bio-based supports. Palladium nanoparticles immobilized on rice husk silica, banana pseudostem cellulose, and pine needle-derived biochar have achieved coupling efficiencies exceeding 95%, with minimal metal leaching and high thermal stability (Afewerki et al., 2020; Kempasiddaiah et al., 2020; Valentini et al., 2025) (Afewerki et al., 2020; Kempasiddaiah et al., 2020; Valentini et al., 2025). The high surface area and bio-functional anchoring of these materials promote uniform nanoparticle dispersion, while the renewable origin of the supports further enhances sustainability metrics.

Michael additions, both aza- and spiro-variants have similarly been catalyzed by agro-waste-derived bases and acids. Calcined bone meal, for instance, provides

CaO-based basicity for high-yield reactions under mild thermal conditions, whereas sulfonated lignin, with its robust $\text{--SO}_3\text{H}$ acidity, has enabled solvent-free or aqueous-phase additions of comparable efficiency (Khalil & Al-Matar, 2013; Riadi et al., 2012). Mechanochemical variants employing potassium-rich ash-based catalysts have also been developed, minimizing energy inputs and solvent waste while maintaining excellent product selectivity (Ki et al., 2022). These catalytic systems share mechanistic commonalities with transesterification and PET depolymerization reactions, in which activation of electrophilic carbon centers and nucleophilic enhancement are critical steps.

Aldol condensations, central to constructing extended carbon frameworks from aldehyde and ketone precursors, represent a particularly relevant transformation in the context of both biomass and PET valorization. Porous CaO catalysts derived from calcined eggshells have demonstrated high activity in facilitating the formation of enolates and stabilizing transition states, while sulfonated glucose-derived carbons have achieved comparable efficacy in catalyzing condensation reactions under solvent-free and low-temperature conditions (Clarina et al., 2014; ZALI et al., 2008). More advanced materials, such as nitrogen-doped carbon catalysts embedded with K_2O have shown exceptional selectivity in furfural condensations, offering robust thermal stability and reusability across multiple reaction cycles (Zhan et al., 2019). These systems are of particular interest for the upgrading of PET-derived BHET or DMT through condensation pathways to yield value-added polymeric intermediates.

To better understand and optimize the activity of biomass-derived catalysts in these reactions, the use of a comprehensive analytical toolkit is essential. Techniques such as XRD, SEM/TEM, BET surface area analysis, FTIR, and XPS provide critical insights into crystalline phase composition, morphology, porosity, and surface functionalization. While GC, HPLC, and NMR analyses of product distributions help correlate these features with catalytic performance. These methods, already established in biodiesel research, are directly applicable to emerging PET recycling strategies, where surface activation, carbonyl reactivity, and leaching stability are equally significant (Sheldon, 2016).

Biomass-derived heterogeneous catalysts have demonstrated extensive utility in a range of carbon–carbon bond-forming reactions, highlighting their adaptability across diverse chemical domains. Their success in Aldol condensations, Michael additions, and cross-couplings offers valuable mechanistic parallels to PET glycolysis and methanolysis, where ester bond cleavage and nucleophile activation are similarly essential. As the field progresses, the intersection of organic transformation chemistry and plastic upcycling offers fertile ground for the continued evolution of agro-waste-based catalytic platforms and thus cementing their relevance in both academic and industrial contexts.

1.2.5. Comparative Evaluation of Biomass-Derived Catalysts Against Conventional and Nanostructured Systems

As the landscape of catalytic technologies in chemical recycling continues to evolve, the comparison between biomass-derived catalysts, traditional metal-based homogeneous systems, and nanostructured heterogeneous catalysts becomes increasingly relevant. Each class of catalysts presents distinct characteristics in terms of activity, reusability, toxicity, economic feasibility, and environmental sustainability.

Homogeneous catalysts, such as zinc acetate or cobalt salts, have long served as performance benchmarks due to their high activity and reaction rates (Imran et al., 2013; H. Wang et al., 2009). However, their inherent non-recyclability, metal contamination of the product stream, and environmental toxicity pose significant challenges for large-scale deployment especially in food-grade or pharmaceutical-grade applications of recycled PET.

In contrast, nanostructured catalysts, including zero-valent metals, spinel ferrites, and oxide–carbon nanocomposites offer superior surface-area-to-volume ratios, tailorable surface chemistry, and high catalytic selectivity (Du et al., 2020; Yun et al., 2023). They are capable of achieving rapid depolymerization under mild conditions with excellent recyclability. Nevertheless, their preparation typically involves energy-intensive synthetic protocols, use of toxic solvents, or incorporation of rare earth metals, thereby raising concerns about cost, scalability, and

environmental impact. Moreover, their high performance may not always justify the complex post-reaction separation procedures or long-term stability under industrial stress conditions (Kumari et al., 2024).

Biomass-derived solid catalysts, on the other hand, emerge as a sustainable midpoint balancing catalytic efficiency with economic and ecological viability. These catalysts are sourced from renewable, low-cost agro-waste, including eggshells, banana peels, lignocellulosic residues, and marine biomass, and often require minimal processing for activation (e.g., calcination, sulfonation) (Boro et al., 2014; Dulymahakamtorn et al., 2025; Y. Kim et al., 2022; Yunita et al., 2019). Their low carbon footprint, non-toxic composition, and compatibility with aqueous or solvent-free systems make them especially attractive for green industrial applications. Importantly, many biomass-derived systems exhibit bifunctionality, offering both acid and base sites that facilitate complex reaction mechanisms including transesterification, ester hydrolysis, and carbon–carbon bond formation (Chandra Kishore et al., 2022; Tobío-Pérez et al., 2022).

Performance-wise, several studies have reported that bio-ash-based CaO or K₂O catalysts achieve PET glycolysis or methanolysis efficiencies comparable to or exceeding those of metal oxides and IL-modified nanoparticles (Khiangte et al., 2023; Y. Kim et al., 2022; Yunita et al., 2019). In cases such as the present work, the developed OPA@Fe₃O₄ catalyst and orange peel ash, yields over 80 to 90% were obtained at moderate temperatures within short reaction times, often with minimal catalyst degradation across reuse cycles (Lalmangaihzualla et al., 2023). In addition to their comparative strengths, both biomass-derived catalysts and nanocatalysts are actively addressing several previously identified research gaps in sustainable catalysis. For instance, recent advancements in surface engineering, magnetic support incorporation, and hybrid designs are beginning to resolve limitations in catalyst recovery, structural integrity, and operational stability (Pham et al., 2024; T. Wang et al., 2021).

Recent literature underscores that integrating life cycle assessment, techno-economic analysis, and catalyst recyclability evaluations is becoming

standard in biomass catalyst research. Galiwango et al., (2024) highlight the need to bridge LCA and TEA with catalyst integration in biomass hydrothermal systems (Galiwango et al., 2024), while Osman et al. (2024) stress that combined LCA-TEA approaches are crucial for assessing sustainability across full biorefinery pathways (Osman et al., 2024). These methodologies are essential in affirming the long-term sustainability credentials of these systems compared to traditional homogeneous or synthetic nanocatalysts.

1.3. Scope of the Present Investigation

The present study explores the design, development, and application of biomass-derived heterogeneous catalysts for sustainable chemical transformations, with a particular emphasis on the chemical recycling of polyethylene terephthalate (PET) and the catalysis of carbon–carbon bond-forming reactions, specifically Aldol condensation. The overarching aim is to harness the catalytic potential of agro-waste-derived materials (orange peel bamboo leaf) to address critical environmental challenges namely, plastic pollution and waste valorization, through green and scalable chemical processes.

This research primarily focuses on the synthesis and performance evaluation of novel solid catalysts derived from naturally occurring, calcium- and carbon-rich biomass wastes. Two core biomass-derived catalyst systems, Orange Peel Ash (OPA) and Bamboo Leaf Ash (BLA), are developed via thermal calcination and optimized for physicochemical activity. In addition, a nanostructured magnetically separable catalyst (OPA@Fe₃O₄) is engineered to further enhance catalytic efficiency and facilitate recovery in liquid-phase reactions. These catalysts are investigated for their application in two major areas: (1) the depolymerization of PET via glycolysis and methanolysis, and (2) the Aldol condensation, a fundamental carbon–carbon bond-forming reaction in organic synthesis, with broad utility in pharmaceuticals, agrochemicals, perfumery, materials sciences.

In the context of PET recycling, the study evaluates the ability of these biomass-based catalysts to catalyze the transesterification of PET with ethylene glycol and methanol to produce BHET and DMT, respectively. Reaction parameters

such as temperature, catalyst loading, time, and reactant ratio are systematically optimized to achieve high depolymerization efficiency and selectivity toward the desired monomers. The recyclability and thermal stability of the catalysts are also assessed over multiple reaction cycles to demonstrate their long-term applicability.

Parallel to this, the study investigates the use of OPA as active base catalyst in Aldol condensation reactions. As a fundamental C–C bond-forming reaction, Aldol condensation serves as a model transformation to evaluate the basic strength, surface accessibility, and reusability of the catalysts. Its inclusion demonstrates the broader applicability of biomass-derived catalysts beyond polymer recycling and underscores their potential in green organic synthesis.

To provide comprehensive insight into structure-activity relationships, the catalysts are thoroughly characterized using a suite of analytical techniques, including X-ray Diffraction (XRD) for crystallinity, Fourier Transform Infrared Spectroscopy (FTIR) for surface functional groups, Scanning and Transmission Electron Microscopy (SEM/TEM) for morphology, X-ray Photoelectron Spectroscopy (XPS) for surface elemental states, Brunauer-Emmett-Teller (BET) analysis for surface area, Thermogravimetric Analysis (TGA) for thermal stability, Energy Dispersive X-ray Spectroscopy (EDX) for elemental composition, and High- Performance Liquid Chromatography (HPLC) for product quantification.

This thesis presents a critical comparison between biomass-based catalysts and synthetic nanoparticle catalysts, emphasizing their respective advantages in activity, sustainability, reusability, and ease of preparation. While synthetic nanoparticles typically offer higher surface areas and faster reaction kinetics, biomass-derived catalysts stand out for their eco-friendly preparation, low-cost feedstocks, and ability to valorize waste materials. Beyond this comparison, the study advances sustainable catalysis by enhancing PET recycling and the Aldol reaction through biomass-derived solid catalysts. It demonstrates how waste biomass can be transformed into efficient, recoverable catalysts, contributing simultaneously to environmental remediation and the development of value-added materials, thus supporting the principles of circular chemistry and resource-efficient synthesis.

CHAPTER 2

METHODOLOGY

2.1. Chemicals and reagents

All chemicals and reagents obtained are of analytical or equivalent grade and are used without further purification.

Table 2.1: Lists the details of all the chemicals used for the present work.

Sl. No.	Chemicals	Formula	Brand	Cas No.
1.	Ferrous sulfate heptahydrate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Himedia	7782-63-0
2.	Ferric chloride	FeCl_3	Himedia	7705-08-0
3.	Ethylene glycol	$\text{C}_2\text{H}_6\text{O}_2$	Merck	107-21-1
4.	Methanol	CH_3OH	Merck	67- 56-1
5.	Ammonia	NH_3	Merck	1336-21-6
6.	Dichloromethane	CH_2Cl_2	Merck	75- 09-2
7.	Sodium sulfate	Na_2SO_4	Merck	7757-82-6.
8.	Ethyl acetate	$\text{C}_4\text{H}_8\text{O}_2$	Merck	141- 78-6
9.	n-Hexane	C_6H_{14}	Merck	110- 54-3
10.	Acetonitrile	CH_3CN	Merck	75-05-8
11.	Chloroform	CH_3Cl	Merck	Chloroform
12.	Dimethyl formamide	$\text{HCON}(\text{CH}_3)_2$	Sigma-Aldrich	68-12-2
13.	Dimethyl sulfoxide	$(\text{CH}_3)_2\text{SO}$	Merck	67-68-5
14.	4-Nitrobenzaldehyde	$\text{C}_7\text{H}_5\text{NO}_3$	Sigma Aldrich	555- 16-8
15.	3-Nitrobenzaldehyde	$\text{C}_7\text{H}_5\text{NO}_3$	Sigma Aldrich	99- 61-6
16.	2-Nitrobenzaldehyde	$\text{C}_7\text{H}_5\text{NO}_3$	Sigma Aldrich	552- 89-6
17.	4-Chlorobenzaldehyde	$\text{C}_7\text{H}_5\text{ClO}$	Sigma-Aldrich	104-88-1

18.	3-Chlorobenzaldehyde	C_7H_5ClO	Sigma Aldrich	587-04-2
19.	2-Chlorobenzaldehyde	C_7H_5ClO	Sigma-Aldrich	89-98-5
20.	4- Bromobenzaldehyde	C_7H_5BrO	Sigma Aldrich	1122 -91-4
21.	Benzaldehyde	C_7H_6O	Sigma-Aldrich	100-52-7
22	4- Methylbenzaldehyde	C_8H_8O	Sigma-Aldrich	104- 87-0
23.	4-Methoxybenzaldehyde	4- $(CH_3O)C_6H_4CHO$	Sigma-Aldrich	123-11-5
24.	Acetone	C_3H_6O	Merck	67- 64-1
25.	Acetophenone	$CH_3COC_6H_5$	Merck	98-86-2
26.	Cyclohexanone	$C_6H_{10}O$	Merck	108- 94-1
27.	Silica Gel (60-120 mesh)	SiO_2	Merck	7631 -86-9
28.	Silica Gel (For TLC)	SiO_2	Merck	7631 -86-9
29.	bis(2-hydroxyethyl terephthalate)	$C_{12}H_{14}O_6$	Sigma-Aldrich	959-26-2

2.2. Instruments

All samples were weighed using an electronic balance (ME204, Mettler Toledo, Switzerland). The collected biomass samples were dried in a hot air oven IGENE LABSERVE IG 225LHS, while calcination was carried out at muffle furnace (LMF-B22). Powder X-ray diffraction (XRD) analysis was performed with a Philips Xpert MPD instrument to determine crystalline structures. Wavelength dispersive X-ray fluorescence (XRF) analysis of the prepared catalyst was carried out using a PANalytical Axios mAX system. Scanning Electron Microscope (SEM) images and elemental compositions were obtained with a JSM-6360, Jeol, and ESEM EDAX XL-30. Transmission Electron Microscope (TEM) imaging was performed on a JEM-2100 at 200 kV. Fourier-transform infrared (FT-IR) spectra were recorded on a

Spectrum BX FT-IR instrument (wavenumber in cm^{-1}) using KBr disks. Nitrogen adsorption-desorption isotherms were measured with a Quanta chrome Nova-1000 surface area and porosity analyzer; samples were pre-treated at 150 °C for 10 hours. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer TGA 4000, monitoring weight loss from 30 °C to 995 °C at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analysis of post-consumed PET was performed using a PerkinElmer DSC 6000. Nuclear magnetic resonance (NMR) spectra (^1H and ^{13}C) were acquired on a Bruker 400 MHz Avance III spectrometer in DMSO- d_6 and acetone, with TMS as an internal standard. High-performance liquid chromatography (HPLC) analysis was conducted using a Waters 1525 binary pump with a Spherisorb ODS2 5 μm , 4.6 x 250 mm column and a Waters UV detector set at 254 nm.

2.3. Preparation of the catalysts

2.3.1. Collection and Preparation of biomass wastes

Orange (*Citrus sinensis*) peels were collected from the local vendors in Aizawl, Mizoram, India. While, bamboo (*Melocanna baccifera*) leaves were gathered from Pachhunga University College Campus, Aizawl, Mizoram, India. The collected samples were cleaned thoroughly with distilled water, and then dried inside hot air oven at 60 °C for 24 hours or until dry (for orange peel). The dried bamboo leaves were stored for further use.

2.3.2. Synthesis of catalysts

Three different processes are employed for the preparation and synthesis of biomass-derived solid catalysts in this project.

2.3.2.1. Preparation of Orange peel ash (OPA) Using *Combustion*

Orange peel ash (OPA) was prepared using simple combustion method. The dried orange peels were burned in open air and the dark grey colour ash was collected and then sieved using 100 British Standard Sieve (BSS). The finely divided orange peel ash was stored in a closed container at room temperature.

2.3.2.2. Preparation of Bamboo leaf ash (BLA) Using *Calcination*

The dried bamboo leaves were burnt in open air, the black-coloured ash originally formed as a result of incomplete combustion was calcined at 700 °C for 4 hours. The grey-coloured ash obtained after calcination was then sieved using 100 BSS and the collected ash was stored in a sample vial at room temperature.

2.3.2.3. Synthesis of magnetic iron oxide (Fe₃O₄) nanoparticles

The magnetic Fe₃O₄ NPs was synthesized by following the traditional co-precipitation technique with small changes to the reported methodology (Changmai et al., 2021).

2.3.2.3.1. Preparation of orange peel ash extracts

OPA collected after combustion (10 g) was added to 100 mL deionized water, the mixture was then stirred using an overhead stirrer for 1 h at 80 °C to extract the basic portions from the ash. The mixture was filtered and the orange peel extract was collected.

2.3.2.3.2. Synthesis of orange peel impregnated iron oxide nanoparticle OPA@Fe₃O₄

A mixture of FeSO₄·7H₂O (5 mmol) and FeCl₃ (10 mmol) were added to 100 mL of deionized water which was pre-heated at 90 °C with vigorous stirring. To this, 20 mL of the OPA extract was added dropwise until the solution changes from brownish color to dark brown. Then a small amount of 1M ammonia solution was added dropwise till the color of the solution changes from dark brown to fully dark. The prepared Fe₃O₄ NPs was allowed to settle; the solution was decanted and the solid part at the bottom was collected. The magnetite nanoparticle was mixed with 50 mL of orange peel extract and then stirred at room temperature for another 30 minutes. The water was evaporated using a rotary evaporator and the dried OPA coated nano catalyst (OPA@ Fe₃O₄) was collected and stored in vacuum at room temperature.

2.3.3. Characterization of PET waste

The thermal analysis of the post consumed PET was carried out using PerkinElmer DSC 6000 under an inert atmosphere with nitrogen flow of 20 mL min⁻¹. PET samples (2-4 mg) were then heated from 50 °C to 300 °C at a rate of 20 °C min⁻¹ using indium (In) as a standard for measuring enthalpy of fusion (ΔH_f). Degree of Crystallinity of PET was calculated from the enthalpy change obtained from DSC analysis by taking 140 J g⁻¹ as ΔH_f of pure crystalline PET using the following equation (Panowicz et al., 2021):

$$\text{Crystallinity \%} = \frac{\text{Enthalpy of fusion}}{140 \text{ J/g}} \times 100 \quad (2.1)$$

2.3.4. Catalyst characterization

The synthesized catalysts Orange Peel Ash (OPA), Bamboo Leaf Ash (BLA), and Orange Peel-based Fe₃O₄ Nanocomposites were thoroughly characterized using a suite of advanced analytical techniques to elucidate their morphological, structural, compositional, and surface properties.

2.3.4.1. Surface Morphology and Microstructure

The external morphology of the catalysts was investigated using Scanning Electron Microscopy (SEM) on a JEOL JSM-6360, which provided insights into surface texture, particle distribution, and agglomeration. High-Resolution Transmission Electron Microscopy (HR-TEM) was performed using a JEOL JEM 2100 (200 kV) to study the internal microstructure and particle size at the nanoscale. Elemental composition and mapping were carried out using Energy-Dispersive X-ray Spectroscopy (EDS) coupled with ESEM EDAX XL-30.

2.3.4.2. Crystallinity and Elemental Composition

Crystalline phases of the catalysts were determined using Powder X-ray Diffraction (XRD) on a Philips X'Pert MPD diffractometer, with phase identification conducted via the JCPDS database. To assess the oxide composition and elemental distribution, Wavelength Dispersive X-ray Fluorescence (XRF) analysis was performed using a PANalytical Axios mAX spectrometer.

2.3.4.4. Functional Group Analysis

Surface functionalities were examined by Fourier Transform Infrared Spectroscopy (FT-IR) using a PerkinElmer Spectrum BX spectrometer. Spectra were recorded over the range of 4000-400 cm^{-1} using the KBr pellet method, and characteristic absorption bands (λ_{max} in cm^{-1}) were used to identify functional groups present on the catalyst surface.

2.3.4.5. Porosity and Surface Area

The specific surface area, pore volume, and average pore diameter of the catalysts were analyzed using N_2 adsorption–desorption isotherms recorded on a QuantaChrome NOVA-1000 surface area and porosity analyzer. Prior to measurement, samples were degassed at 150 °C for 10 hours. Surface area was calculated by the Brunauer-Emmett-Teller (BET) method, while Barrett-Joyner- Halenda (BJH) analysis was employed to determine pore size distribution. These analyses provided critical insight into the textural properties and mesoporosity of the materials.

2.3.4.6. Surface Chemistry and Elemental States

Surface elemental composition and chemical bonding states were evaluated using X-ray Photoelectron Spectroscopy (XPS), performed on a PHI 5000 VersaProbe III (Physical Electronics) under ambient conditions (room temperature, ~40% relative humidity).

2.3.4.7. Thermal Stability

Thermal degradation behavior and stability of the catalysts were assessed via Thermogravimetric Analysis (TGA) using a PerkinElmer TGA 4000 system under a nitrogen atmosphere. Catalyst samples were heated from 30 °C to 995 °C at a uniform heating rate of 10 °C/min.

2.4. Recycling of Plastic waste

The present study explores greener route for the chemical recycling of polyethylene terephthalate (PET) plastic using glycolytic and methanolytic method to

yield respective monomer bis(hydroxy)ethyl terephthalate (BHET) and dimethyl terephthalate (DMT). Cast-off PET bottles were gathered from the streets of Aizawl, Mizoram, India. The bottles were washed repeatedly with distilled water, dried and then cut into pieces of ~1 mm squares.

2.4.1. Glycolysis of Polyethylene terephthalate

A two necked 100 mL round bottom flask fitted with thermometer and reflux condenser was loaded with 480 mg (2.5 mmol) of PET flakes, 2.25 mL of ethylene glycol and the prepared catalysts. The mixture was immersed in an oil bath and the reaction was carried out at 190 °C in atmospheric pressure. After completion of the reaction (as shown by the disappearance of PET flakes), the compound (BHET) obtained was purified by either of the following two methods (Fukushima, Coulembier, Lecuyer, Almegren, Alabdulrahman, Alsewailem, McNeil, et al., 2011).

Method 1: The catalyst was separated quickly *via* filtration and then washed with 100 mL of hot deionized water. After the mixture was cooled down, the white precipitate insoluble in water was filtered. The filtrate was then concentrated to about 40 mL and stored in a refrigerator at 2 °C for 12 hours. The white crystalline product formed in the filtrate was separated, dried and then weighed.

Method 2: After filtration, the residue was washed with 15 mL of methanol. The filtrate was collected and the solvent was evaporated under reduced pressure. The crude solid was dissolved in warm CH₂Cl₂ (150 mL) and then washed with water (2 times). The aqueous portion was extracted with 50 mL of CH₂Cl₂, the organic fractions were combined, dried with Na₂SO₄, and then evaporated to give BHET as a white powder.

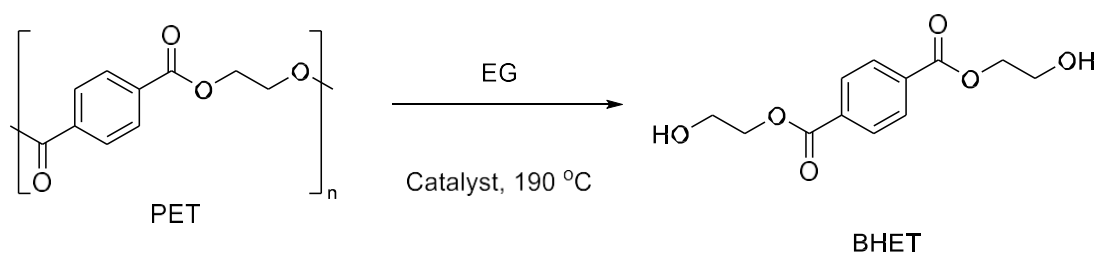
The conversion % of PET and yield % of the recrystallized product were calculated using the following equations (2.2, 2.3):

$$\text{Conversion of PET \%} = \frac{\text{weight of initial PET} - \text{undepolymerized PET}}{\text{weight of initial PET}} \times 100 \quad (2.2)$$

$$\text{Yield of BHET \%} = \frac{\text{No. of mol of BHET monomer}}{\text{Mol of PET}} \times 100 \quad (2.3)$$

The water insoluble product % was also calculated from the total amount of solid obtained by using the following equation (2.4):

$$\text{Yield of water insoluble part \%} = \frac{\text{water insoluble product}}{\text{BHET} + \text{water insoluble product}} \times 100 \quad (2.4)$$



Scheme 2.1: Glycolysis of PET.

2.4.1.1 Optimization of reaction condition

The glycolysis of polyethylene terephthalate (PET) utilizing ethylene glycol involves the cleavage of ester bonds, followed by the synthesis of bis-(2-hydroxyethyl terephthalate) (BHET) monomers through transesterification. Reaction parameters such as temperature, duration, solvent choice, catalyst concentration, and particle size are reported to significantly influence the efficiency and yield of the process for such reactions (Imran et al., 2013). The investigation further focused on optimizing the glycolytic recycling process of PET utilizing the prepared catalysts. This was achieved through systematic repetitive experiments, during which variations in reaction progress and product yield were meticulously recorded. The study examined the influence of key parameters, including catalyst loading, ethylene glycol (EG) content, reaction duration, and temperature. The optimal conditions identified, along with the effects of each parameter, are comprehensively discussed. Glycolysis of color PET bottles:

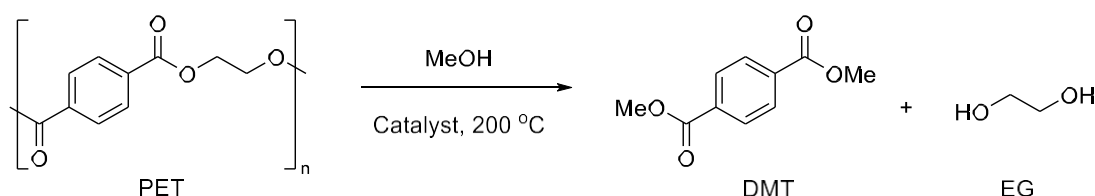
Color bottles are reported to contain acidic components which could hamper the catalytic activity of some catalysts towards PET depolymerization. (Fukushima, Coulembier, Lecuyer, Almegren, Alabdulrahman, Alsewailem, McNeil, et al., 2011). The efficacy of the synthesized catalyst and the impact of colored PET was tested on

glycolytic recycling of red, light-yellow and green hues following the observed optimum reaction conditions. Residual color if persists after recrystallization and filtration process could be eliminated by adding 30 mg of activated charcoal followed by filtration. The findings of this study are detailed further in **chapter 3 Section 3**.

2.4.2. Methanolysis of Polyethylene terephthalate

A Shilpent Teflon Lined Hydrothermal Autoclave (50 mL) was charged with 500 mg of PET flakes, 100 mg of catalyst and 5 mL of methanol. The autoclave was immersed in an oil bath preheated at 200 °C and the reaction was kept constant for 1 hour. After completion, it was allowed to cool down and 40 mL hot methanol was added to the reaction mixture and then filtered. The filtrate was cooled to room temperature and then placed in a refrigerator for 2 hours where dimethyl terephthalate (DMT) crystals out from the solution. The filtrate was distilled under reduced pressure to recover methanol followed by isolation of ethylene glycol. The obtained DMT was characterized using IR, NMR and HPLC analyses and the percentage of yield was calculated using the following equation (2.5):

$$\text{Yield of DMT monomer (\%)} = \frac{\text{Actual yield of DMT monomer}}{\text{Theoretical Yield of DMT}} \times 100 \% \quad (2.5)$$



Scheme 2.2: Methanolytic recycling of PET.

2.4.2.1. Optimization of reaction condition

To enhance the reaction condition for the selective formation of DMT monomer, the effect of different parameters such as catalyst loading, methanol content, reaction time and reaction temperature were investigated and the detailed results are depicted in **Chapter 3 Section 4**.

2.4.2.2. Methanolysis of Color PET Bottles

The influence of different coloration on the methanolysis process of PET was systematically evaluated using bottles in red, light-yellow and green hues under the optimized conditions. The color retention of DMT monomer, was assessed through UV-Vis spectroscopy, comparing the spectral data of monomers derived from colored PET bottles with those obtained from clear PET samples. The samples were dissolved in chloroform (5 mg/mL) and the absorbance of DMT obtained from colored as well as clear bottle was recorded on UV-Vis spectrophotometer at 350- 800 nm wavelength range. The findings are discussed briefly in **Chapter 3 Section 4**.

2.4.3. Reusability of catalysts

The reusability of catalysts is a critical consideration for chemists, particularly regarding their industrial and environmental applications. Following separation from the reaction mixture, catalysts were washed with methanol two to three times to eliminate organic impurities, then dried in a hot air oven at 80 °C for five hours. Any weight loss during filtration and recovery was compensated by adding fresh catalyst. The reusability of the recovered catalyst was evaluated under each optimized conditions for the corresponding catalysts. Additionally, the regenerated catalyst underwent SEM, TEM, and EDX analyses to assess changes in morphological structure and atomic composition. The findings are detailed in **Chapter 3 Section 4**.

2.4.4. Characterization of recycled products

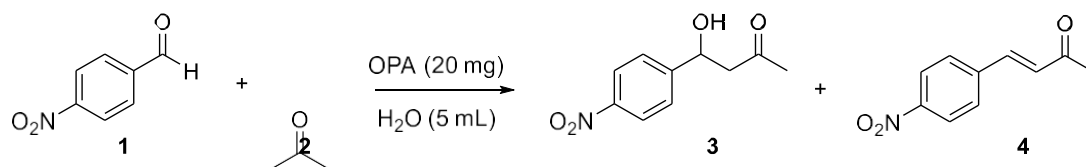
The analysis of the BHET and DMT products was conducted utilizing advanced spectroscopic and chromatographic techniques. To identify functionality and assess molecular structures, ^1H NMR and ^{13}C NMR spectroscopy was performed on a Bruker 400MHz Avance III spectrometer in DMSO- d_6 (chemical shift in δ with TMS as internal standard).

FTIR spectroscopy, conducted within the 4000-500 cm^{-1} range on a Spectrum BX FT-IR instrument by Perkin Elmer, further confirmed the presence of specific functional groups.

The purity of the monomers obtained through glycolysis and methanolysis processes was evaluated by comparing their chromatograms with those of commercial BHET and DMT standards. HPLC, employing a Waters 1525 binary pump and Waters UV detector 2489, was used for this purpose. An analytical column (Spherisorb ODS2, 5 μm , 4.6 x 250 mm) facilitated separation at 254 nm detection wavelength, with a mobile phase consisting of a methanol-water mixture (70/30 v/v) flowing at 1 mL/min. Additionally, the product monomer BHET and DMT, crude reaction product, and byproducts of the reaction were analyzed through their HPLC chromatograms to determine the composition of residual compounds.

2.5. Procedure for Aldol reaction:

In a 25 mL round-bottom flask, a mixture comprising 2 mmol of ketone, 20 mg of catalyst, and 5 mL of water was prepared. An aldehyde (1 mmol) was subsequently added, and the reaction was maintained under stirring at ambient temperature. The reaction progress was monitored via thin-layer chromatography (TLC). Upon completion, ethyl acetate was introduced to solubilize the reaction mixture, followed by filtration to remove the catalyst. The organic phase was separated, and the aqueous phase was washed with ethyl acetate (2 x 30 mL). The combined organic layers were then washed with water (2 x 50 mL), dried over sodium sulfate (Na_2SO_4), and concentrated under reduced pressure to yield the desired product.



Scheme 2.3: Aldol reaction using OPA.

2.5.1. Characterization of aldol product:

The synthesized aldol condensation products were characterized using Nuclear Magnetic Resonance (NMR) spectroscopy to confirm structural identity and verify the presence of key functional groups.

The products obtained from reactions using acetone as the substrate were directly analyzed without further purification. In contrast, crude reaction mixtures derived from cyclohexanone and acetophenone were purified by column chromatography using silica gel (60-120 mesh) as the stationary phase. A solvent system consisting of hexane and ethyl acetate in a 1:5 v/v ratio was used as the mobile phase. Elution was monitored using thin-layer chromatography (TLC), and the developed plates were visualized by exposure to iodine vapors as a staining agent. Relevant fractions were pooled and concentrated under reduced pressure prior to spectroscopic analysis.

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer using DMSO- d_6 as the solvent. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard.



Figure 2.1: Collected samples a) color variant PET bottles, b) shredded PET flakes, c) dried orange peel, d) dried bamboo leaves.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. CHARACTERIZATION OF THE CATALYSTS

3.1.1. Characterization of Orange peel ash (OPA)

This section details the physicochemical, morphological, and thermal characterization of the synthesized orange peel ash (OPA) catalyst, using a suite of analytical techniques including XRF, XPS, XRD, FTIR, SEM-TEM, BET, EDX, and TGA. The findings provide insight into the structural features, elemental composition, surface properties, and catalytic potential of OPA as a sustainable heterogeneous catalyst for depolymerization and C–C bond-forming reactions.

3.1.1.1. Morphological Analysis (SEM and TEM)

Scanning Electron Microscopy (SEM) images (**Figure 3.1a and 3.1b**) revealed a cloud-like, agglomerated morphology with a rough and porous surface texture. The porous framework suggests a high external surface area, which enhances adsorption and accessibility to active sites. Transmission Electron Microscopy (TEM) (**Figures 3.1c and 3.1d**) further revealed a squashy, deformable matrix with clearly defined mesoporous and microporous domains. The combination of hierarchical porosity and surface irregularity in OPA is beneficial for facilitating mass transfer and increasing contact between reactants and catalytic sites, ultimately improving its catalytic performance in liquid-phase reactions.

3.1.1.2. Chemical Composition (XRF Analysis)

The elemental composition of OPA was assessed by X-ray Fluorescence (XRF) spectroscopy (**Table 3.1**). The catalyst was found to be rich in calcium oxide (CaO, 32.87%) and potassium oxide (K₂O, 30.87%), both of which contribute significantly to its basic character. Other major components include SO₃ (15.79%) and MgO (7.04%), along with minor levels of Na₂O, Al₂O₃, SiO₂, P₂O₅, Fe₂O₃, and transition metal oxides. The high content of alkaline and alkaline-earth metal oxides is characteristic of strong base catalysts and supports the material's suitability for base-driven transformations such as aldol reaction and PET depolymerization.

These results are consistent with previous reports on plant-waste-derived ashes and confirm the mineral-rich nature of the catalyst (Changmai et al., 2020).

Table 3.1: Determination of OPA composition using XRF analysis

Sl. No.	Compound	Concentration (%)
1	Na ₂ O	0.108
2	MgO	7.037
3	Al ₂ O ₃	0.123
4	SiO ₂	1.115
5	P ₂ O ₅	5.188
6	SO ₃	15.792
7	K ₂ O	30.866
8	CaO	32.868
9	Cr ₂ O ₃	0.129
10	MnO	0.268
11	Fe ₂ O ₃	2.152
12	CuO	0.201
13	ZnO	0.223
14	Rb ₂ O	0.579
15	SrO	1.855
16	BaO	0.465

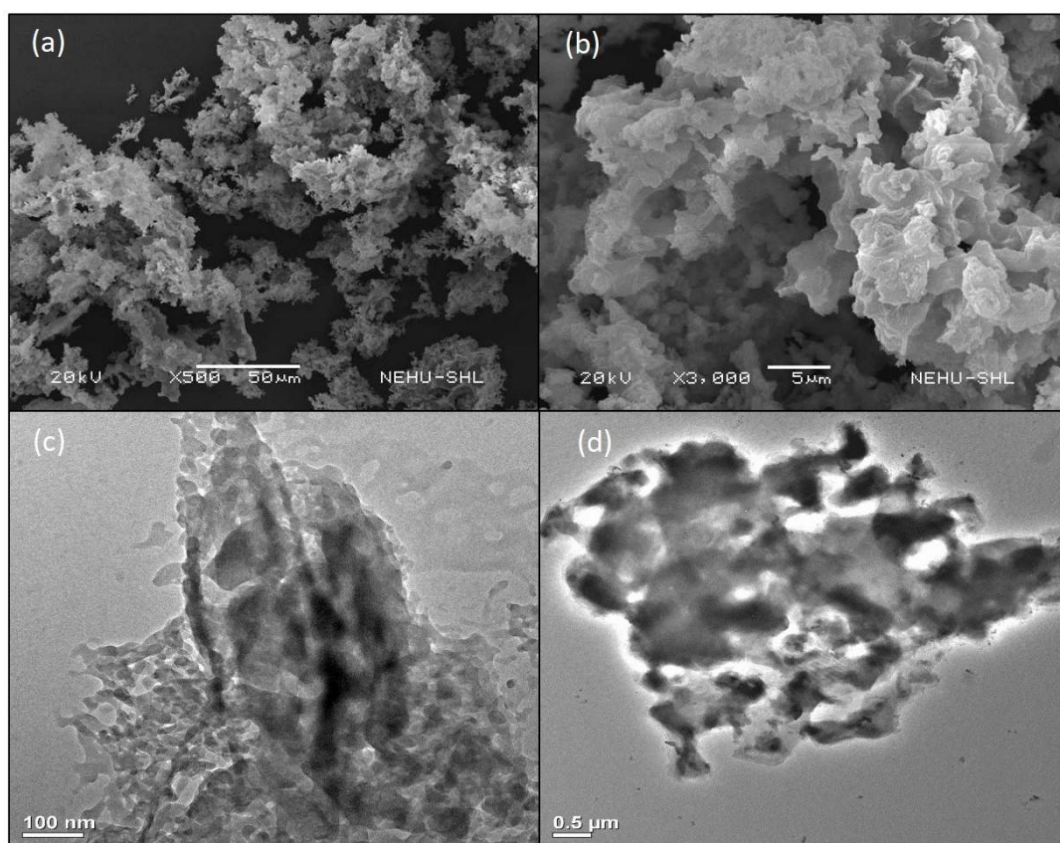


Figure 3.1: SEM (a) and (b) images of OPA and TEM (c) and (d) images of OPA

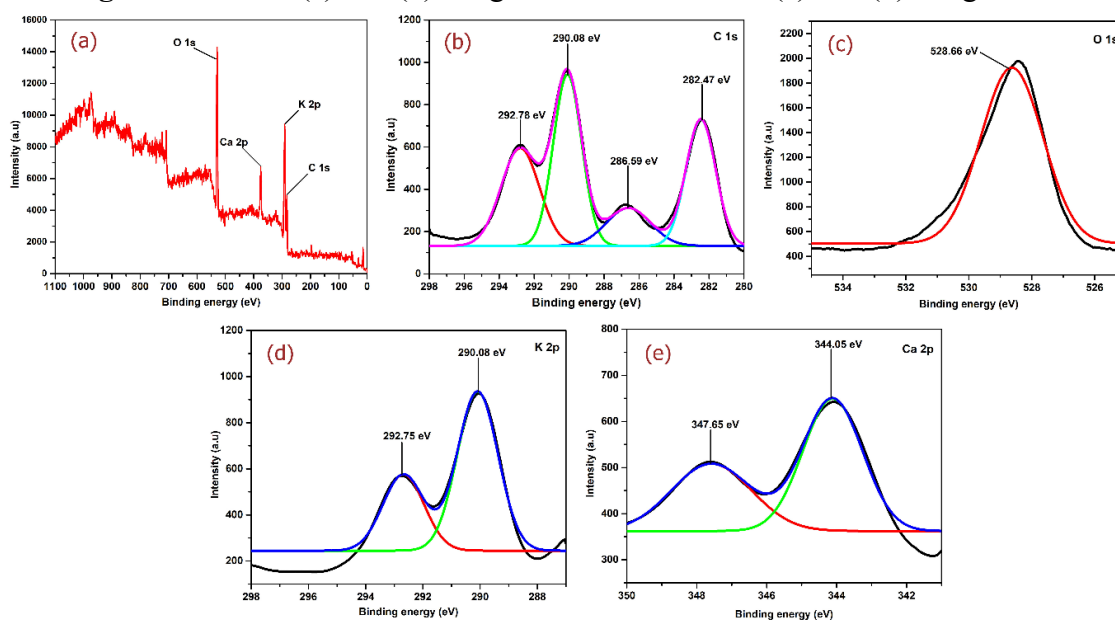


Figure 3.2: XPS Analysis of OPA Catalyst

3.1.1.3. Surface Composition and Functional Groups (XPS Analysis)

X-ray Photoelectron Spectroscopy (XPS) was used to determine the surface elemental composition and oxidation states of key components in OPA (**Figure 3.2**). The survey spectrum confirmed the presence of carbon (C), oxygen (O), calcium (Ca), and potassium (K) as major surface constituents.

The C 1s spectrum exhibited two peaks at 286.59, and 282.47 eV, where the peak at 286.59 were attributed to C–C and C=O bonds, commonly associated with carbonate groups while 282.47 eV could be due to the adventitious organic matter left behind by incomplete combustion (the two peaks at 292.78, 290.08 overlaps with K 2p). The O 1s deconvoluted peak appeared at 528.66 eV, representing lattice oxygen in metal oxides (**Figure 3.2c**). The K 2p peaks at 292.75 and 290.08 eV corresponded to K₂O and K₂CO₃ (Pathak et al., 2018), while the Ca 2p peaks at 347.65 and 344.05 eV confirmed the presence of CaCO₃ and CaO, respectively (Changmai et al., 2020).

3.1.1.4. Crystalline Structure (XRD Analysis)

The crystalline phases of OPA were identified via X-ray Diffraction (XRD) (**Figure 3.3a**). The pattern evidences a multiphase inorganic ash comprising crystalline oxides and carbonates. Distinct reflections attributable to CaCO₃ and CaO are observed at $2\theta = 27.233^\circ$, 32.322° , 39.508° , and 48.177° (JCPDS 76-0606, 86-2341, 82-1691, 28-0775). Peaks consistent with K₂O and K₂CO₃ appear at $2\theta = 29.311^\circ$, 30.222° , 40.708° , and 41.605° (JCPDS 77-2176, 87-0730). Additional features at $2\theta = 26.506^\circ$ and 34.222° match SiO₂ (JCPDS 89-8936, 89-3609), while reflections at $2\theta = 44.422^\circ$ and 53.560° are consistent with MgO (JCPDS 30-0794, 76-1363). A minor peak at $2\theta = 30.243^\circ$ suggests P₂O₅ (JCPDS 85-1120).

The XRD pattern confirmed that OPA possesses a crystalline and multi-phase structure, dominated by thermally stable alkaline metal oxides and carbonates. These phases contribute to the catalyst's thermal resistance and chemical robustness under reaction conditions.

3.1.1.5. Functional Group Identification (FTIR Analysis)

Fourier-transform infrared (FTIR) spectroscopy was employed to detect functional groups present in the OPA catalyst (**Figure 3.3b**). A broad band at 3412 cm^{-1} and a smaller one at 2958 cm^{-1} were indicative of O–H stretching vibrations due to surface-adsorbed moisture (Maneerung et al., 2016). Peaks observed at 1440, 1048, and 874 cm^{-1} were attributed to asymmetric and symmetric stretching of carbonate groups (Changmai et al., 2021). Lower frequency peaks at 811 cm^{-1} and 688 cm^{-1} were assigned to K–O and Ca–O bonds, respectively, corroborating the XPS findings of potassium and calcium oxides on the surface (Changmai et al., 2019).

3.1.1.6. Porosity and Surface Area (BET and BJH Analysis)

The Brunauer Emmett Teller (BET) surface area analysis, along with Barrett Joyner Halenda (BJH) pore distribution (**Figures 3.3c and 3.3d**), revealed that OPA exhibits a type-IV isotherm, with a distinct H1 hysteresis loop, characteristic of mesoporous materials. The BET analysis provided a surface area of $4.97\text{ m}^2/\text{g}$, an average pore diameter of 25.22 Å , and a pore volume of $0.022\text{ cm}^3/\text{g}$.

Although the surface area is relatively modest compared to other biomass-derived catalysts, the well-developed mesoporosity ensures accessibility to active sites. This is particularly beneficial for liquid-phase reactions, where mass transfer is critical. The hierarchical pore structure, combined with strong basicity, contributes significantly to catalytic efficiency.

3.1.1.7. Elemental Distribution (EDX Analysis)

Energy-dispersive X-ray spectroscopy (EDX) was used to validate the elemental composition of the catalyst (**Figure 3.4**). The major elements detected were oxygen (51.73%), potassium (21.32%), calcium (13.73%), and carbon (6.86%), aligning well with the findings from XRF and XPS (**Table 3.2**). Minor elements such as Na, Mg, P, S, Cl, Fe and trace metals were also detected, indicating the multi-metallic nature of the ash. The presence of alkali and alkaline-earth metals further reinforces its basic character and catalytic potential.

Table 3.2: EDX data for elemental composition of OPA

Sl No.	Elements	Weight %	Atomic %
1	C	6.86	11.66
2	O	51.73	65.97
3	Na	0.67	0.60
4	Mg	1.30	1.09
5	Si	0.10	0.07
6	P	1.60	1.06
7	S	0.30	0.19
8	Cl	1.82	1.05
9	K	21.32	11.13
10	Ca	13.73	6.99
11	Fe	0.57	0.21

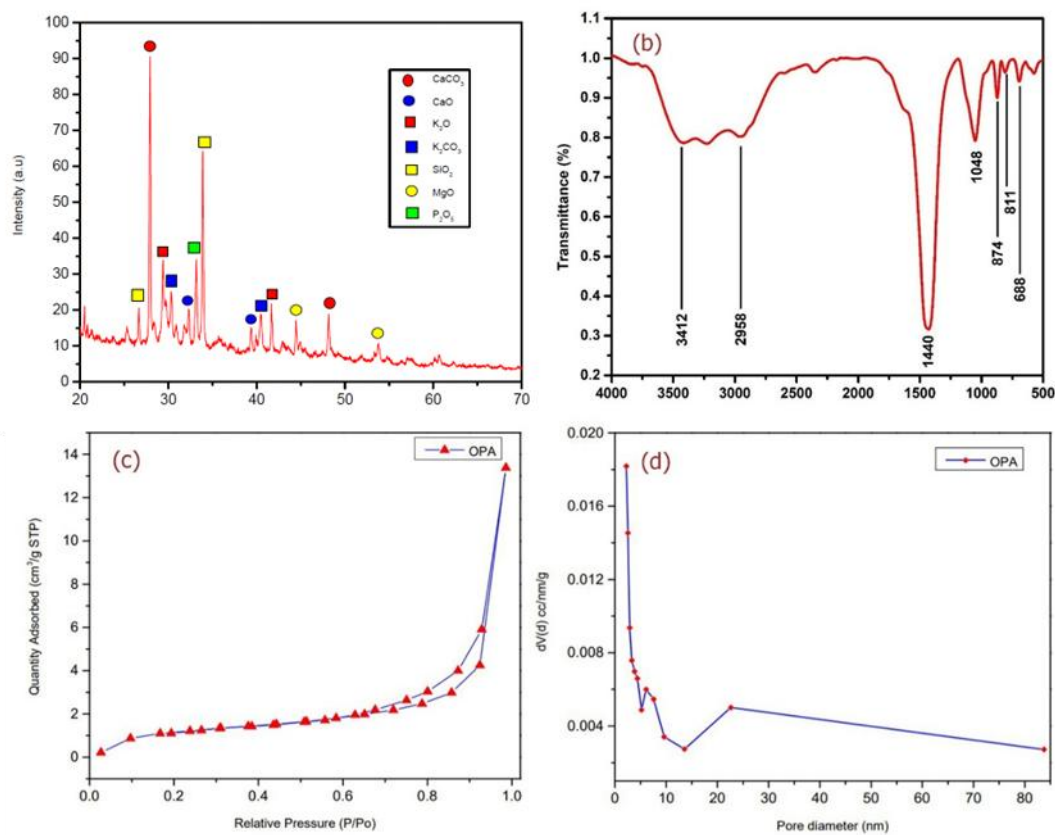


Figure 3.3: (a) XRD Data of OPA (b) FT-IR Spectra of OPA (c) Nitrogen Adsorption-Desorption Isotherm, and (d)

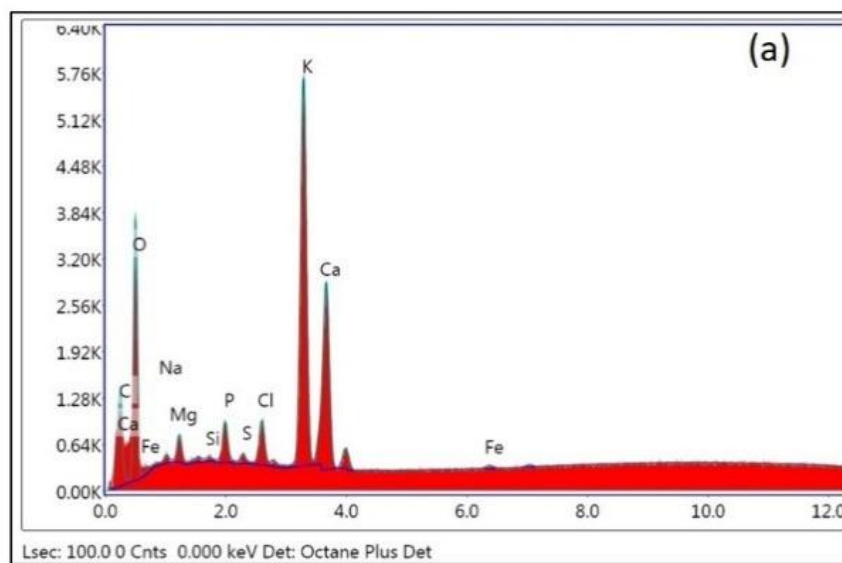


Figure 3.4: EDX spectrum of OPA

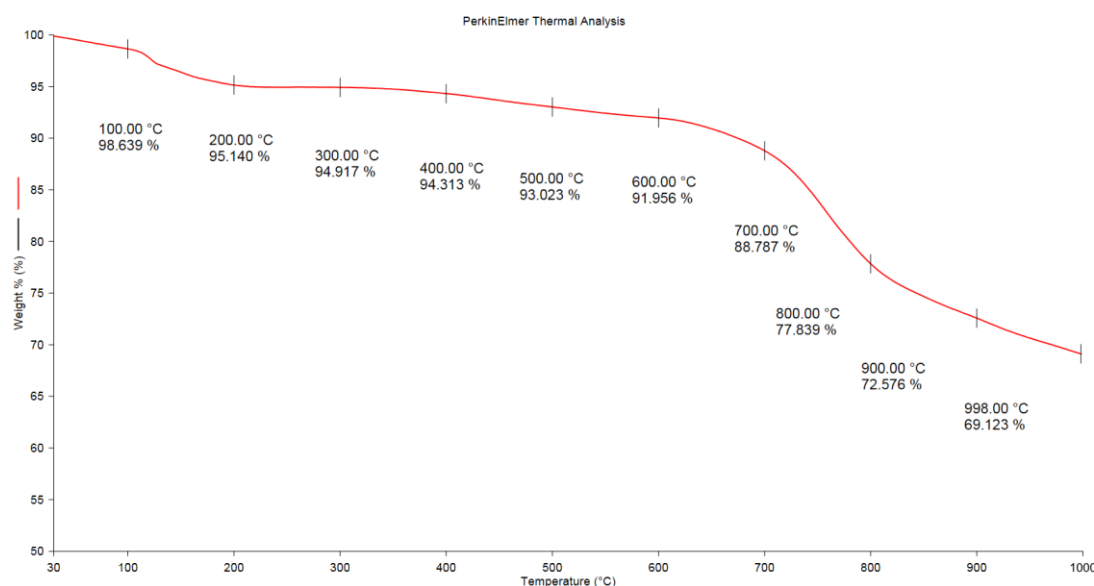


Figure 3.5: TGA thermogram of OPA

3.1.1.8. Thermal Stability (TGA Analysis)

The thermal stability of OPA was investigated using thermogravimetric analysis (TGA) (**Figure 3.5**). The TGA profile showed a ~5% weight loss below 190°C, attributed to the evaporation of surface-adsorbed water. The sample remained thermally stable up to approximately 600°C, after which a second major weight loss (~21%) was observed between 650-900°C, corresponding to the oxidation and decomposition of carbonaceous residues (Chouhan & Sarma, 2013).

These results confirm that OPA possesses moderate to high thermal stability, making it suitable for thermal catalytic processes such as methanolysis and glycolysis of PET under elevated temperature conditions.

3.1.2 Analysis of Bamboo Leaf Ash (BLA)

This section presents and interprets the physicochemical, morphological, and structural characteristics of the synthesized bamboo leaf ash (BLA) catalyst. A range of analytical techniques, including XRF, XPS, XRD, FTIR, BET, SEM-TEM, EDX, and TGA, were employed to explore the catalytic material's composition, morphology, surface functionalities, porosity, and thermal stability.

3.1.2.1 Chemical Composition (XRF Analysis)

The chemical constituents of the BLA catalyst were determined using X-ray fluorescence (XRF) spectroscopy (**Table 3.3**). The catalyst was found to be silica- rich, with SiO₂ content at 76.02%, indicating that silica forms the primary matrix of the material. Additional components include SO₃ (6.89%), CaO (4.78%), K₂O (2.88%), and Fe₂O₃ (2.34%), followed by trace amounts of MnO, MgO, P₂O₅, Al₂O₃, Na₂O, Cr₂O₃, and TiO₂. The high silica content enhances the thermal durability, while the basic metal oxides (CaO, K₂O, MgO) introduce active sites for base- catalyzed reactions. These findings are in line with previous studies on ash-based catalysts (Changmai et al., 2020).

Table 3.3: XRF analysis of BLA catalyst.

Sl. No	Chemical Formula	Concentration (%)
1	SiO ₂	76.02
2	SO ₃	6.892
3	CaO	4.783
4	K ₂ O	2.876
5	Fe ₂ O ₃	2.341
6	MnO	1.888
7	MgO	1.277
8	P ₂ O ₅	0.64
9	Al ₂ O ₃	0.529
10	Na ₂ O	0.134
11	Cr ₂ O ₃	0.124
12	TiO ₂	0.117
13	CuO	0.114
14	ZnO	0.092
15	SrO	0.053

3.1.2.2 Surface Composition and Chemical States (XPS Analysis)

To probe the surface chemical states, X-ray photoelectron spectroscopy (XPS) was conducted (**Figure 3.6**). The wide-scan spectrum confirmed the presence of Si, O, C, Ca, and K. Deconvolution of the Si 2p peak revealed a binding energy of 100.68 eV, characteristic of silicon dioxide. The C 1s spectrum displayed two peaks, with notable peak at 285.38 eV associated with C–C and C=O bonds in carbonate environments. The O 1s peak at 529.94 eV indicated the presence of metal oxides. The K 2p spectrum showed peaks at 293.84 eV and 291.12 eV, suggesting both K₂O and K₂CO₃ forms, while Ca 2p peaks at 348.63 eV and 344.56 eV corresponded to CaCO₃ and CaO, respectively. These results confirm the availability of catalytically active basic sites on the BLA surface, which are critical for transesterification, aldol condensation, and PET depolymerization.

3.1.2.3 Crystalline Phases (XRD Analysis)

The XRD diffraction pattern of BLA (**Figure 3.7b**) revealed a complex crystalline structure. The most prominent peaks at $2\theta = 20.82^\circ$, 26.58° , and 50.09° were assigned to SiO₂ (JCPDS Nos. 89-1961, 89-8936, 89-8945). Peaks at 29.42° , 42.36° , and 45.69° confirmed the presence of CaO and CaCO₃, while K₂O and K₂CO₃ were identified from peaks at 39.42° and 40.22° . Additional diffraction peaks indicated trace crystalline phases of Fe₂O₃, Na₂CO₃, Al₂O₃, and MnO₂. The coexistence of crystalline silicates and carbonates in BLA implies a robust catalytic matrix, combining both thermal stability and reactive basic centers.

3.1.2.4 Functional Groups (FTIR Analysis)

The FTIR spectrum of BLA (**Figure 3.7a**) confirmed the presence of several surface functional groups. A broad band centered at 3442 cm^{-1} was attributed to O–H stretching of surface-adsorbed water (Maneerung et al., 2016). Peaks at 1641 cm^{-1} and 1446 cm^{-1} signified C–O stretching vibrations in carbonate structures (Rajkumari et al., 2019). The Si–O–Si network was indicated by peaks at 1082 cm^{-1} (stretching) and 796 cm^{-1} (bending), reinforcing the silica-rich composition (Fatimah et al., 2019; Tran et al., 2013). The presence of carbonate and silicate functionalities is consistent with the material's alkaline reactivity and mesoporous framework.

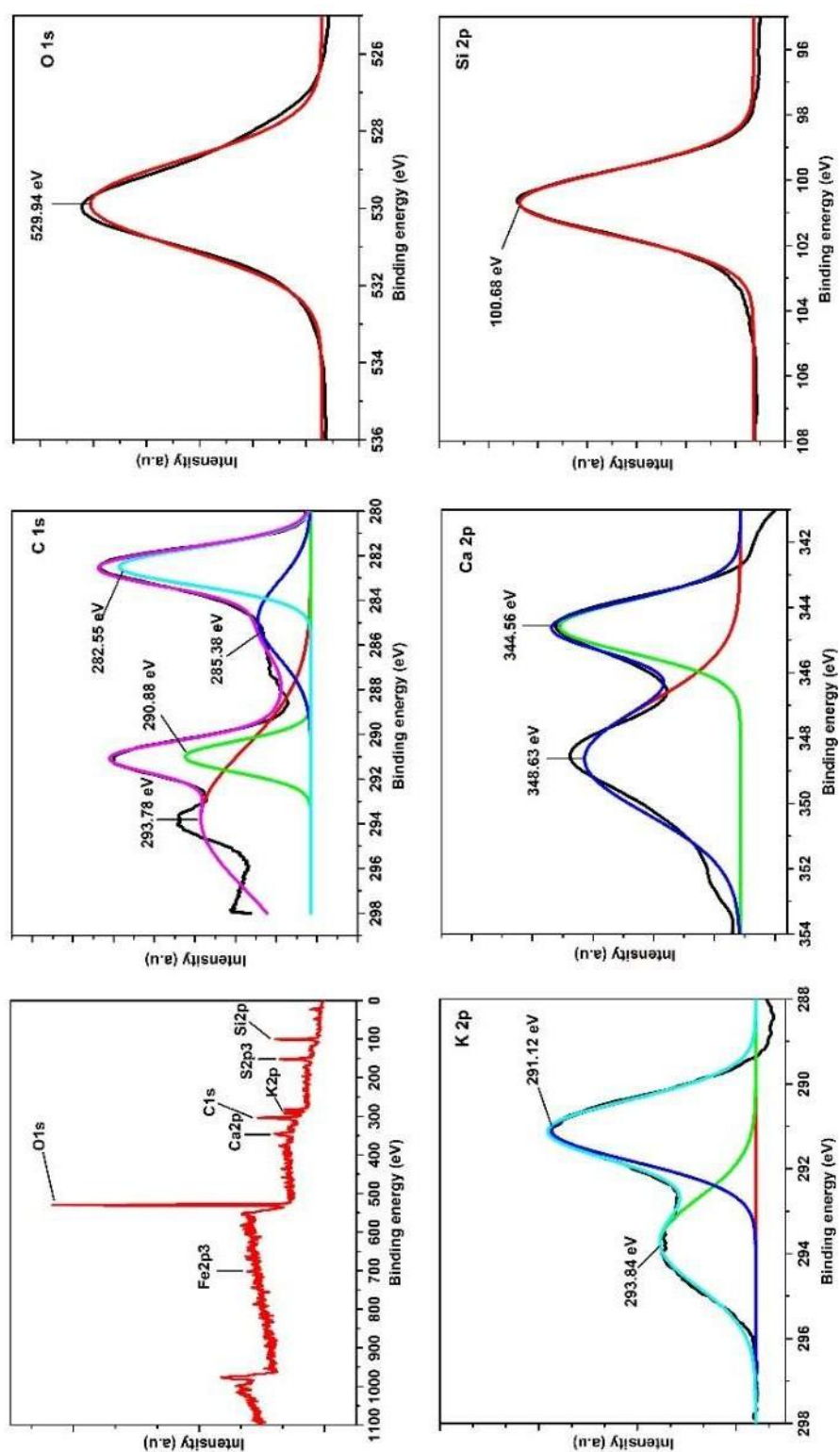


Figure 3.6: XPS analysis of BLA catalyst.

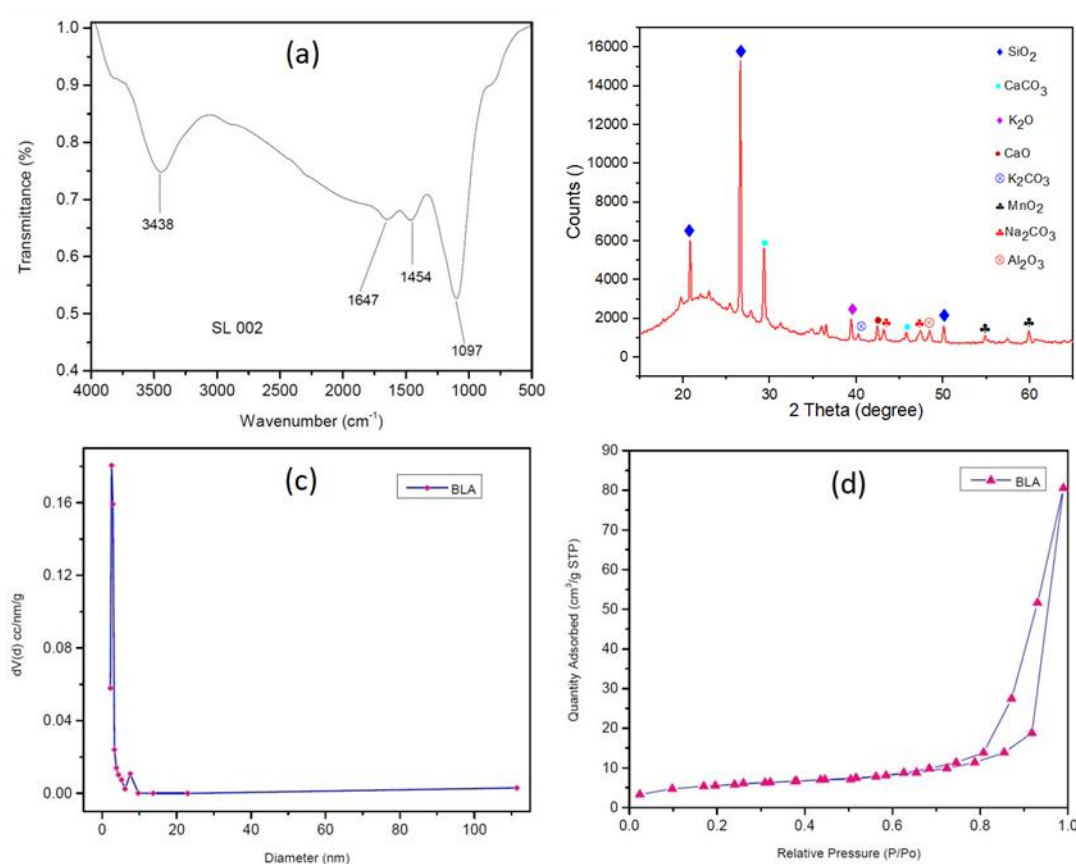


Figure 3.7: Figure 1: (a) IR data of BLA, (b) XRD data of BLA c) BJH pore size distribution of BLA, and d) N2 adsorption-desorption isotherm of BLA.

3.1.2.5 Surface Area and Porosity (BET and BJH Analysis)

The BET nitrogen adsorption-desorption isotherm (**Figure 3.7d**) exhibited a type IV profile with an H1 hysteresis loop, typical of mesoporous materials. The BJH pore size distribution (**Figure 3.7c**) showed a relatively uniform distribution with an average pore diameter of 13.68 nm, total pore volume of 0.127 cm³/g, and specific surface area of 21.85 m²/g. These values indicate that BLA possesses moderate surface area and accessible porosity, suitable for adsorption-driven catalytic processes. The hierarchical structure facilitates the diffusion of bulky molecules, enhancing reactivity in liquid-phase organic reactions.

3.1.2.6 Morphological Analysis (SEM and TEM)

SEM micrographs (**Figures 3.8a and 3.8b**) showed that BLA particles possess a rough, porous exterior and appear as agglomerated clusters composed of irregular micro- and mesoporous domains. TEM imaging (**Figures 3.8c and 3.8d**) confirmed an aggregated, globular morphology, with particle sizes ranging from 10 to 50 nm. The microstructure supports a high surface-to-volume ratio, facilitating enhanced contact between catalytic sites and reactants. The heterogeneous particle shape and rough texture are advantageous for anchoring active species and adsorbing reactants.

3.1.2.7 Elemental Distribution (EDX Analysis)

To validate the elemental profile, EDX spectroscopy was performed (Figure 3.9). The analysis revealed oxygen (48.01%), silicon (32.27%), calcium (8.98%), and potassium (4.61%) as the principal constituents. Trace elements such as Mg, Mn, Al, P, S, Cl, and Fe were also detected (**Table 3.5**). These results are consistent with XRF and XPS findings and confirm the multicomponent composition of BLA, providing both structural (SiO₂) and catalytic (metal oxides) features.

Table 3.4: EDX data of BLA

Sl No.	Elements	Weight %	Atomic %
1	O	48.01	64.01
2	Mg	1.59	1.42
3	Al	1.12	0.87
4	Si	32.27	24.53
5	P	0.83	0.56
6	S	0.49	0.32
7	Cl	0.32	0.20
8	K	4.61	2.48
9	Ca	8.89	4.74
10	Mn	1.25	0.51
11	Fe	0.52	0.35

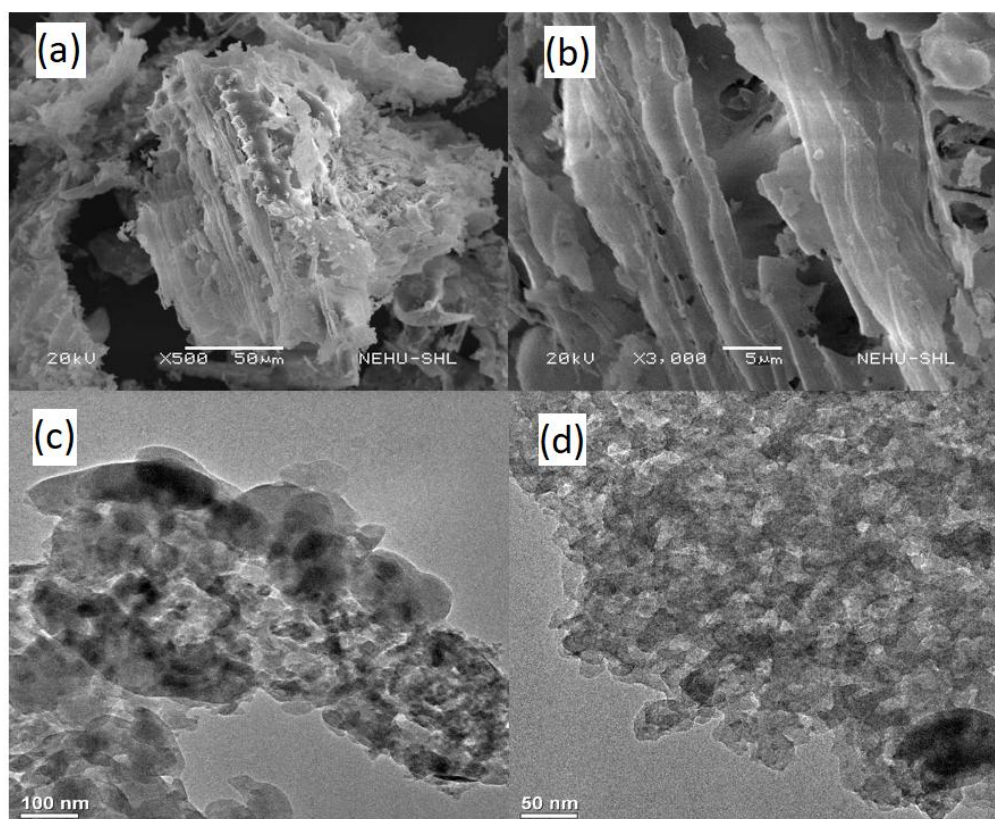


Figure 3.8: SEM [a) and b)] and TEM [c) and d)] micrographs of BLA

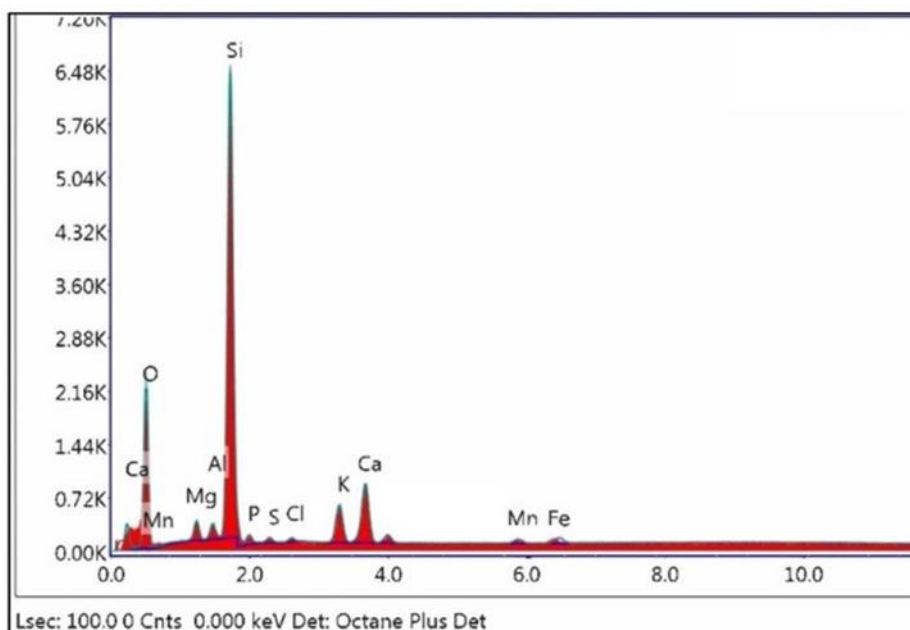


Figure 3.9: EDX spectra of BLA

3.1.2.8 Thermal Stability (TGA Analysis)

Thermogravimetric analysis (TGA) (**Figure 3.10**) was used to assess the catalyst's stability across a wide temperature range (30-1000°C). A minor weight loss of ~6% occurred below 200°C due to moisture desorption. A secondary weight loss of ~7% above 600 °C was attributed to the oxidative degradation of residual carbon. The total weight loss of 13% indicates that BLA is thermally stable up to 1000 °C, making it suitable for high-temperature catalytic processes. In contrast, the OPA catalyst showed a greater total weight loss (~21%), likely due to lower SiO₂ content and the thermal degradation of more volatile carbonaceous species.

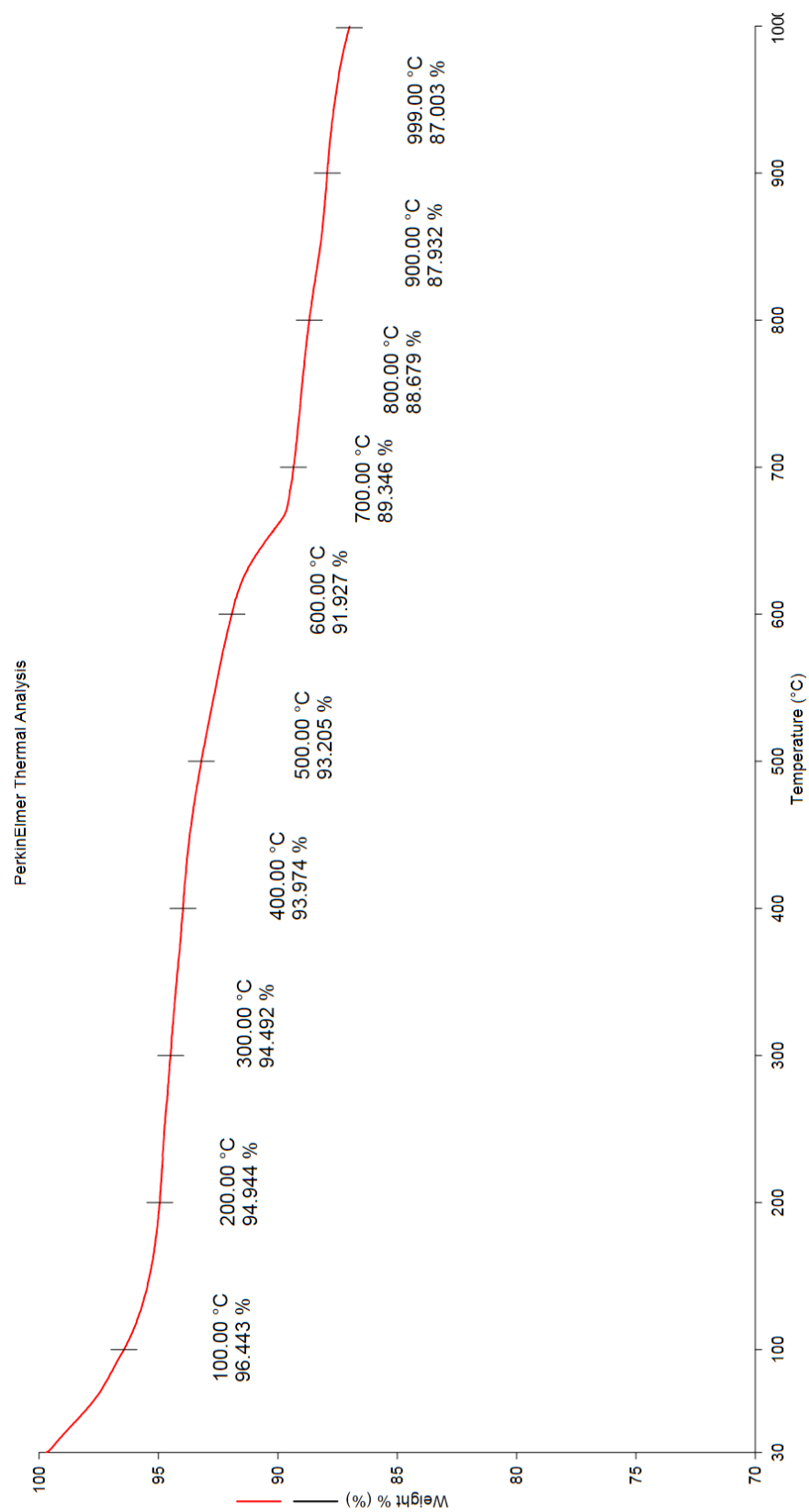


Figure 3.10: TGA thermogram of BLA

3.1.3 Analysis of Orange peel extract impregnated magnetic iron nanoparticles

OPA@Fe₃O₄.

The orange peel extract-impregnated Fe₃O₄ nanoparticles (OPA@Fe₃O₄) were characterized using a range of physicochemical and structural techniques to evaluate their catalytic suitability for PET depolymerization. The following sections detail the elemental composition, crystallinity, surface functionalities, morphology, thermal stability, and porosity of the synthesized nanocatalyst.

3.1.3.1 Chemical Composition (XRF Analysis)

The chemical oxide content of the synthesized OPA@Fe₃O₄ was analyzed by X-ray fluorescence (XRF) spectroscopy (**Table 3.5**). The results confirmed that Fe₃O₄ was the predominant oxide, comprising 55.79% of the total composition, followed by significant quantities of K₂O (26.17%) and SO₃ (8.86%). Minor constituents such as Na₂O, P₂O₅, MgO, SiO₂, CaO, and trace amounts of other transition metal oxides were also present. The presence of Fe₃O₄, a magnetic iron oxide with inherent basicity, is critical in enhancing the catalytic base strength of the material. Additionally, the synergy between basic metal oxides (K₂O and CaO) and transition metals in the OPA@Fe₃O₄ provides an effective active site environment for promoting PET depolymerization. Coating basic orange peel ash (OPA) with Fe₃O₄ nanoparticles further amplifies this effect, combining magnetic recoverability with high catalytic performance.

Table 3.5: XRF data of OPA@Fe₃O₄.

Sl. No	Metal Oxides	Concentration %
1	Na ₂ O	0.129
2	MgO	0.077
3	Al ₂ O ₃	0.026
4	SiO ₂	0.129
5	P ₂ O ₅	0.046
6	SO ₃	8.857
7	K ₂ O	26.17
8	CaO	0.031
9	MnO	0.296
10	Fe ₃ O ₄	55.786
11	Co ₃ O ₄	0.097
12	NiO	0.048
13	CuO	0.034
14	ZnO	0.021
15	Rb ₂ O	0.026
16	Y ₂ O ₃	0.082
17	Nb ₂ O ₅	0.013
18	Na ₂ O	0.129
19	MgO	0.077

3.1.3.2 Surface Chemical States (XPS Analysis)

X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface chemistry of the OPA@Fe₃O₄ (**Figure 3.11**). The survey scan identified the presence of K, C, and O as the major surface elements. Deconvolution of the K 2p spectrum revealed two peaks at 290.61 eV and 293.08 eV, confirming the existence of K₂O and K₂CO₃ on the surface. The C 1s spectrum showed two distinct peaks, with the most relevant ones at 282.76 eV and 286.75 eV attributed to C–C and C=O functionalities typical of metal carbonates. A higher-energy peak at 293.02 eV and 293.08 eV are the overlapped K 2p bands. The O 1s region displayed two major peaks at 527.03 eV and 528.77 eV, indicating the co-presence of metal oxides and carbonate species. These XPS results substantiate the findings from XRF, confirming the high basicity and heterogeneity of the catalyst surface.

3.1.3.4 Crystallinity (XRD Analysis)

The X-ray diffraction (XRD) pattern of the nanocatalyst (**Figure 3.11e**) confirmed its crystalline nature. Sharp diffraction peaks at $2\theta = 40.00^\circ$, 57.18° , 28.39° , 38.83° , 35.50° , and 62.78° were matched with K₂O, CaO, and Fe₃O₄ phases (JCPDS Nos. 77-2151, 65-2992, 02-1088, 89-0691). Additional peaks at 12.97° , 25.89° , 29.65° , 32.00° , 50.27° , 66.45° corresponded to SiO₂, P₂O₅, CaCO₃ and K₂CO₃, confirming the incorporation of multiple active phases into the catalyst. The crystalline profile supports the material's thermal and mechanical stability, while the dispersion of carbonate and oxide crystals reflects its multi-functionality as both a support and active site reservoir.

3.1.3.5 Functional Group Analysis (FTIR)

Fourier-transform infrared (FTIR) spectroscopy of OPA@Fe₃O₄ revealed several characteristic vibrational modes (**Figure 3.11f**). The broad absorption band at 3419 cm^{-1} was indicative of O–H stretching due to adsorbed moisture. Peaks at 1646 , 1391 , 1119 , and 886 cm^{-1} were attributed to carbonate stretching and bending vibrations, confirming the presence of metal carbonates on the catalyst surface (Balajii & Niju, 2020; Changmai et al., 2021; Gohain et al., 2017). A distinct absorption at 615 cm^{-1} corresponded to the stretching of metal–oxygen bonds, reinforcing the

presence of metal oxides such as Fe_3O_4 and CaO (Changmai et al., 2021; Vasantharaj et al., 2019).

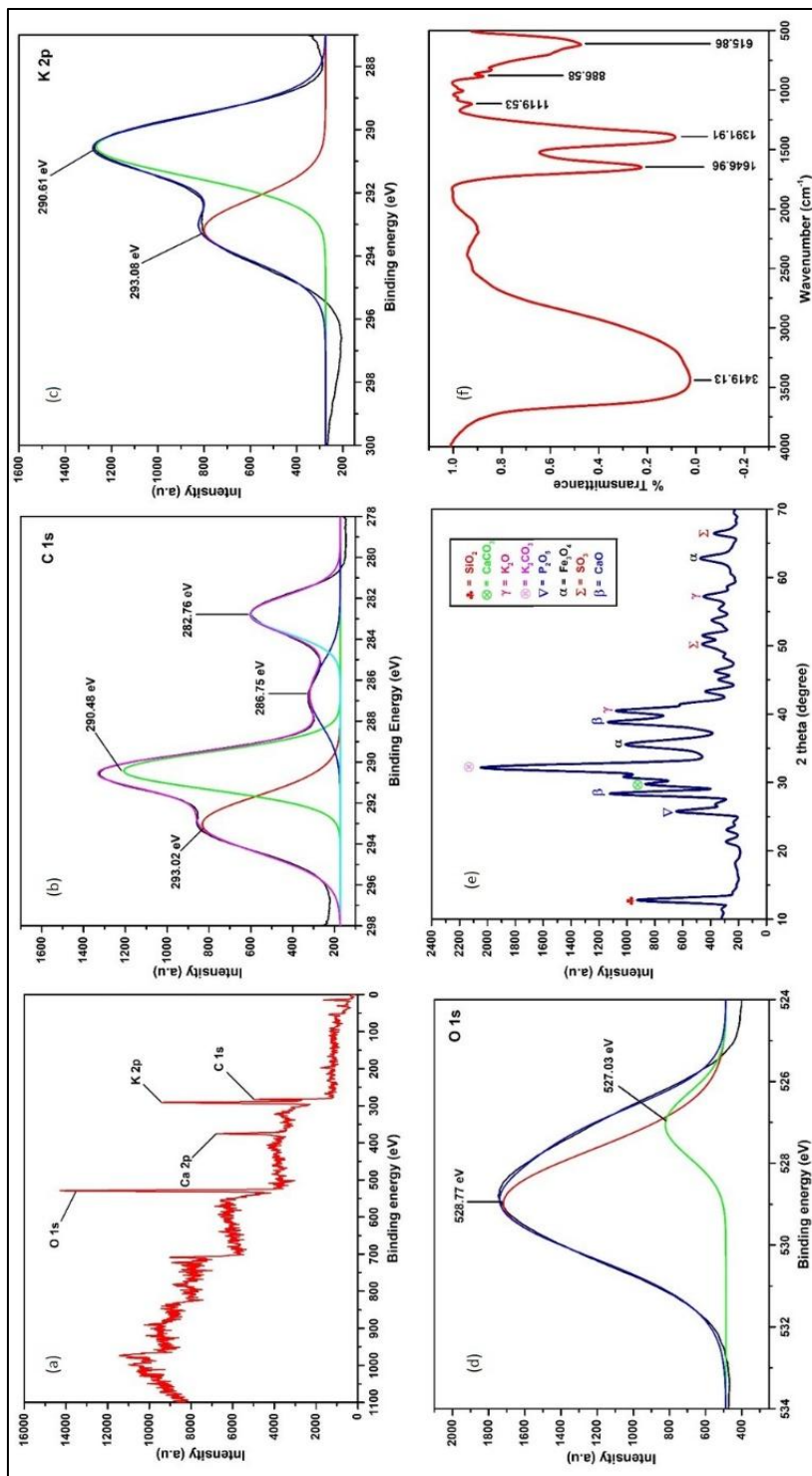


Figure 3.11: (a-d) XPS analysis of OPA@Fe₃O₄, (e) XRD data of OPA@Fe₃O₄, (f) FT-IR spectrum of OPA@Fe₃O₄.

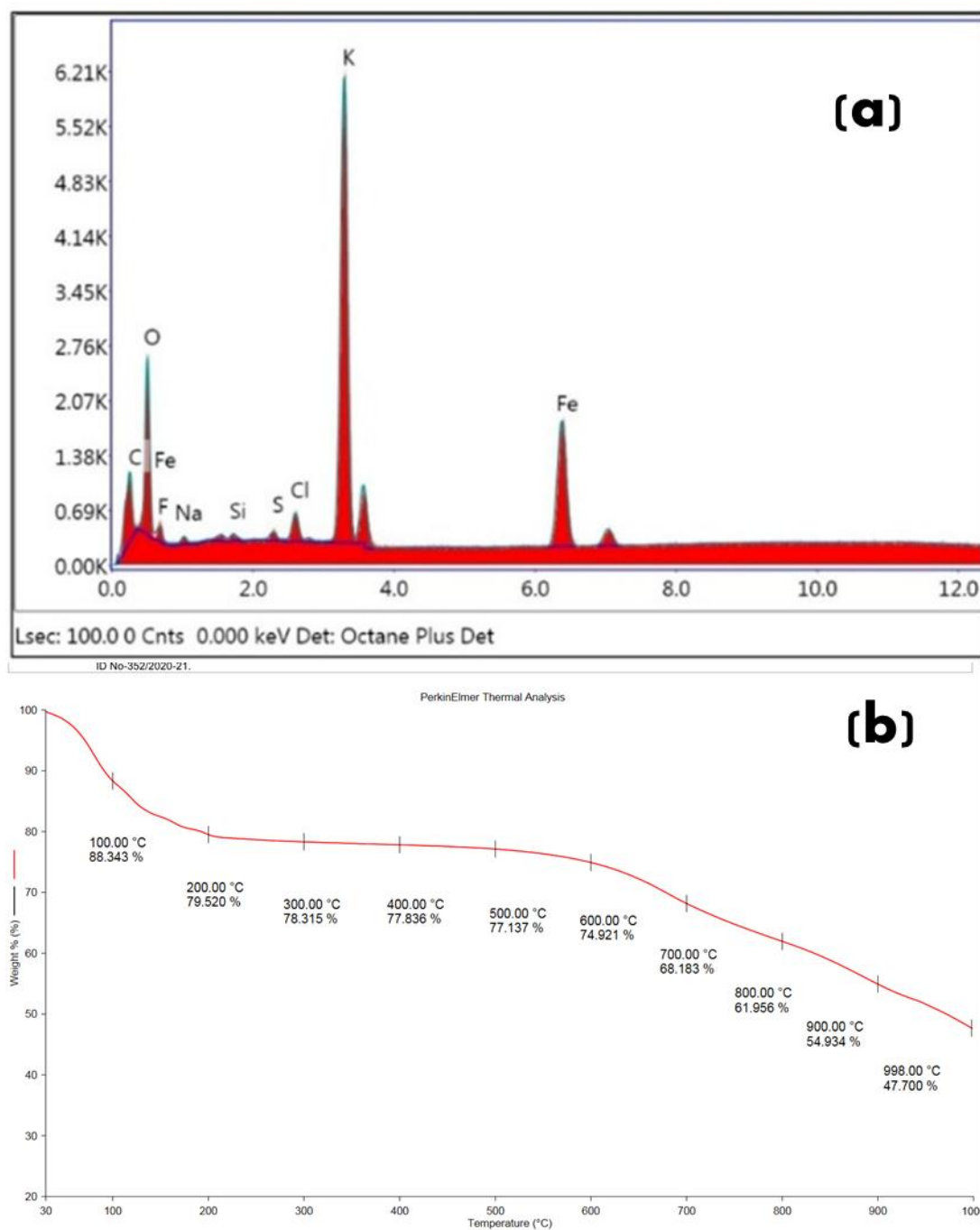


Figure 3.12: (a) EDX data of OPA@Fe₃O₄, (b)TGA thermogram of OPA@Fe₃O₄.

3.1.3.6 Elemental Distribution (EDX Analysis)

Energy-dispersive X-ray spectroscopy (EDX) was used to validate the elemental content of the nanocatalyst (**Table 3.6 & Figure 3.12**). Major elements identified included oxygen (34.36%), potassium (28.82%), iron (25.95%), and carbon (8.18%), along with traces of sodium, silicon, sulfur, chlorine, and aluminium. The elemental ratios confirmed consistency with both XRF and XPS analyses, indicating successful synthesis of OPA@Fe₃O₄ nanocomposite, with homogeneously distributed active components across the catalyst surface.

Table 3.6: EDX data for elemental composition of OPA@Fe₃O₄.

Sl No.	Elements	Weight %	Atomic %
1	C	8.18	16.52
2	O	34.36	52.11
3	F	0.00	0.00
4	Na	0.84	0.89
5	Si	0.21	0.18
6	S	0.34	0.26
7	Cl	1.30	0.89
8	K	28.82	17.88
9	Fe	25.95	11.28
10	C	8.18	16.52

3.1.3.7 Thermal Stability (TGA Analysis)

Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere from 30-1000 °C to assess the thermal robustness of OPA@Fe₃O₄ (**Figure 3.12b**). An initial weight loss of ~12% below 200 °C was associated with the desorption of surface moisture. The catalyst remained thermally stable up to 600 °C, after which a notable mass reduction of ~27.2% was observed between 600–900 °C, likely due to oxidation of carbonaceous residues (Chouhan & Sarma, 2013).

These results indicate that the OPA@Fe₃O₄ are thermally resilient up to moderate-to-high temperatures, making them well-suited for thermal catalytic processes, including PET methanolysis and glycolysis.

3.1.3.8 Morphology (SEM and TEM Analysis):

SEM micrographs (**Figure 3.13a and 3.13b**) revealed that the OPA@Fe₃O₄ possess an irregular, rod-like morphology with significant surface roughness and porosity. The particles were observed to be agglomerated, a common feature in biomass-derived magnetic nanocatalysts.

TEM analysis (**Figure 3.13c and 3.13d**) showed shell-like, polycrystalline structures with an average particle size of 10-20 nm. The SAED (Selected Area Electron Diffraction) pattern displayed diffused rings, confirming the polycrystalline nature of the OPA@Fe₃O₄ nanocomposite. These nanostructures provide abundant exposed active sites, improving surface interactions during catalytic cycles (Changmai et al., 2021).

3.1.3.9 Surface Area and Porosity (BET Analysis)

Brunauer–Emmett–Teller (BET) analysis was conducted to determine the specific surface area, pore size, and pore volume of OPA@Fe₃O₄ (**Figure 3.14**). The isotherm exhibited a type-IV hysteresis loop (H1), characteristic of mesoporous materials (Sing & Williams, 2004). The catalyst was found to have:

- i. Surface area: 31.23 m²/g
- ii. Pore volume: 0.085 cm³/g
- iii. Average pore diameter: 5.123 nm

These values highlight a significant improvement over OPA and BLA catalysts, where surface areas were approximately six times lower. The enhanced surface area and mesoporosity of OPA@Fe₃O₄ are expected to accelerate reaction rates by increasing the number of accessible active sites, making them highly effective in base-catalyzed PET depolymerization and aldol reactions.

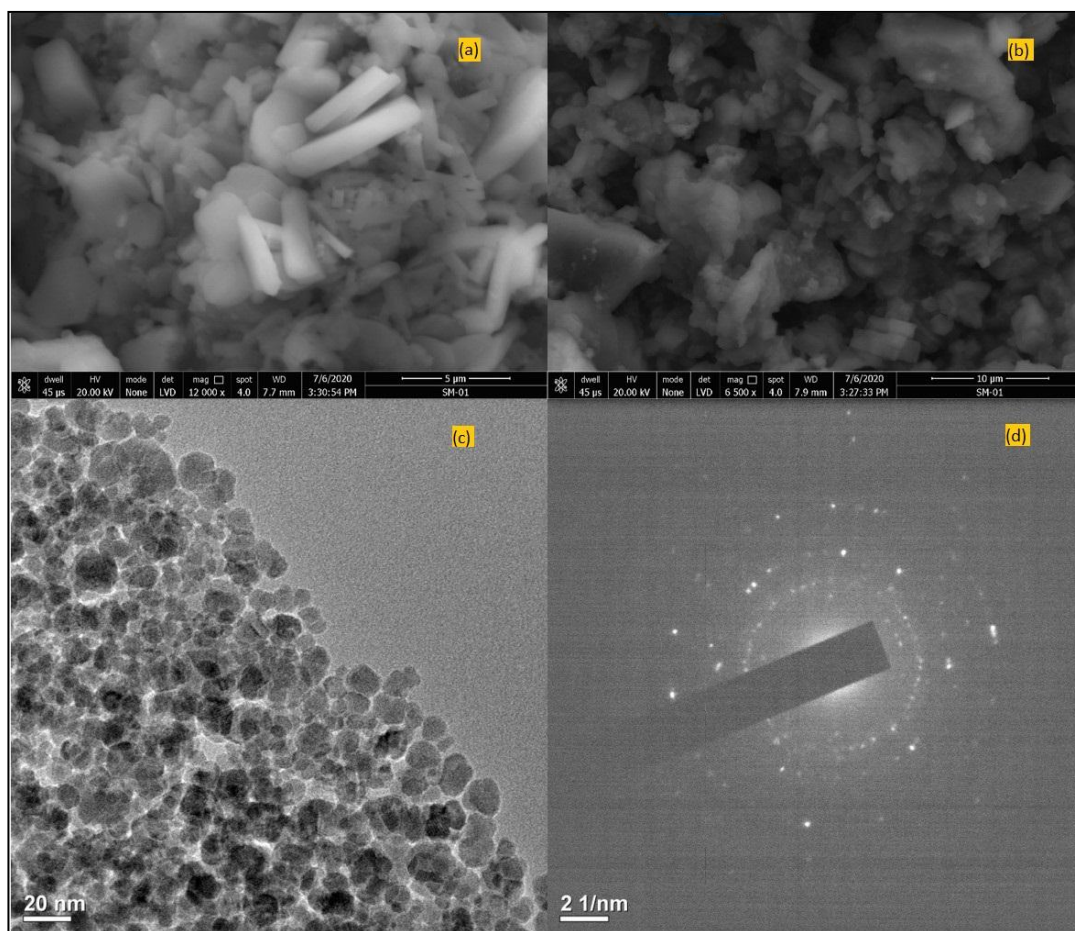


Figure 3.13: SEM (a) and (b) and TEM (c) and (d) images of OPA@Fe₃O₄

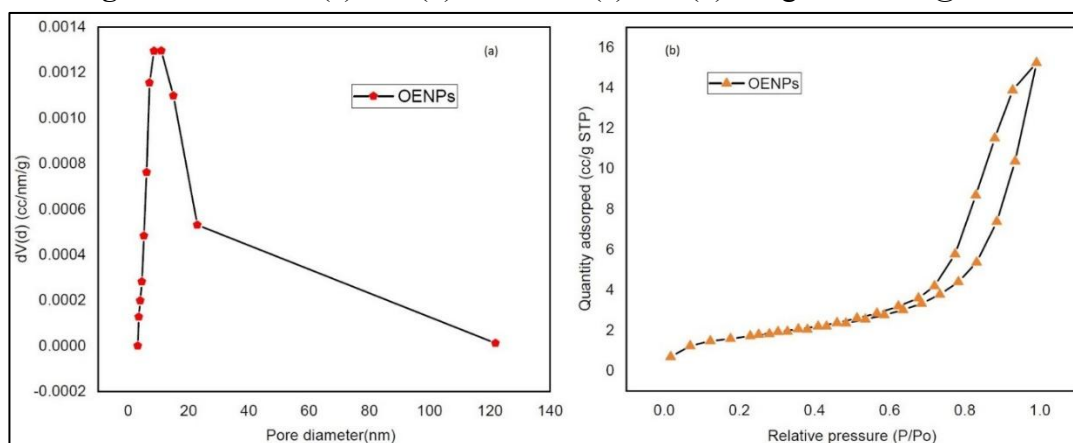


Figure 3.14: (a) BJH pore size distribution of OPA@Fe₃O₄, (b) Nitrogen adsorption-desorption isotherm of OPA@Fe₃O₄.

3.1.4. Comparative Summary of OPA, BLA, and OPA@Fe₃O₄ Catalysts

A comparative analysis of the three synthesized heterogeneous catalysts: Orange Peel Ash (OPA), Bamboo Leaf Ash (BLA), and Orange Peel Extract-Impregnated Fe₃O₄ Nanoparticles (OPA@Fe₃O₄), highlights distinct physicochemical features, catalytic potential, and thermal and morphological advantages for use in PET depolymerization and base-catalyzed organic reactions.

3.1.4.1. Elemental and Oxide Composition (XRF, EDX)

OPA is highly enriched in CaO (32.87%) and K₂O (30.87%), indicating a strong basic nature suitable for base-catalyzed reactions. BLA is predominantly composed of SiO₂ (76.02%), giving it a silicate matrix with moderate basicity, supported by smaller amounts of SO₃, CaO, and K₂O. Meanwhile, OPA@Fe₃O₄ show the highest concentration of Fe₃O₄ (55.79%), along with K₂O (26.17%) and SO₃ (8.86%), confirming the successful impregnation of magnetic iron oxide and enhancement of base strength through composite formation.

3.1.4.2. Surface Chemistry (XPS)

All three catalysts exhibit surface C–C, C=O, metal oxide, and metal carbonate functionalities, critical for catalytic performance. OPA and BLA showed pronounced Ca–O and K–O bonds, while OPA@Fe₃O₄ displayed additional Fe–O signals and distinct K₂CO₃ and K₂O surface peaks, highlighting its hybrid surface reactivity.

3.1.4.3. Crystalline Phases (XRD)

OPA contained crystalline phases of CaCO₃, K₂O, CaO, Fe₂O₃, and MgO. BLA was dominated by SiO₂ and secondary phases like K₂CO₃, CaCO₃, Al₂O₃, and MnO₂, offering a rigid silicate framework. OPA@Fe₃O₄ demonstrated well-defined peaks of Fe₃O₄, K₂O, CaO, and carbonate species, confirming a polycrystalline magnetic structure, and suggesting greater phase heterogeneity.

3.1.4.4. Surface Functional Groups (FTIR)

All three catalysts displayed broad O–H bands and characteristic peaks for carbonate and metal–oxygen vibrations.

OPA and BLA showed K–O and Ca–O bonds, while OPA@Fe₃O₄ presented stronger, well-defined signals for metallic oxides and carbonates, reinforcing its multifunctional nature.

3.1.4.5. Morphology (SEM and TEM)

OPA exhibited a cloud-like agglomerated structure with moderate porosity while BLA appeared rough, microporous, with globular aggregates of 10–50 nm. OPA@Fe₃O₄ showed rod-like nanostructures, shell-like morphology, and polycrystalline nano-sized particles (10–20 nm) with well-distributed active sites which are ideal for efficient catalysis.

3.1.4.6. Porosity and Surface Area (BET)

OPA@Fe₃O₄ exhibited the highest surface area, followed by BLA and OPA. The mesoporosity of all three catalysts is suitable for diffusion-controlled catalysis, with OPA@Fe₃O₄ having the best surface-to-volume ratio as shown in **Table 3.7**.

Table 3.7: Comparative studies of different catalysts using BET

Catalyst	Surface Area (m ² /g)	Pore Diameter (nm)	Pore Volume (cm ³ /g)	Isotherm Type
OPA	4.97	2.52	0.022	Type IV (H1)
BLA	21.85	13.68	0.127	Type IV (H1)
OPA@Fe ₃ O ₄	31.23	5.12	0.085	Type IV (H1)

3.1.4.7. Thermal Stability (TGA)

OPA was found to be stable up to 600 °C; with a total weight loss ~21%. While BLA exhibit superior stability and a total weight loss of ~13%, which is attributed to high SiO₂ content. OPA@Fe₃O₄ was also found to be stable up to

600 °C and shows a total weight loss of ~27.2%, with enhanced resistance up to 900 °C due to Fe₃O₄ disintegration.

3.1.5. Comparative Implications for Catalytic Applications

OPA is a low-cost, highly basic catalyst, suitable for reactions requiring strong base sites but is limited by lower surface area and moderate thermal stability.

BLA, with its silica-rich matrix and higher porosity, is thermally stable and moderately active, making it effective for liquid-phase reactions with a preference for structural integrity.

OPA@Fe₃O₄, combining the strengths of both, offer high surface area, magnetic recovery, enhanced thermal and phase stability, and abundant basic and redox-active sites, making it the most promising catalyst for PET depolymerization and aldol condensation reactions under both thermal and green conditions.

3.2. POST-CONSUMER PET CHARACTERIZATION.

Differential Scanning Calorimetry (DSC) was employed to evaluate the crystallinity levels in post-consumer PET samples by measuring thermal transitions such as glass transition temperature (T_g), enthalpy of fusion (ΔH_f), and melting temperature, as summarized in **Table 3.8**. The T_g values varied depending on the PET color: clear PET showed the highest T_g (79 °C), followed by light-yellow (78 °C), and green PET (75 °C). To determine ΔH_f, each sample underwent a heating–cooling–reheating cycle from 50 °C to 300 °C, using indium as the calibration reference. Among the samples, green PET exhibited the highest ΔH_f (60.01 J/g), while clear and light-yellow PET showed slightly lower values (55.10 J/g and 54.52 J/g, respectively). These enthalpy values were then used to estimate the degree of crystallinity, reflecting the extent of molecular order. Green PET had the highest crystallinity (42.86%), followed by clear (39.35%) and light-yellow (38.94%) samples. As established in prior studies, crystallinity is inversely related to degradation rate, more crystalline PET tends to degrade more slowly rates (Jenkins & Harrison, 2008). However, the relatively small differences observed across the color variants suggest comparable depolymerization behavior.

Table 3.8: Thermal properties of poly(ethylene terephthalate) PET samples obtained from DSC analysis

Sample	Weight of sample (in mg)	T_{mo} (°C) ^a	T_m (°C) ^a	ΔH_f (J g ⁻¹) ^a	T_g (°C) ^a	Crystallinity (%) ^b
Clear PET	3.200	239.11	255.38	55.1033	79	39.35
Green color PET	2.600	237.63	253.81	60.0128	75	42.86
Light-yellow color PET	2.000	236.05	254.24	54.5185	78	38.94

^aMelt onset temperature (T_{mo}), melt end temperature (T_m), enthalpy (ΔH_f) and glass transition temperature (T_g) measured at a heating rate of 20 °C min⁻¹ by DSC.

^bDegree of crystallinity was determined based upon 140 Jg⁻¹ for the 100% crystalline PET.

3.3. GLYCOLYSIS OF POLYETHYLENE TEREPHTHALATE (PET)

The chemical depolymerization of polyethylene terephthalate (PET) was carried out *via* glycolysis as discussed in the previous chapter. Upon completion, the crude product mixture underwent separation and purification using two distinct methodologies – aqueous separation and solvent extraction. The aqueous method provided a superior BHET yield in each case compared to the solvent-based method. The higher performance of the aqueous method is likely due to efficient crystallization driven by BHET's limited solubility in water at low temperatures. Consequently, the aqueous work-up was selected for subsequent experiments due to higher recovery, lower solvent use, and better operational safety.

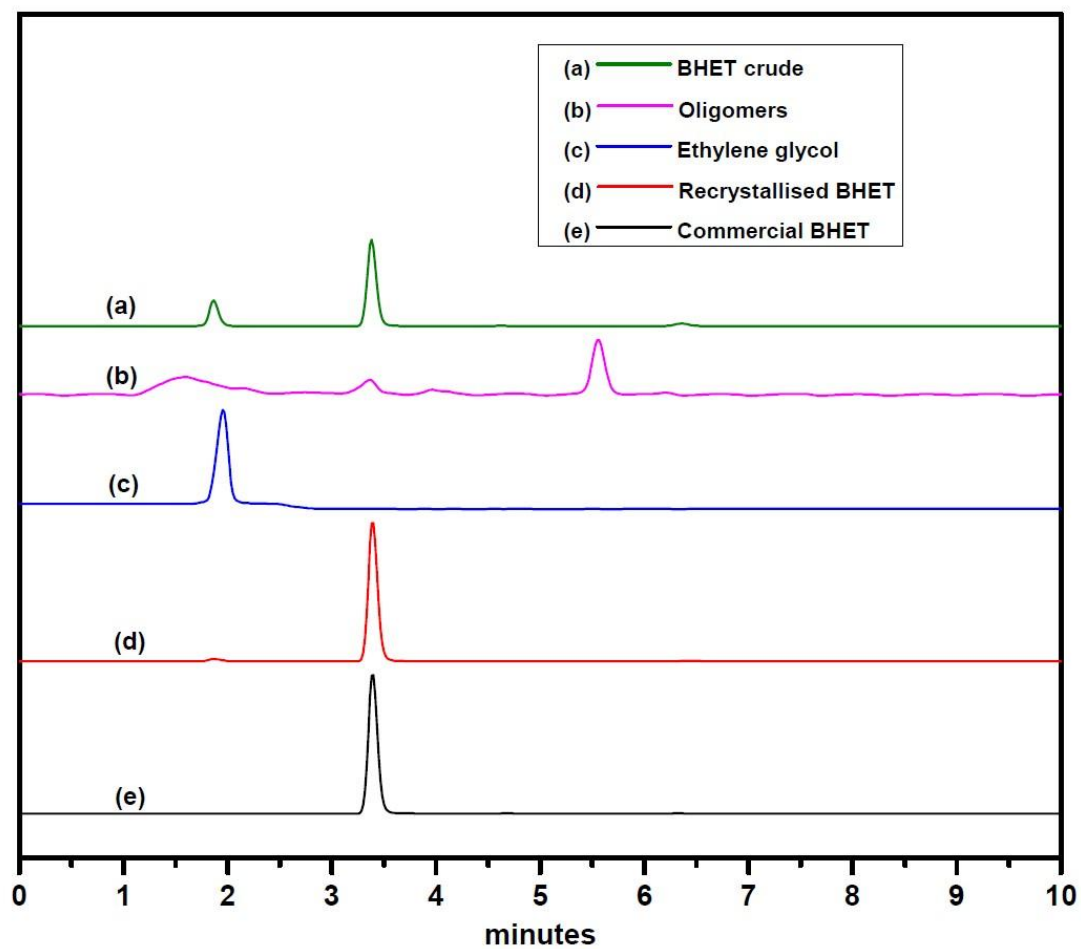


Figure 3.15: HPLC data of- (a) the crude product, (b) water-insoluble part, (c) ethylene glycol, (d) recrystallized BHET, and (d) commercially available BHET

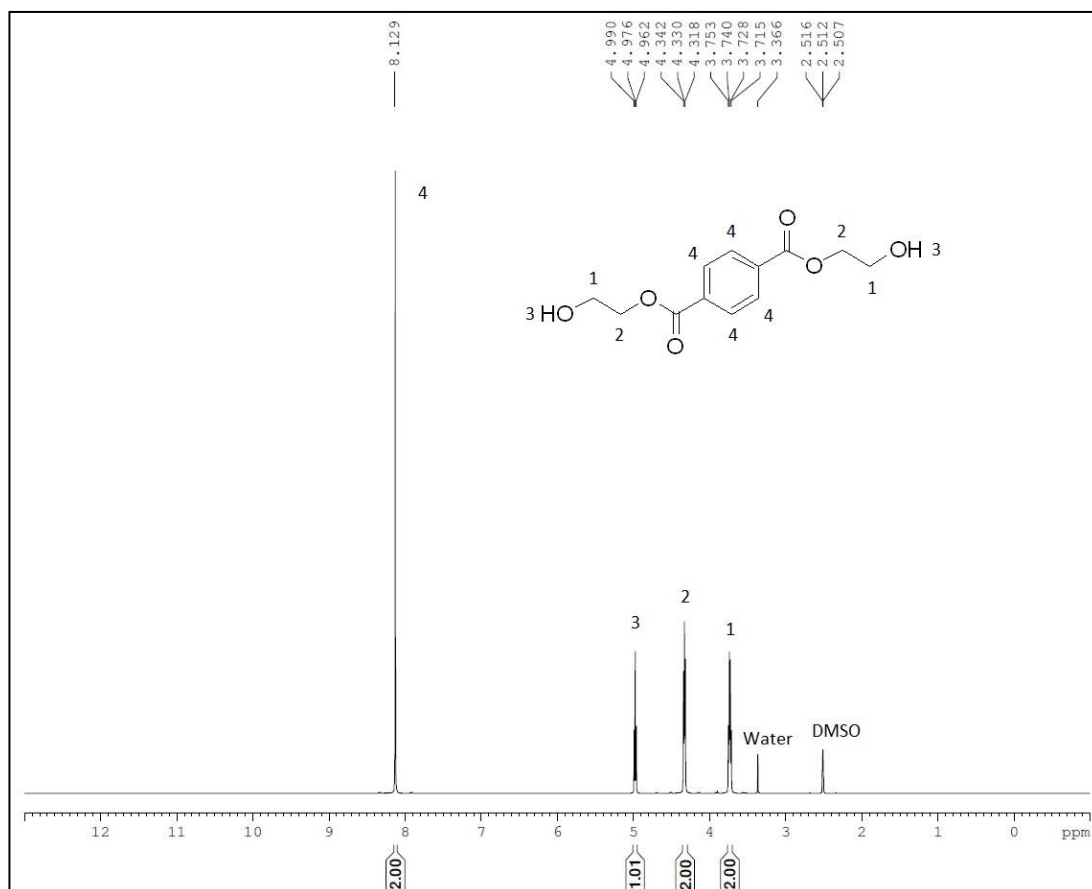


Figure 3.16: ¹H NMR spectra of recrystallized BHET

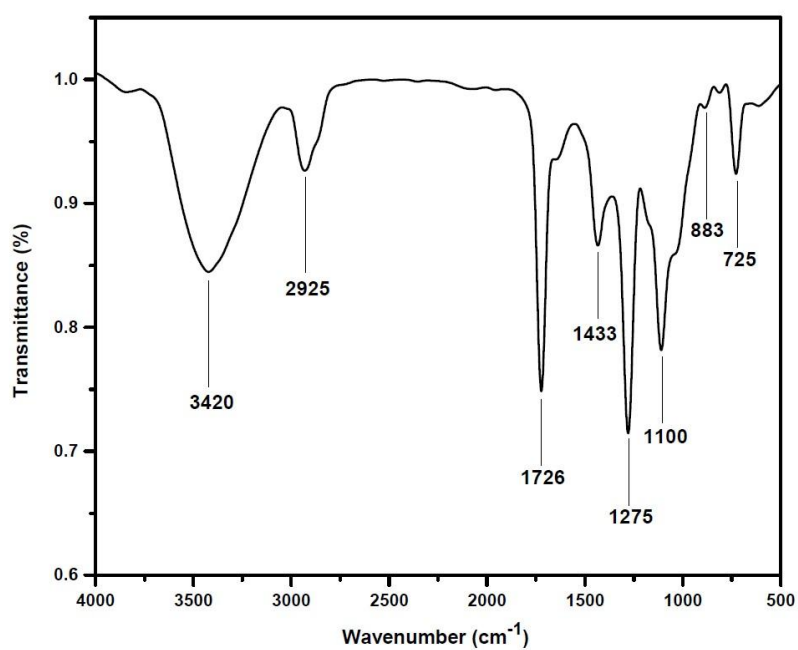
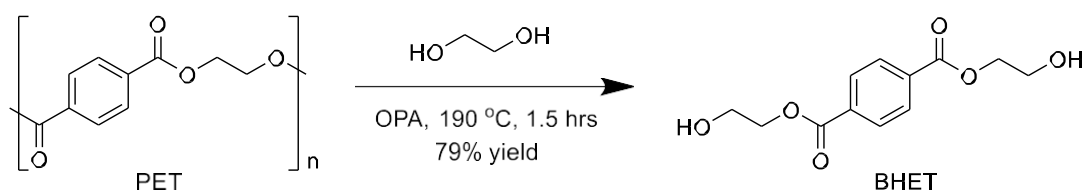


Figure 3.17: IR spectra of recrystallized BHET

3.3.1. PET Glycolysis using OPA as a catalyst

Glycolysis of PET was carried out under atmospheric pressure in the presence of excess ethylene glycol at 190 °C (**Scheme 1**). After the disappearance of PET flakes, the reaction mixture was filtered to separate out the catalyst. Analysis of the final crude product by HPLC (**Figure 3.15**) using reversed phase column revealed the presence of two smaller peaks at a retention time of 1.866 and 6.361 minutes which might be due to the presence of EG and oligomers, respectively. A major peak at a retention time of 3.382 minute is assigned to BHET monomer. Further analysis of the recrystallized product, along with commercially available BHET, EG, and water-insoluble fractions, indicated the presence of BHET as well as additional products beyond the monomeric form, suggesting complex reaction pathways or impurities within the sample matrix.

Scheme 3.1: Glycolysis of PET using OPA



The process of recrystallization of the crude product using water as a solvent yields a highly purified BHET. The purified BHET exhibits characteristic nuclear magnetic resonance (NMR) spectral features that are consistent with established literature data, thereby confirming its structural integrity. In the ¹H NMR spectrum (Figure 3.16), key resonances are observed at $\delta = 2.51$ ppm corresponding to the methyl protons in DMSO, at $\delta = 3.74$ ppm indicative of the methylene protons adjacent to hydroxyl groups (CH₂-OH), at $\delta = 4.33$ ppm associated with the methylene protons attached to the ester carbonyl group (COO-CH₂), at $\delta = 5.00$ ppm representing the hydroxyl protons (-OH), and at $\delta = 8.09$ ppm corresponding to aromatic protons (Ar-H). These spectral features align with previously reported data (Jehanno, Flores, et al., 2018; Yue et al., 2013). The ¹³C NMR spectra display a prominent peak at $\delta = 165.12$ ppm attributable to the carbonyl carbon, along with aromatic carbons resonating at $\delta = 133.70$ ppm and $\delta = 129.47$ ppm. Additional

resonances at $\delta = 66.99$ ppm and 58.95 ppm are indicative of the methylene carbons linked to hydroxyl groups, specifically ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$), confirming the successful synthesis of the target compound. The analysis of the water-insoluble fraction reveals that it predominantly consists of BHET dimers, with minor quantities of residual impurities. These impurities are likely derived from the PET feedstock, which commonly contains trace amounts of additives and contaminants introduced during manufacturing to enhance moldability. The presence of such impurities is typical and does not significantly detract from the purity of the isolated BHET, as evidenced by the spectral data and the purification process employed.

The Fourier Transform Infrared (FT-IR) spectroscopic analysis of recrystallized BHET monomer (**Figure 3.17**) revealed four distinct and prominent absorption peaks. These peaks were observed at wavenumbers $\nu = 3420\text{ cm}^{-1}$, 1726 cm^{-1} , 1275 cm^{-1} , and 1100 cm^{-1} . The peak at 3420 cm^{-1} is indicative of the O-H stretching vibration, which confirms the presence of hydroxyl functional groups within the molecular structure. The absorption at 1726 cm^{-1} corresponds to the C=O stretching vibration characteristic of carbonyl groups, a key functional group in ester compounds. The peaks at 1275 cm^{-1} and 1100 cm^{-1} are associated with C-O stretching vibrations, which are typical of ester linkages and confirm the molecular integrity of the recrystallized BHET. These spectral features collectively validate the chemical structure and purity of the synthesized compound, providing essential insights into its molecular composition and functional group distribution, which are critical for understanding its physicochemical properties and potential applications in polymer synthesis and related fields.

3.3.1.1 Optimization of the reaction parameters

To enhance the reaction condition for the selective formation of BHET monomer, the effect of different parameters such as catalyst loading, EG content, reaction time and reaction temperature were investigated and the results are depicted in **Table 3.9**.

In the context of catalytic depolymerization of polyethylene terephthalate (PET), it has been systematically observed that variations in catalyst concentration

exert a significant influence on the efficiency and yield of the resulting bis(2-hydroxyethyl) terephthalate (BHET). Experimental investigations were meticulously designed to evaluate the impact of different catalyst loadings during the glycolysis process, which employed 14 equivalents (2 g) of ethylene glycol (EG) at a temperature of 190 °C maintained for a duration of one hour under atmospheric pressure conditions. The progression of the reaction was monitored through the rapid degradation of PET, with the disappearance of PET flakes serving as a practical visual indicator of reaction completion (Fukushima et al., 2013). Analytical assessment of the crude reaction products via high-performance liquid chromatography (HPLC) revealed the formation of BHET monomer, along with its dimeric and oligomeric derivatives. Results indicated that a catalyst loading as low as 4 weight percent (20 mg) was sufficient to complete the glycolysis process within the stipulated time frame. However, subsequent purification procedures involving aqueous recrystallization of the monomer demonstrated that increasing the catalyst concentration to 10 weight percent (50 mg) yielded the most effective and consistent performance, as evidenced by the highest purity and yield of BHET. Consequently, this optimal catalyst loading was selected for further parameter optimization to enhance process efficiency and product quality in subsequent experimental iterations.

Table 3.9: Optimization of BHET^a

Sl. No.	Catalyst loading (mg)	EG loading (in g)	Time (h)	Conversion (%)	BHET yield (%)
1	20	2	1	100	63
2	30	2	1	100	71
3	50	2	1	100	75
4	70	2	1	100	69
5	100	2	1	100	71
6	50	1	1	100	61
7	50	1.5	1	100	73
8	50	2.5	1	100	78
9	50	3	1	100	76
10	50	2.5	0.5	80	54
11	50	2.5	1.5	100	79
12	50	2.5	2	100	76
13	50	2.5	2.5	100	71

^a Reactions were conducted at 190 °C under atmospheric pressure

The process of glycolysis of polyethylene terephthalate (PET) utilizing ethylene glycol (EG) involves a dynamic equilibrium between the monomer bis(hydroxyethyl) terephthalate (BHET) and various oligomeric species, notably its dimer form. Achieving a high yield of BHET necessitates an excess of reagent to suppress the formation of undesired oligomers and by-products, as supported by prior studies (Fukushima et al., 2013; López-Fonseca et al., 2009). Our experimental findings corroborate these reports, demonstrating that increasing the molar ratio of EG to PET enhances the monomer yield. Specifically, the reaction proceeds efficiently even with six equivalents of EG, as documented in **Table 3.9, entry 6**; however, the final yield of BHET remains significantly lower compared to reactions employing higher reagent equivalents. A notable correlation exists between the reduction of PET/EG ratio and the increased formation of water-soluble by-products, which often contain detectable amounts of BHET dimers and oligomers upon

recrystallization. The optimal conditions identified involved using sixteen equivalents of EG, which resulted in a pure BHET monomer with a yield of 78% within a one-hour reaction period, as shown in **Table 3.9, entry 8**. Increasing the reagent loading beyond this optimal point did not yield further improvements in monomer recovery, as evidenced by the data in **Table 3.9, entry 9**, indicating a plateau in the reaction efficiency at higher reagent concentrations.

Analysis of the data presented in **Table 3.9**, specifically entries 8, 10, and 11, indicates a clear trend whereby the conversion rate of polyethylene terephthalate (PET) and the subsequent yield of bis(2-hydroxyethyl) terephthalate (BHET) exhibit a progressive increase with the extension of reaction duration. Notably, the optimal yield of BHET, reaching 79%, was observed after a reaction time of 90 minutes under conditions where the temperature was maintained at 190 °C and the ethylene glycol (EG) loading was fixed at 16 equivalents, as detailed in **Table 3.9, entry 11**. Furthermore, the process demonstrated flexibility, as effective degradation could be achieved at a lower temperature of 150 °C, albeit necessitating a longer reaction period, as illustrated in **Figure 3.18a**. It is also important to note that elevating the reaction temperature beyond 190 °C tends to promote the formation of water-insoluble by-products, which could potentially impact the purity and yield of the desired BHET, as documented in **Table 3.10**. These findings underscore the importance of optimizing reaction parameters to balance efficiency and product quality in the chemical recycling of PET materials.

Table 3.10: Effect of reaction temperature on the degradation of PET^a

Sl. No	Reaction temperature (°C)	Reaction time (in h)	BHET yield in mg
1	150	48	51.98
2	160	24	57.55
3	170	8	65.89
4	180	3	72.12
5	190	1.5	79.00
6	200	1.5	75.68

^aReaction condition: 2.5 mmol of PET, 16 equivalents of EG, 10 wt % of OPA.

3.3.1.2. Recycling of EG and catalyst

The evaluation of catalyst and reagent recyclability has garnered significant attention among chemists, primarily due to considerations of economic efficiency and environmental sustainability. In this context, the reusability and recovery of the orange peel ash (OPA) catalyst and ethylene glycol (EG) under optimized reaction conditions were systematically examined to facilitate subsequent glycolysis of polyethylene terephthalate (PET), as detailed in **Table 3.11**. Post-reaction, the catalyst was subjected to filtration, followed by washing with methanol and drying in an oven maintained at 80 °C for a duration of five hours. It was observed that catalyst loss ranged between 5% and 10%, a deficit that was compensated by supplementing with fresh catalyst. The reusability of OPA was tested up to five cycles in which 62.66% of BHET monomer was obtained during 21 h reaction time. Notably, the catalyst's selectivity towards the formation of (BHET) exhibited only marginal decline after multiple cycles; however, the reaction time required for completion progressively increased, as illustrated in **Figure 18b**. This trend, characterized by increased reaction times and reduced yields across successive cycles, may be attributed to the leaching of active catalytic sites during the reaction and purification processes. Following the separation of BHET crystals, the residual aqueous phase was evaporated under vacuum at 60 °C to recover unreacted EG, which was subsequently stored in an oven at 50 °C for 12 hours. The recovered residual reagent was then reused in subsequent glycolysis reactions, thereby enhancing process sustainability and resource efficiency.

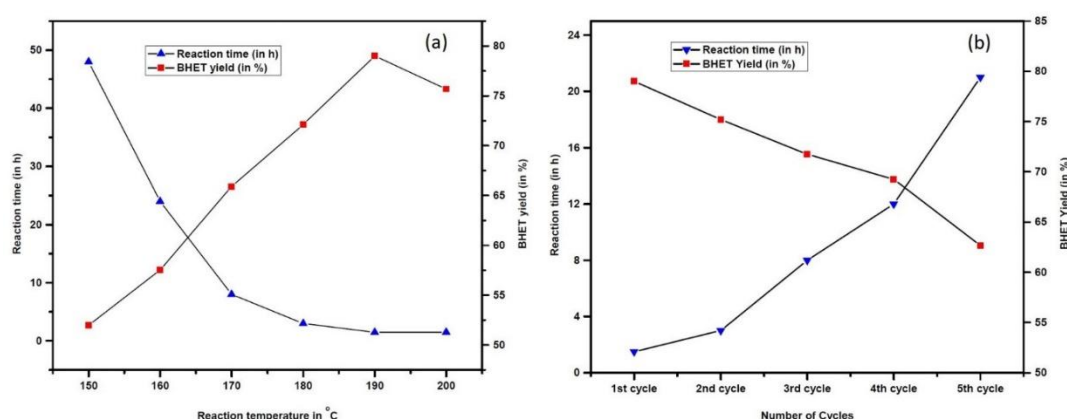


Figure 3.18: (a) Effect of reaction time on PET depolymerization. The reaction was conducted using 2.5 mmol of PET, 16 equivalents of EG and 10 wt % of OPA, and

(b) Reusability of OPA catalyst. The reaction was conducted using 2.5 mmol of PET, 16 equivalents of EG and 10 wt% of OPA catalyst.

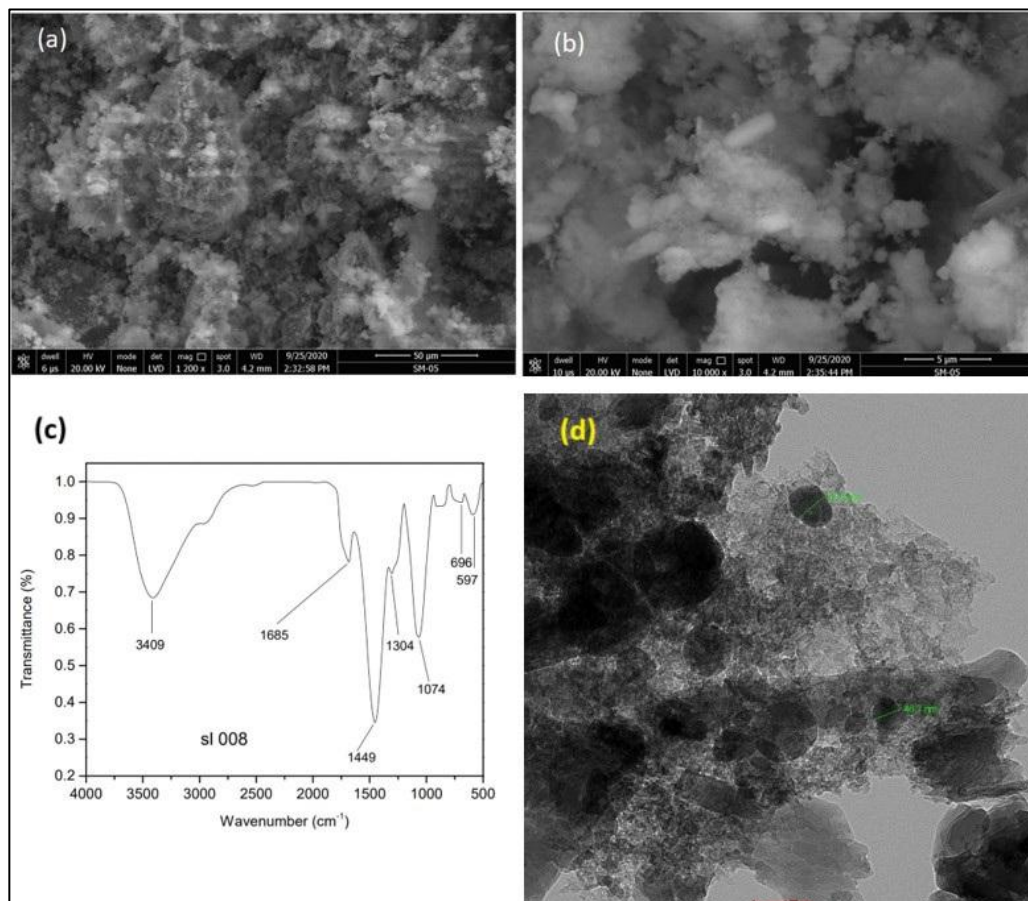


Figure 3.19: (a) SEM & (b) TEM images of recovered OPA after the 5th cycle, (c) FT-IR spectra after the 5th cycle, (d) TEM image of recovered OPA after the 5th cycle

Table 3.11: Reusability of OPA catalyst^a

No. of cycle	Time (in hour)	BHET yield %
1st cycle	1.5	79.00
2 nd cycle	3	75.20
3 rd cycle	8	71.75
4 th cycle	12	69.25
5 th cycle	21	62.66

^aReaction condition: 2.5 mmol of PET, 16 equivalents of EG, 10 wt % of OPA, 190 °C.

Following the fifth catalytic cycle, comprehensive analytical techniques including Fourier Transform Infrared (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Energy Dispersive X-ray (EDX) analysis were employed to evaluate the alterations in the physicochemical properties of the reused catalyst. The FT-IR spectra of the regenerated OPA catalyst demonstrated minimal deviations from those observed in the pristine catalyst, indicating preservation of the functional groups essential for catalytic activity (**Figure 3.19c**). EDX analysis revealed a significant reduction in potassium (K) content, with the weight percentage decreasing markedly from 21.32% to 0.48%, suggesting substantial leaching of potassium ions during the catalytic cycles (**Figure 3.20**). Morphological assessments via SEM and TEM imaging indicated that the catalysts maintained an uneven, mesoporous structure characteristic of the fresh material, implying structural stability despite chemical modifications incurred during reuse (**Figure 3.19a & 3.19b and 3.19d**). These findings underscore the catalyst's resilience and provide insights into its structural and compositional stability over multiple cycles, which are critical parameters for evaluating its practical applicability in continuous catalytic processes.

Table 3.12: EDX data of recovered OPA after 5th cycle.

Sl No.	Elements	Weight %	Atomic %
1	C	30.74	42.92
2	O	41.94	45.00
3	Mg	1.29	0.89
4	Si	0.68	0.41
5	P	3.82	2.07
6	S	0.84	0.44
7	K	0.48	11.13
8	Ca	19.04	7.96

3.3.2. PET Glycolysis using BLA as a catalyst

Glycolysis of PET was performed in a two necked round bottom flask containing EG, PET and BLA at 190 °C under atmospheric pressure. The disappearance of PET flakes was once again used as a visible indicator for the end of the reaction. After completion of the reaction, the crude product was purified by either recrystallization or extraction methods and the pure product was characterized using HPLC, IR, ^1H and ^{13}C NMR. The crude product and water-insoluble part obtained in the recrystallization process were also characterized using HPLC and NMR.

The High-Performance Liquid Chromatography (HPLC) analysis was carried out in a reversed-phase column using a mixture of methanol/water at a volume fraction of 70/30 as a mobile phase at a flow rate of 1 mL/min. The crude product showed three major peaks at the retention time of 1.872, 3.385 and 6.363 minutes which corresponds to ethylene glycol, BHET monomer and BHET dimer, respectively (**Figure 3.21b**). HPLC analysis of commercially available BHET monomer, ethylene glycol and recrystallized product (**Figure 3.21a**), as well as the water insoluble fraction is in accord with the findings. Three prominent bands at $\nu = 3441\text{cm}^{-1}$ (OH), 2950 cm^{-1} (CH_2) and 1693 cm^{-1} ($\text{C}=\text{O}$) were observed in its IR spectra and a strong absorption peak at 1260 cm^{-1} was assigned to esters C-O bond.

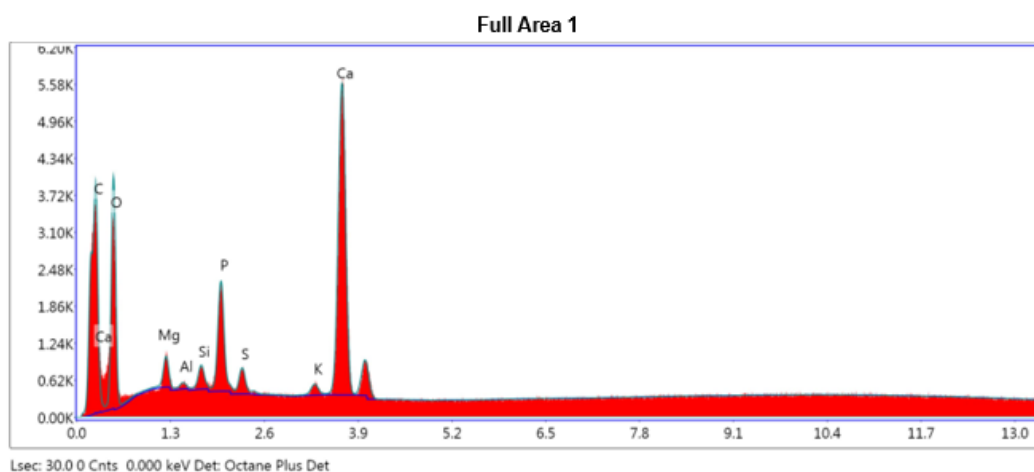


Figure 3.20: EDX spectra of OPA after the 5th cycle

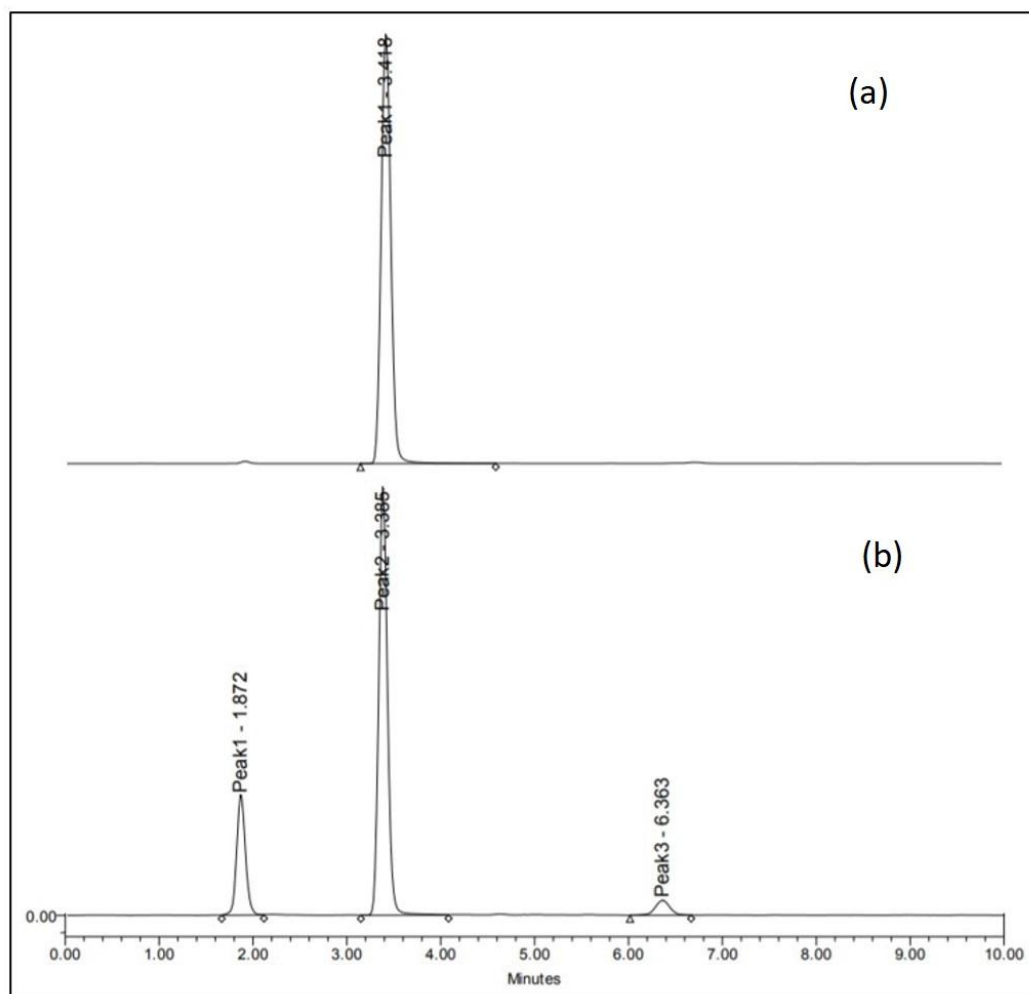


Figure 3.21: HPLC data of (a) the recrystallized product and (b) the crude product

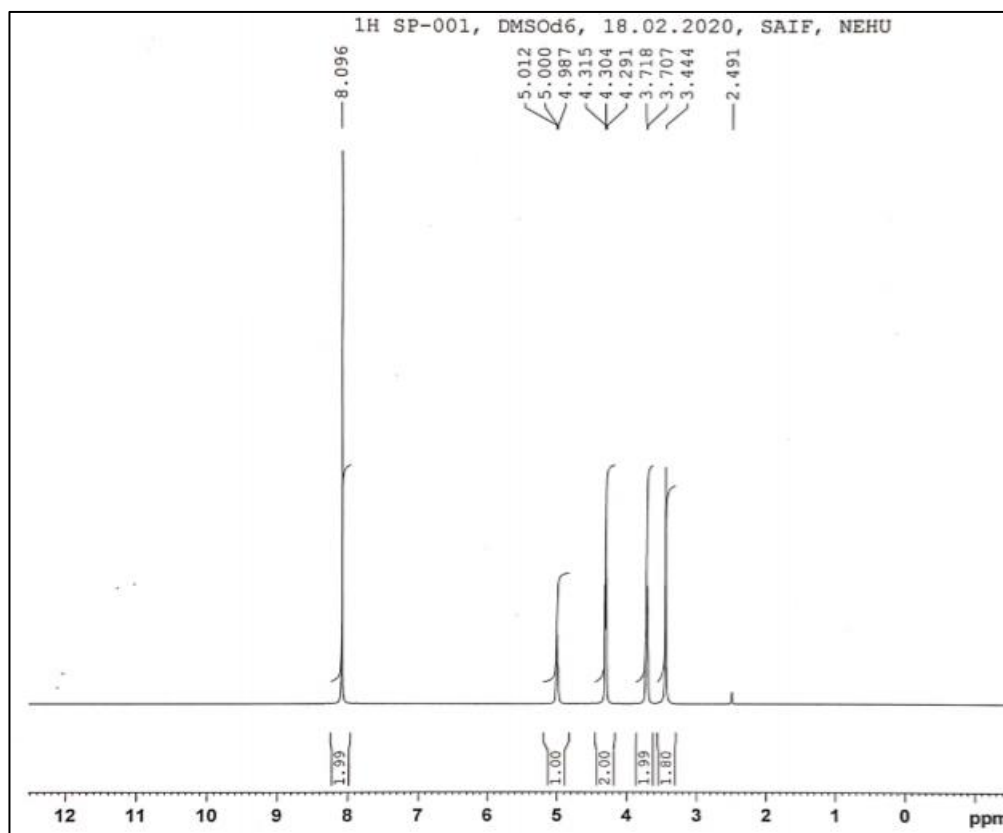


Figure 3.22: ^1H NMR spectra of recrystallized BHET

^1H NMR spectra of the recrystallized product (**Figure 3.22**) using $\text{DMSO-}d_6$ as solvent revealed resonances at $\delta = 8.09$, 5.00, 4.30, 3.70 and 2.49 ppm and assigned to aromatic protons, hydroxyl protons, methylene protons of COO-CH_2 and $\text{CH}_2\text{-OH}$ and DMSO, respectively. In its ^{13}C NMR, distinctive peaks at $\delta = 165.09$ (carbonyl), 133.63 and 129.43 (aromatic carbons), 66.95 and 58.91 ppm were also detected (methylene carbons). The water insoluble fraction was found to be composed mainly of BHET dimer, but most probably other oligomers and terephthalic esters are also present in it (Fukushima, Coulembier, Lecuyer, Almegren, Alabdulrahman, Alsewailem, McNeil, et al., 2011).

3.3.2.1. Investigation of the catalyst loading

Initially, the conversion of PET waste to its monomer was carried out in the presence of 16 equivalent of ethylene glycol and 15 wt % BLA at 190 $^\circ\text{C}$ and after 3 hours, 77% yield of BHET monomer was obtained (**Table 3.13, entry 4**). When the same reaction was performed in the absence of our catalyst, even after 100 hours of

reaction time at 190 °C, only 74% PET conversion and 41% BHET yield were achieved (**Table 3.13, entry 2**). So, while keeping other parameters such as EG loading and reaction time constant, optimization of the catalysts loading was performed and the result is shown in **Table 3.13**. Previous studies have shown that an equilibrium exists between BHET monomer and oligomers particularly its dimer during glycolysis (Ghaemy & Mossaddegh, 2005; Raheem et al., 2019; Xi et al., 2005b). Our results were also on a par with an earlier report that increasing the catalyst loading accelerates the reaction but shortens the equilibration time (Al-Sabagh, Yehia, Eissa, Moustafa, Eshaq, Rabie, & Elmetwally, 2014a; Zhou et al., 2012). **Table 3.13, entry 3-5** clearly exhibited this trend as enhancing the amount of catalyst from 10 wt % to 20 wt % led to the improved formation of BHET monomer with a decreased in the production of water insoluble part. The best result was obtained with 20 wt % of the catalyst giving 79% BHET yield (**Table 3.13, entry 5**) and we choose this catalyst loading for further study. However, an additional increase in the catalyst amount led to the reduction of BHET yield (**Table 3.13, entry 6 and 7**). This might be attributed to the fact that, after crossing the optimal catalyst loading, the reaction progressed more rapidly to form BHET monomer. As the reaction proceeds further, BHET then repolymerized into its dimer and oligomers, which plummets the BHET yield while increasing the water insoluble product at the same time (Al-Sabagh, Yehia, Eissa, Moustafa, Eshaq, Rabie, & Elmetwally, 2014b; H. Wang et al., 2010).

Table 3.13: Optimization of the catalyst loading^a

Entry	Catalyst loading (in mg)	Reaction time (in h)	Yield of water insoluble product %	BHET yield %
1	-	24 ^b	<1	2
2	-	100 ^c	2	41
3	50	3	7	72
4	70	3	5	77
5	100	3	3	79
6	120	3	4	78
7	140	3	6	76

^aReaction condition: 480 mg (2.5 mmol) of PET, and 2.25 mL of ethylene glycol at 190 °C; ^b16% PET conversion; ^c74% PET conversion

3.3.2.2. Optimization of the reagent loading and reaction time

The impact of EG loading and reaction time on glycolysis of PET were examined and the results are shown in **Figure 3.23a and 3.23b**. It has been observed in the previous reports that the ratio of ethylene glycol to PET influences both the conversion and yield of the product (Ghaemy and Mossaddegh, 2005; Xi et al., 2005). This is consistent with our findings and with an increase in the concentration of ethylene glycol, the formation of oligomer decreases, which also contributes to easy recrystallisation and purification. Even at a low concentration of EG (6 equiv.), the glycolysis proceeded efficiently, but there is some difficulty in the purification process as the recrystallized products usually contain small amount of the dimer and/or oligomers of BHET. We have also observed that the equilibrium between BHET monomer and dimer was reached after 3.5 hours of reaction when the temperature and EG loading were fixed at 190 °C and 16 equivalents, correspondingly. Shorter or longer reaction time results in the increased formation of water-insoluble fraction. This selectivity of BHET monomer to initial increase and then decrease with reaction time can be explained on account of their depolymerization and repolymerization process. During glycolysis, PET first degrades into its oligomers, then to the dimers and lastly, into its monomer. With increasing glycolysis time, BHET repolymerized into its dimers and then into oligomers, forming chemical equilibrium (Al-Sabagh, Yehia, Eissa, Moustafa, Eshaq, Rabie, & Elmetwally, 2014b; H. Wang et al., 2009). Shorter reaction time results in the incomplete degradation of the oligomers or dimers whereas prolonged reaction time beyond 3.5 hours results in the repolymerization of BHET monomer.

3.3.2.2. Effect of reaction temperature

We further examine the effect of temperature for glycolysis of PET and observed that it exponentially affected the reaction time as well as BHET yield. When the reaction was carried out at 190 °C using 2.5 mmol of PET, 100 mg of catalysts and 16 equiv. of EG, depolymerization was completed within 3 hours. But the best result was obtained after prolonging the reaction for another 30 minutes. At 150 °C, depolymerization required 72 hours which indicated that this process can be

performed even at a reduced temperature. But at 200 °C, there is a slight decrease in BHET yield with an increase in BHET dimer and/or oligomer production (**Figure 3.24a**).

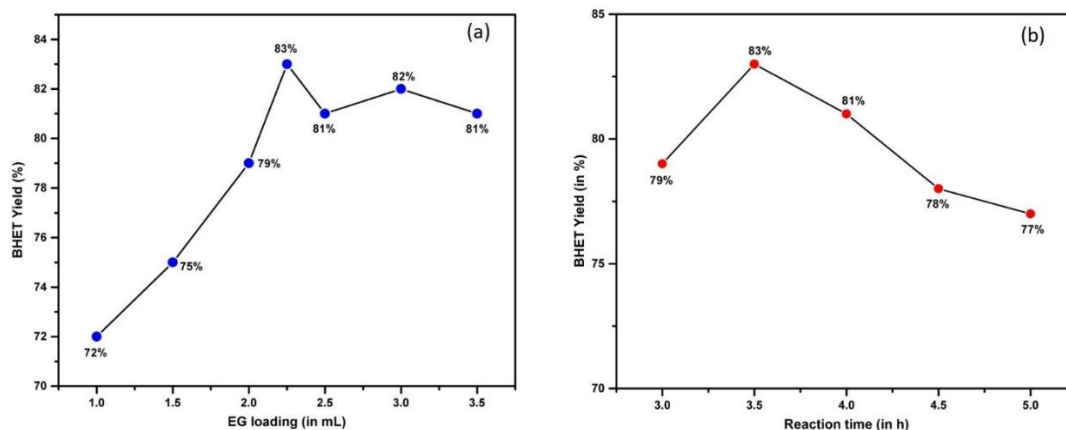


Figure 3.23: (a) Effect of EG loading on glycolysis of PET. The reaction was conducted using varied amount of EG, 480 mg of PET and 100 mg of the catalyst at 190 °C, and (b) Degradation time of PET. The reaction was conducted using 480 mg of PET, 100 mg of the catalyst, 2.25 mL of EG at 190 °C.

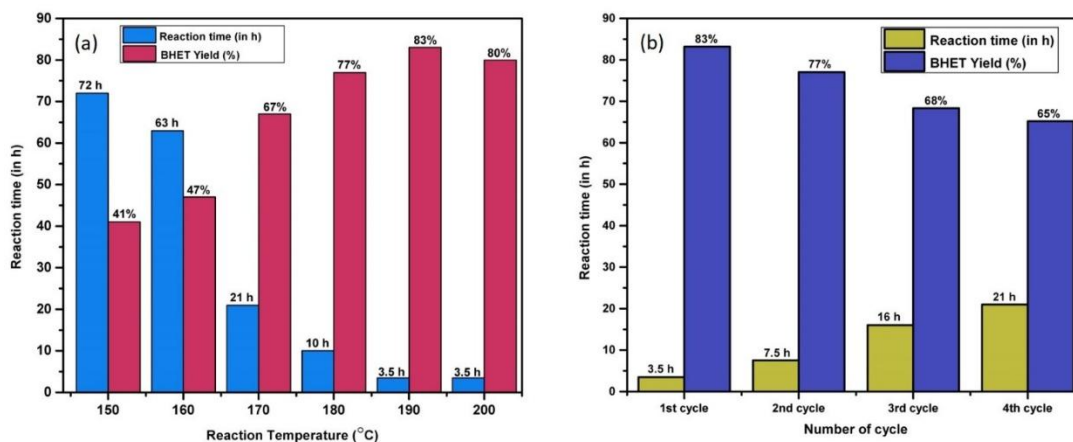


Figure 3.24: (a) Effect of reaction temperature on degradation time of PET. Reaction conditions: PET (2.5 mmol), catalyst (100 mg), EG (16 eq), and (b) Reusability of the catalyst in the degradation of PET.

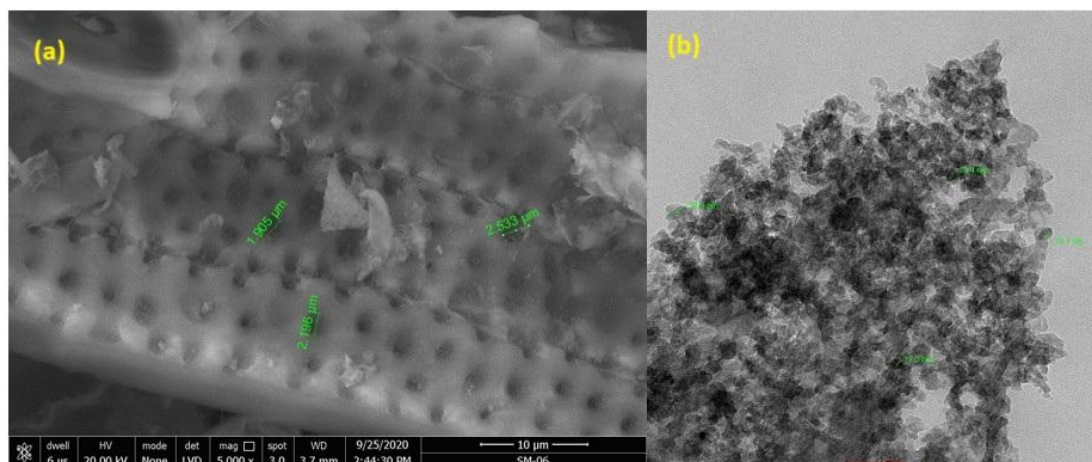


Figure 3.25: (a) SEM image of recovered BLA catalyst after four catalytic cycles, (b) TEM image of recovered BLA catalyst after four catalytic cycles

3.3.2.3. Reusability of the catalyst

Further, the efficacy of the recovered BLA catalyst was investigated for the next subsequent four catalytic cycles under our optimized condition and recovery technique (**Figure 3.24b**). A mixture of PET flakes (480 mg), BLA (100 mg) and EG (2.25 mL) were heated at 190 °C for 3.5 hours. After filtration and washing with methanol, the catalyst was dried in an oven at 80 °C for 5 hours. It was noticed that there was a loss of about 5 to 10% catalyst by weight which was then compensated with a fresh catalyst. For the second run, depolymerization requires 7.5 hours and there was a gradual increase in PET degradation time as well as a slight decreased in BHET yield for the next successive run. This might be due to the leaching of the active components of the catalyst during the reaction and purification processes (Pathak et al., 2018) as shown by EDX analysis after four cycles.

TEM, SEM, and EDX analysis of the recovered catalysts after the 4th cycle were performed to investigate the changes in their morphology and elemental compositions. The reused catalysts after the 4th cycle exhibited an irregular morphological structure with mesoporous characteristic similar to that in the fresh catalyst in its SEM and TEM analyses (**Figure 3.25a and 3.26b**). The elemental composition of the recovered catalysts studied *via* EDX analysis shows a significant loss of Ca concentration from 9.06% to 3.33% in comparison with the fresh catalysts. It also showed a complete loss of potassium (K), magnesium (Mg), manganese (Mn)

and iron (Fe) weight % from the original 4.61%, 1.59%, 1.25% and 0.52 % to an undetectable trace amount in the recovered ash (Figure 3.25a and 3.25b). This significant loss in Ca, K, Mg, Mn and Fe concentration might have directly affected the outcome of the reaction with the recovered catalyst (Ahmed et al., 2013; Bartolome et al., 2014; Farahat & Nikles, 2002; Goje & Mishra, 2003; Nikje & Nazari, 2006). On the other hand, the EDX data clearly indicated that the concentration of Si remains almost the same even after four catalytic cycles (**Figure 3.26**). So, to investigate whether SiO₂ has played an important role in the catalysis (Y. Jin et al., 2015; Kundu et al., 2014) of PET depolymerization, a reaction was carried out in the presence of commercially available silica under our optimized protocol. To our surprise, it was found that even after 5 hours of stirring at high temperature, no conversion of PET was observed and recrystallized BHET monomer could not be isolated from the reaction.

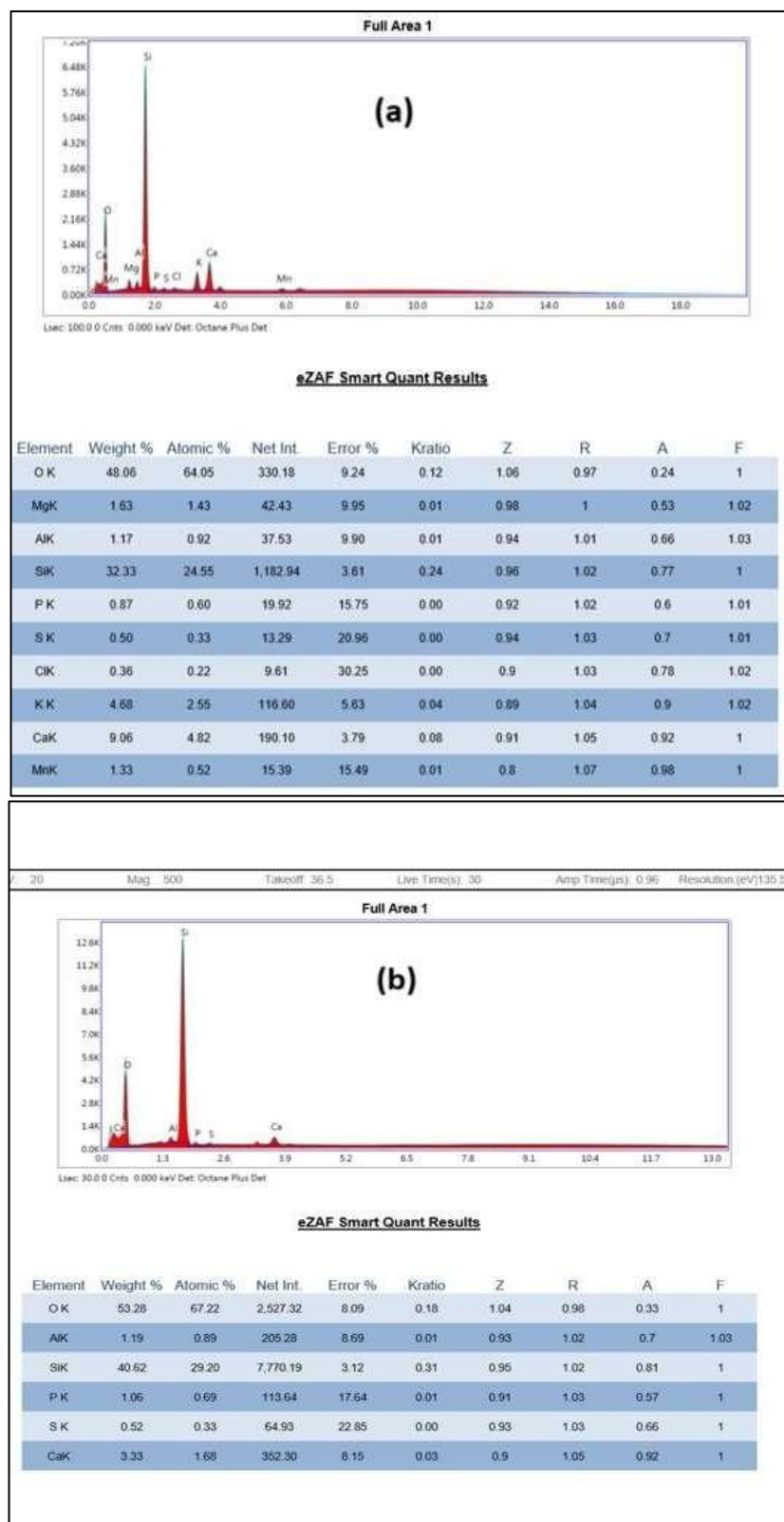


Figure 3.26: (a) EDX data of fresh BLA catalyst, (b) EDX data of recovered BLA catalyst after four catalytic cycles

3.3.2.4. Recovery of the residual reactant

The unreacted ethylene glycol (EG) was recovered by separating the BHET crystal from the aqueous phase followed by evaporation of the filtrate under vacuum at 60 °C (Jehanno, Flores, et al., 2018). The recovered EG was then distilled at 120 °C under reduced pressure and then used for subsequent catalytic depolymerization. This process of recovery and reusability of the residual reactant greatly increases the feasibility of the described protocol towards greener methodology.

Table 3.14: Color bottle recycling^a

Sl. No.	Color of the bottle	Reaction time (in h)	BHET Yield %
1	Red	3.5	75
2	Light-yellow	3	75
3	Green	5	68

^aReaction Condition: 2.5 mmol of PET, 2.25 mL of EG at 190 °C

3.3.2.5. Recycling of color bottle

We also investigated the glycolysis of red, green and light-yellow postconsumer PET bottles under our optimum condition. All the reactions were completed within 3 hours of reaction time, but like before the best results in terms of BHET yield was obtained after 3.5 hours. The recrystallized BHET yield % were almost equivalent to those of clear bottles (**Table 3.14**) and most of the color were removed during recrystallization and filtration (**Figure 3.27**). The residual pigments, if any, can be removed by adding 50 mg of activated carbon after separation of the water insoluble part followed by filtration (Fukushima, Coulembier, Lecuyer, Almegren, Alabdulrahman, Alsewailem, Mcneil, et al., 2011).

3.3.2.6. The proposed reaction mechanism for glycolysis of PET using BLA

Glycolysis of PET proceeds through three stages: breaking into the oligomers, followed by dimer formation and finally, degeneration into the monomer (George & Kurian, 2014). In the current study, PET waste depolymerization was carried out using a recyclable BLA as a heterogeneous catalyst and the proposed

mechanistic pathway is illustrated in **Scheme 3.2**. Heterogeneous catalysis reaction proceeded through diffusion of the reactants to the surface of the catalysts, where they get adsorbed by forming new bonds. The reacting molecules then interact to give new products which was subsequently followed by desorption of the final products from the surface of the catalyst. With BLA, it is assumed that the oxides and carbonates of Ca, K, Mg, Mn and Fe present in the catalyst are the active sites for PET depolymerization (Changmai et al., 2021). These anionic sites abstract the proton of ethylene glycol to generate a nucleophile, 2-hydroxyethanolate. During the degradation process, the glycol itself diffuses into the PET pellets and caused it to swell up (H. Wang et al., 2009). The nucleophile which formed earlier then attacks the carbonyl carbon of the ester bond to form a tetrahedral intermediate, the ester bond in the chain cleaved and reduces the PET polyester into lower fractions. As the acyl group breaks, the $\text{-OCH}_2\text{CH}_2\text{-}$ group gets eliminated and abstract a proton from the catalyst, forming $\text{HOCH}_2\text{CH}_2\text{-}$ group (Al-Sabagh, Yehia, Eissa, Moustafa, Eshaq, Rabie, & Elmetwally, 2014a). The conversion of PET to BHET proceeds through stepwise reaction, where oligomers, dimers, and monomers are produced successively. As the reaction progressed further, BHET can be repolymerized back to its dimers and then oligomers, thereby generating an equilibrium.

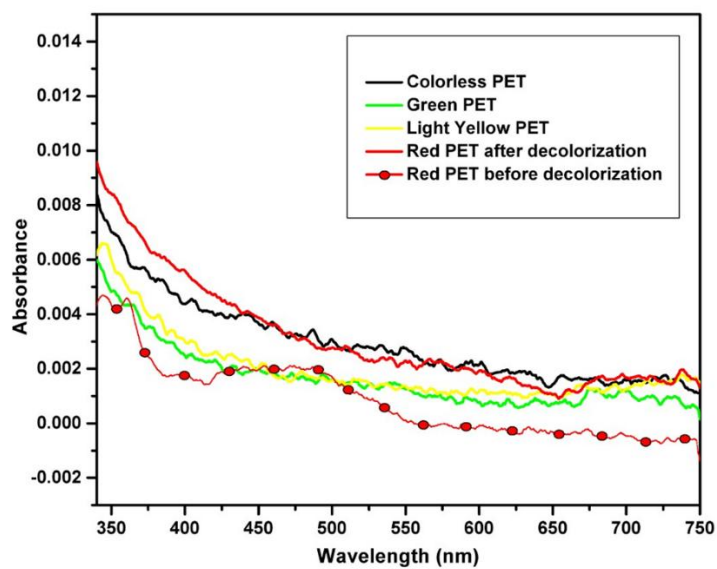
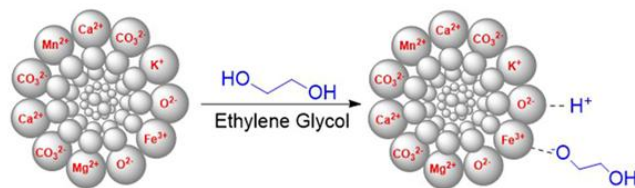
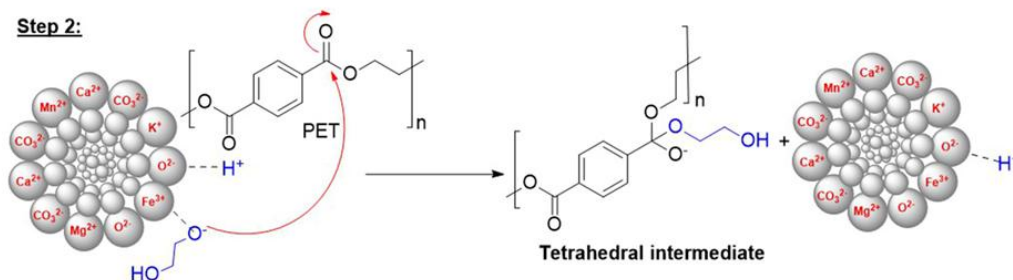


Figure 3.27: UV-vis spectra of BHET monomer derived from colorless, green, light-yellow and red (before and after decolorization) PET bottles. The sample were dissolved in acetone (50 mg/mL).

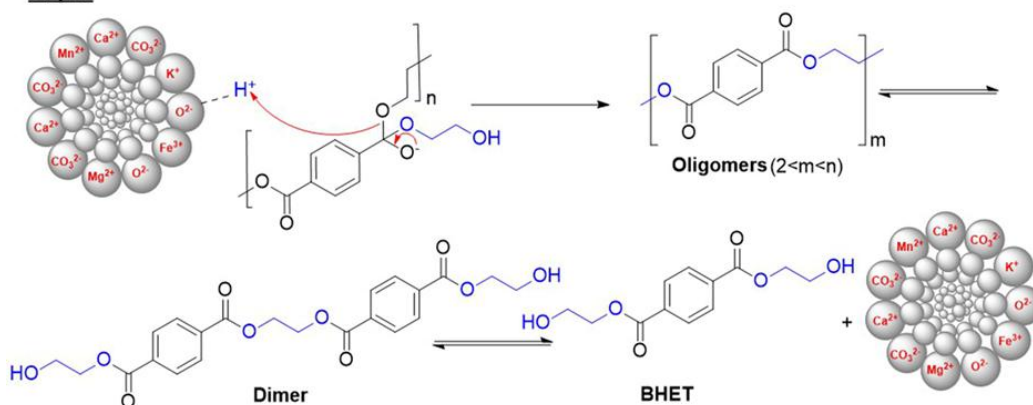
Step 1:



Step 2:



Step 3:



Scheme 3.2: The plausible reaction pathway for glycolysis of PET using BLA

3.3.3. Glycolysis of Polyethylene Terephthalate (PET) Using Orange Peel-Derived Nanoparticles (OPA@Fe₃O₄)

The glycolytic depolymerization of polyethylene terephthalate (PET) was effectively catalyzed by bio-waste-derived orange peel nanoparticles (OPA@Fe₃O₄), whose high surface area, nanostructured morphology (15-17 nm), and rich basic oxide composition (notably K₂O and CaO) contributed to their remarkable catalytic efficiency. Physicochemical analyses including BET, XRD, SEM, TEM, EDX, and FTIR confirmed the mesoporous structure, crystalline oxide phases, and surface –OH and metal–oxygen functionalities, all of which synergistically facilitated the transesterification of PET into bis(2-hydroxyethyl) terephthalate (BHET) under

optimized conditions, thereby highlighting the potential of OPA@Fe₃O₄ as a sustainable catalyst for polymer recycling.

3.3.3.1. Optimization of Reaction Time

A series of time-variation experiments was conducted to determine the optimal reaction duration for maximum BHET yield under the catalytic influence of OPA@Fe₃O₄. The reactions were performed using 10 wt% catalyst, 16 equivalents of ethylene glycol (EG), and 2.5 mmol of PET flakes at 190 °C, varying the reaction time between 1 to 3 hours.

The results, as illustrated in **Figure 3.28(a)**, indicate a marked increase in BHET yield with increasing reaction time, reaching a maximum of approximately 85% at 1.5 hours. Beyond this optimal point, a notable decline in BHET yield was observed, accompanied by the formation of water-insoluble by-products. This trend can be attributed to the reversible nature of the glycolysis reaction, where prolonged heating may favor the re-polymerization of BHET into oligomers and dimers, thereby reducing monomeric recovery. These findings are in alignment with previous reports indicating that precise temporal control is essential to favor depolymerization over repolymerization (Al-Sabagh, Yehia, Eissa, Moustafa, Eshaq, Rabie, & Elmetwally, 2014a; Z. Laldinpui et al., 2021; Lalmangaihuala et al., 2021; Zhou et al., 2012).

3.3.3.2. Optimization of Catalyst Loading

The catalytic efficacy of OPA@Fe₃O₄ was further examined by varying the catalyst concentration between 2 wt% to 16 wt%, while keeping other parameters constant (16 equivalents EG, 1.5 hours, 190 °C). As depicted in **Figure 3.28(b)**, the BHET yield improved significantly with increasing catalyst loading, peaking at 91% at 4 wt%.

However, a further increase in catalyst quantity resulted in a decrease in BHET yield. This inverse behavior is likely due to an overabundance of basic sites on the catalyst surface, which, while initially promoting PET depolymerization, also enhanced reverse reactions, such as re-polymerization of BHET into oligomers. This phenomenon underscores the delicate balance between catalytic activity and

selectivity, emphasizing the need for optimal catalyst dosage to maximize BHET yield while suppressing undesirable side reactions (Ghaemy & Mossaddegh, 2005; Xi et al., 2005a).

3.3.3.3. Optimization of Ethylene Glycol Loading and Reaction Temperature

The impact of EG concentration on the efficiency of PET glycolysis was investigated by altering its molar equivalent from 6 to 20 under optimal catalyst loading (4 wt%) and reaction conditions (190 °C, 1.5 hours). The data presented in **Figure 3.29(a)** show that even at 6 equivalents of EG, a substantial BHET yield of 73% was achieved. However, the yield improved consistently with increasing EG concentration, peaking at 91% with 16 equivalents. Beyond this optimum, excess EG likely diluted the catalyst concentration in the medium, reducing the overall catalytic effectiveness.

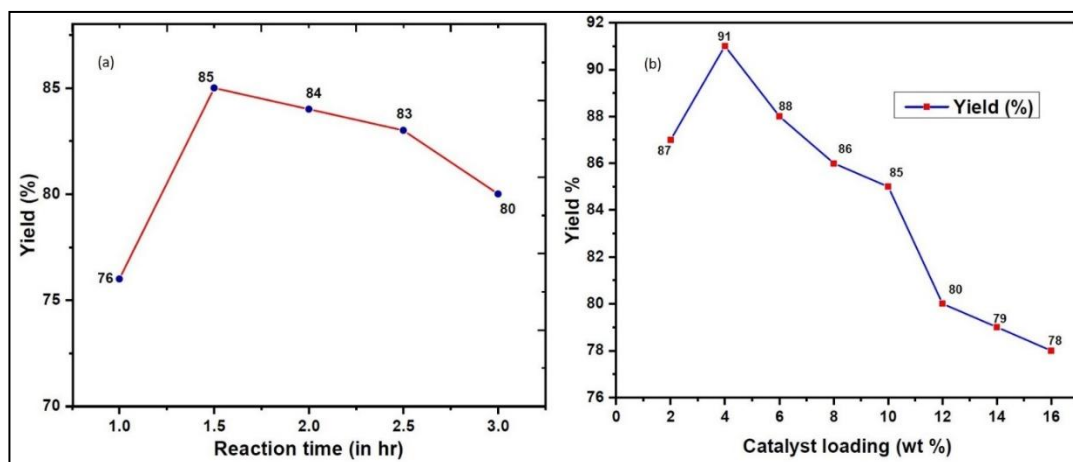


Figure 3.28: (a) Optimization of the reaction time. Reaction condition: 2.5 mmol of PET flakes, 16 equivalent of EG, 10 wt% of catalyst, at 190 °C. (b) Optimization of catalyst loading. Reaction condition: 2.5 mmol of PET flakes, 16 equivalent of EG, 1.5 hrs reaction time, at 190 °C.

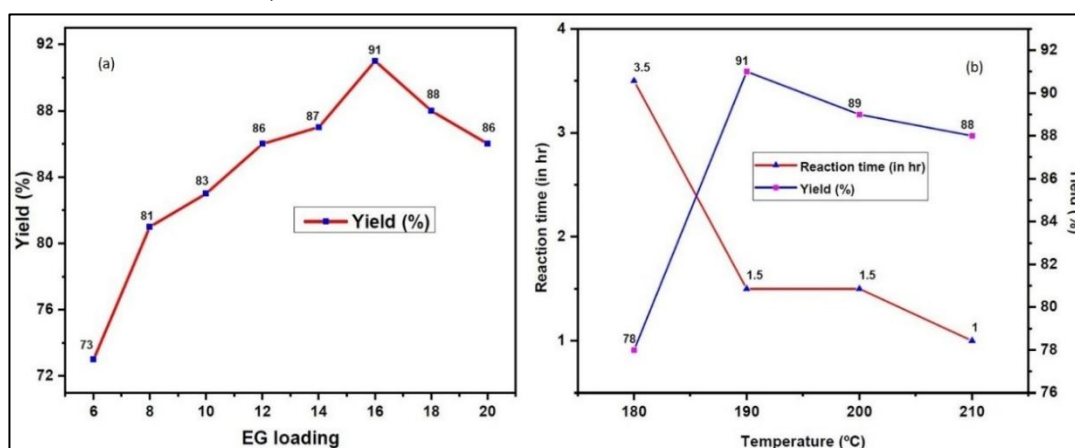


Figure 3.29: (a) Optimization of reagent loading. Reaction condition: 2.5 mmol of PET flakes, 4 wt% catalyst, 1.5 hrs reaction time, at 190 °C. (b) Optimization of reaction temperature. Reaction condition: 2.5 mmol of PET flakes, 4 wt% catalyst, 16 equivalent of EG.

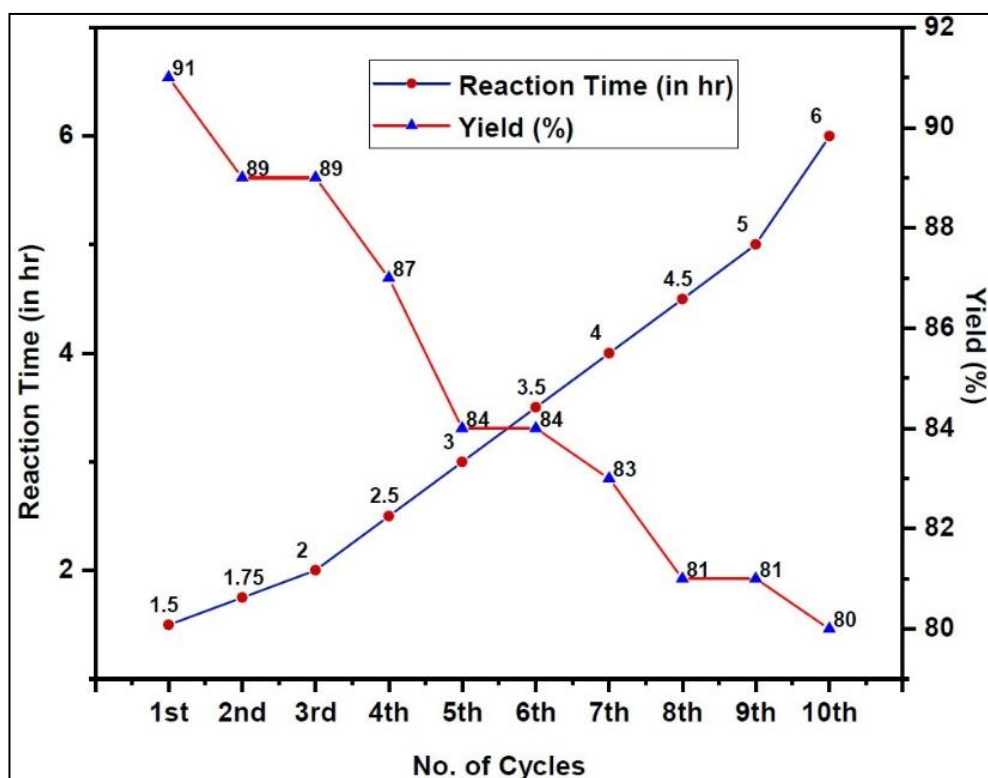


Figure 3.30: Reusability of OPA@Fe₃O₄ catalyst up to 10th catalytic cycles. Reaction condition: 2.5 mmol of PET flakes, 4 wt% catalyst, 16 equivalent of EG, at 190 °C.

Simultaneously, the reaction temperature was optimized within the range of 180-200 °C (**Figure 3.29(b)**). At 180 °C, the reaction required an extended duration (3.5 hours) to achieve 78% BHET yield. In contrast, operation at 200 °C accelerated the process but resulted in increased formation of oligomers, thereby slightly reducing the BHET yield. The optimum temperature was thus established at 190 °C, offering a balance between reaction kinetics and product purity.

3.3.3.4. Catalyst Reusability and Post-Use Analysis

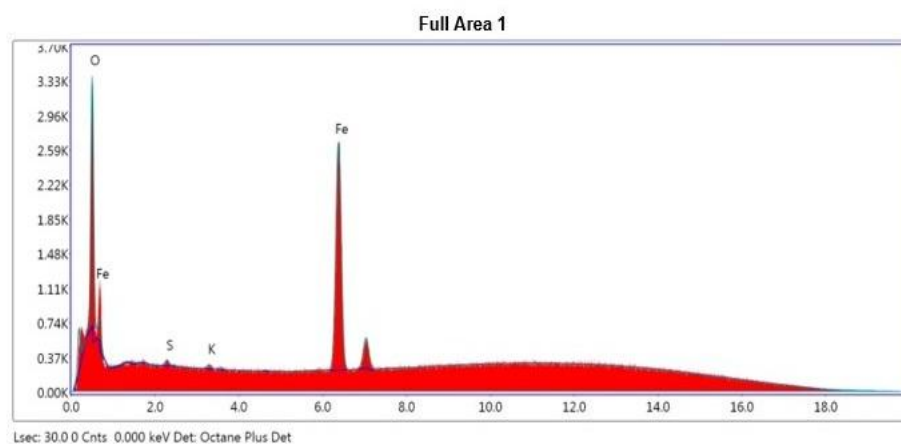
A critical requirement for sustainable catalysis is the ability to recover and reuse the catalyst over multiple cycles. To assess this, the OPA@Fe₃O₄ catalyst was magnetically separated after each reaction cycle, washed thoroughly with hot methanol, and dried at 80 °C before reuse without reactivation. As shown in **Figure 3.30**, the catalyst maintained high catalytic activity over 10 consecutive cycles, consistently yielding over 85% BHET, with only a minor decline observed.

Characterization of the spent catalyst post-10 cycles using SEM and TEM (**Figure 3.32** indicated that the morphology and particle size were largely retained, suggesting minimal structural degradation. EDX analysis (**Table 3.15; Figure 3.31**), however, revealed a significant decrease in potassium content, while the iron and oxygen content remained relatively stable. This leaching of potassium could account for the slight reduction in catalytic performance over time, confirming the role of surface-bound K^+ ions as key active sites in the catalytic process.

Table 3.15: EDX data of recovered catalyst after 10th catalytic cycles

Sl No.	Elements	Weight %	Atomic %
1	O	28.02	57.45
2	Si	0.39	0.40
3	K	0.40	0.34
4	Fe	71.19	41.81

kV: 20 Mag: 5000 Takeoff: 36.1 Live Time(s): 30 Amp Time(μs): 0.96 Resolution:(eV)137.8



eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	R	A	F
O K	28.02	57.45	1,400.35	6.39	0.17	1.18	0.9	0.53	1
S K	0.39	0.40	36.08	49.01	0.00	1.06	0.97	0.73	1.01
K K	0.40	0.34	34.79	54.81	0.00	1.01	0.99	0.91	1.06
FeK	71.19	41.81	2,462.29	2.19	0.66	0.92	1.03	1.01	1

Figure 3.31: EDX spectra of OPA@Fe₃O₄

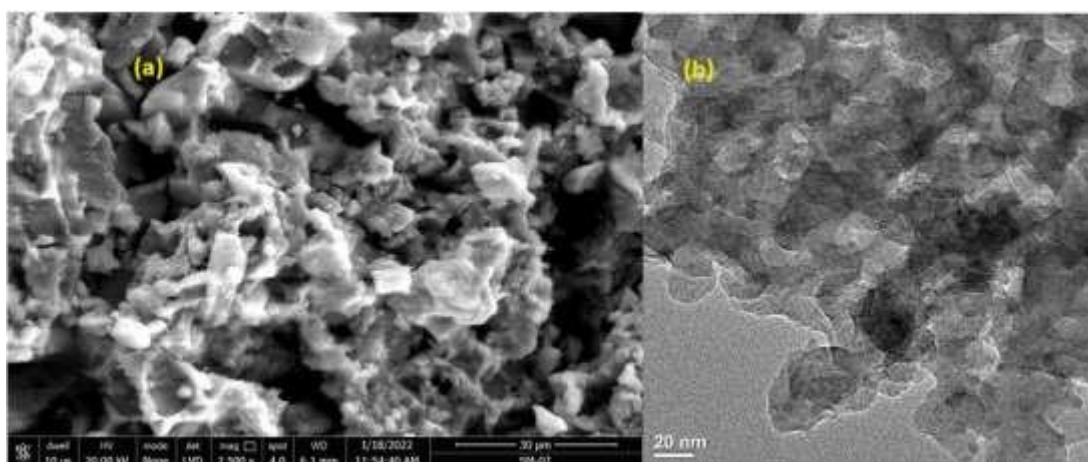


Figure 3.32: SEM (a) and TEM (b) images of OPA@Fe₃O₄ after 10th cycles

3.3.3.5. Glycolysis of Colored PET Bottles

The practical application of OPA@Fe₃O₄ was further validated by employing them in the glycolysis of colored PET bottles, which typically contain metal-based pigments and additives that may hinder catalytic performance. Remarkably, the process achieved complete depolymerization within 1.5 hours under optimized conditions, with BHET yields of 85%, 89%, and 88% for green, red, and light-yellow PET, respectively (**Table 3.16**).

Table 3.16: Glycolysis of color PET bottles^a

Sl No.	Color PET bottles	BHET Yield (%)
1	Green	85
2	Red	89
3	Light-yellow	88

^aReaction condition: 2.5 mmol of PET flakes, 4 wt% catalyst, 16 equivalent of EG, 1.5 hrs reaction time, at 190 °C.

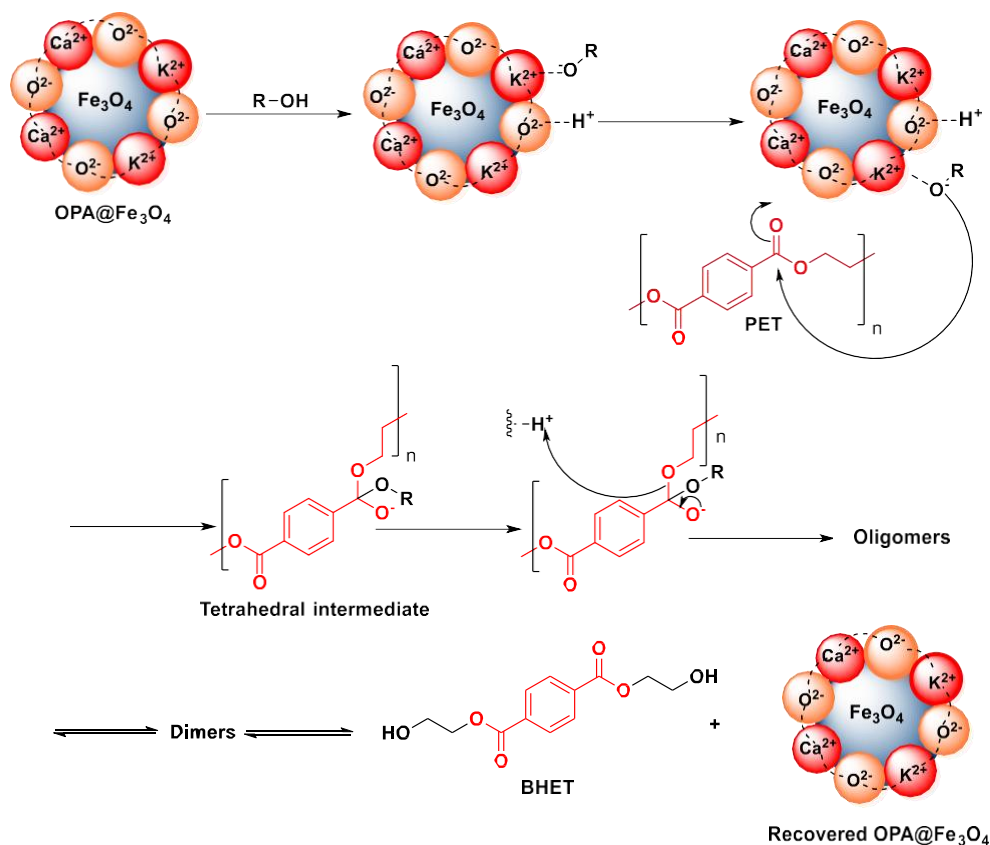
Decolorization was effectively accomplished through a two-step purification process involving recrystallization and treatment with 30 mg of activated charcoal, followed by filtration. The resulting BHET product was nearly colorless and free from pigment-related impurities, demonstrating the adaptability and robustness of OPA@Fe₃O₄ for mixed-PET waste recycling.

3.3.3.6. Proposed Reaction Mechanism

Based on analytical characterization and literature precedent, a mechanistic pathway was proposed for the OPA@Fe₃O₄ -catalyzed glycolysis of PET (**Scheme 3.3**). The process is initiated by the basic surface oxygen species (O²⁻) from metal oxides such as CaO and K₂O present in the OPA@Fe₃O₄. These sites facilitate deprotonation of EG to form nucleophilic ethoxide ions, which subsequently attack the carbonyl carbon of the PET ester bonds.

This nucleophilic substitution leads to the formation of a tetrahedral intermediate, which collapses to generate BHET and liberate smaller ester or hydroxyl-terminated PET fragments. Given the reversibility of the reaction,

equilibrium is established among PET oligomers, dimers, and BHET, necessitating precise reaction condition control to drive depolymerization forward (Changmai et al., 2021; Z. Laldinpui et al., 2021).



Scheme 3.3: Proposed mechanistic pathway for the glycolysis of PET

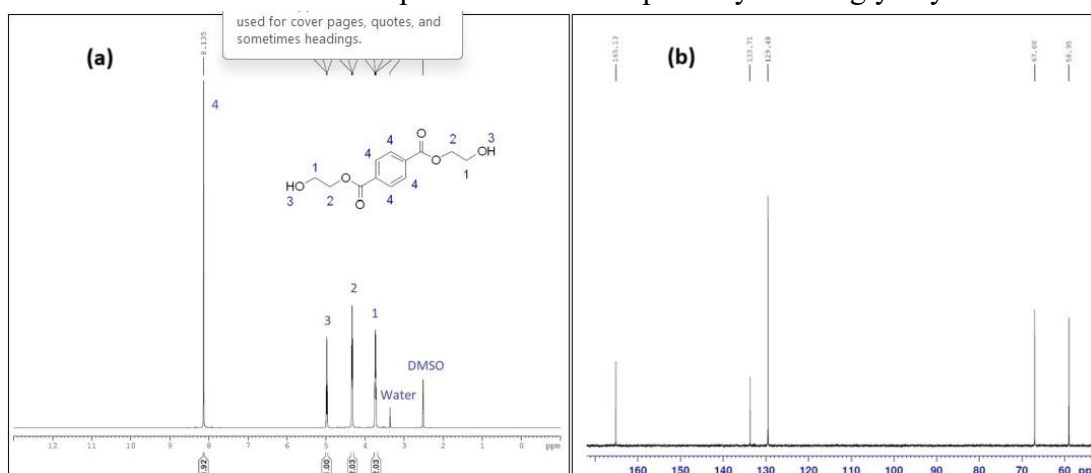


Figure 3.33: (a) ¹H NMR data of recrystallized BHET, (b) ¹³C NMR data of recrystallized BHET

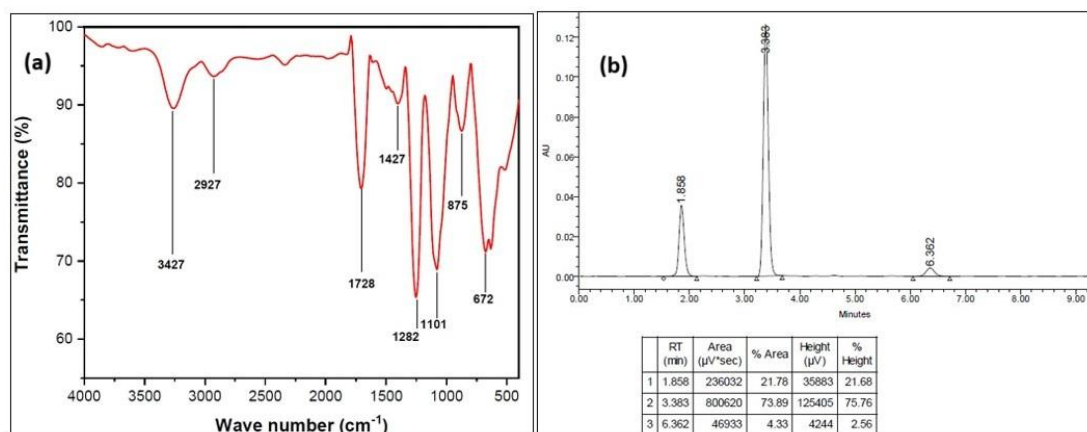


Figure 3.34: (a) FTIR data of recrystallized BHET, (b) HPLC data of the crude product

3.3.3.7. Characterization of the product

The structural integrity of the recrystallized BHET was validated using multiple analytical techniques. In the ^1H NMR spectrum (**Figure 3.33a**), the peaks at δ 8.13 ppm (aromatic protons), 4.98 ppm ($-\text{OH}$), 4.33 ppm ($\text{COO}-\text{CH}_2$), and 3.73 ppm (CH_2-OH) confirmed the expected proton environments. The ^{13}C NMR spectrum (**Figure 3.33b**) showed distinct signals at δ 165.13 ($\text{C}=\text{O}$), 133.71, 129.48 (aromatic carbons), 67.00 (CH_2-O), and 58.95 ppm (CH_2-OH), further corroborating the BHET structure.

FTIR analysis (**Figure 3.35a**) revealed prominent absorption bands at 3427 cm^{-1} ($-\text{OH}$), 2927 cm^{-1} ($\text{C}-\text{H}$), and 1728 cm^{-1} ($\text{C}=\text{O}$ stretching), along with ester $\text{C}-\text{O}$ vibrations at 1282 cm^{-1} and 1101 cm^{-1} . HPLC analysis (**Figure 3.34b**) confirmed the presence of EG (1.858 min), BHET (3.383 min), and its dimer (6.362 min), indicating selective formation and partial condensation of BHET during glycolysis.

3.4. METHANOLYSIS OF POLYETHYLENE TEREPHTHALATE (PET)

3.4.1. Methanolysis of PET Using Orange Peel Ash (OPA)

The methanolytic depolymerization of polyethylene terephthalate (PET) was successfully carried out under hydrothermal conditions using orange peel ash (OPA), a biomass-derived heterogeneous base catalyst rich in alkaline earth and transition metal oxides. The reaction was conducted at 200 °C in a Teflon-lined autoclave, employing 480 mg of PET flakes and an excess of methanol as the solvent, in the presence of OPA catalyst. Following the reaction, the product was extracted with hot methanol and recrystallized by cold precipitation, yielding dimethyl terephthalate (DMT) as the major product in high purity. This process offers an efficient and sustainable route for PET recycling, converting post-consumer plastic waste into valuable monomers suitable for repolymerization or further chemical applications.

3.4.1.1. Product Analysis and Characterization

High-performance liquid chromatography (HPLC) of the crude product confirmed the formation of DMT and ethylene glycol (EG) as the primary depolymerization products, with minor amounts of bis(2-hydroxyethyl) terephthalate (BHET) and 2-hydroxyethyl methyl terephthalate (HEMT) detected as side products. These were identified by comparison with authentic standards (**Figures 3.35**).

Subsequent ^1H and ^{13}C NMR analysis of recrystallized DMT showed distinct peaks at $\delta = 8.012$ ppm (aromatic $-\text{CH}$) and $\delta = 3.860$ ppm (methyl ester $-\text{OCH}_3$), with corresponding carbon signals at $\delta = 166.29$ (carbonyl carbons), 133.89 (quaternary carbon), 129.54 (aromatic carbons), and 52.44 (methyl ester carbon) ppm, conclusively verifying product structure (**Figure 3.35**). These results affirm the selective cleavage of PET ester bonds via a transesterification mechanism catalyzed by OPA.

The FTIR spectra (**figure 3.36**) displayed an absorption band at 1720 cm^{-1} which is characteristic of carbonyl groups; the strong absorption bands at 1262 and 1050 cm^{-1} due to the ester $\text{C}-\text{O}$ and $\text{C}-\text{O}-\text{C}$ stretching vibrations further confirm

DMT ester functionality. Additional peaks observed at 1430 cm^{-1} and 2965 cm^{-1} indicates the presence of aromatic C–H and methyl group, respectively.

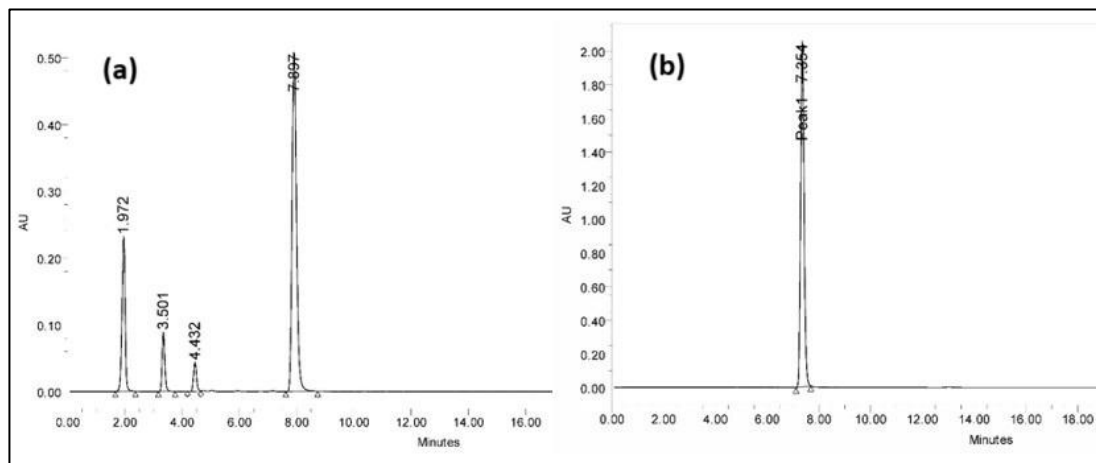


Figure 3.35: (a) HPLC data of the crude product, (b) HPLC data of recrystallized DMT

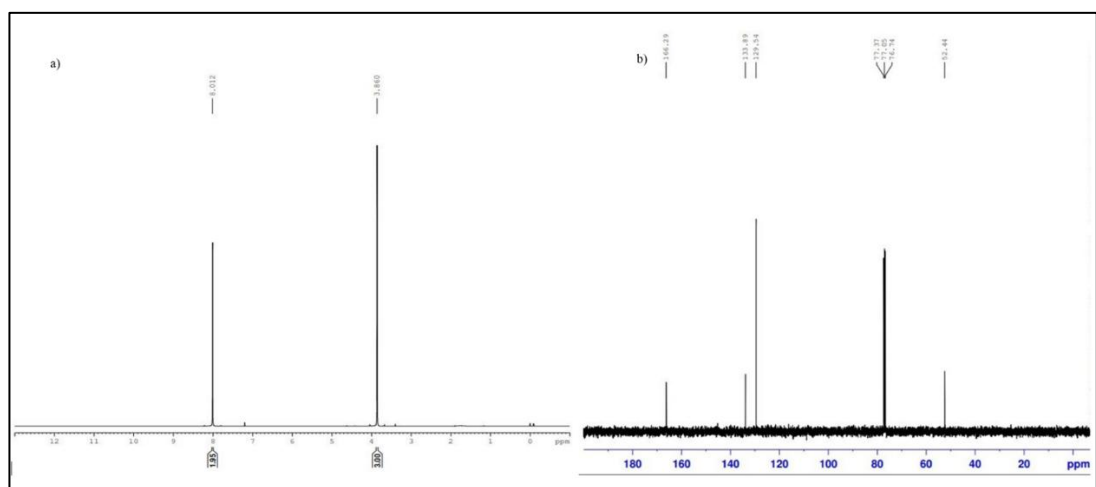


Figure 3.36: (a) ^1H NMR data of DMT, (b) ^{13}C NMR data of DMT

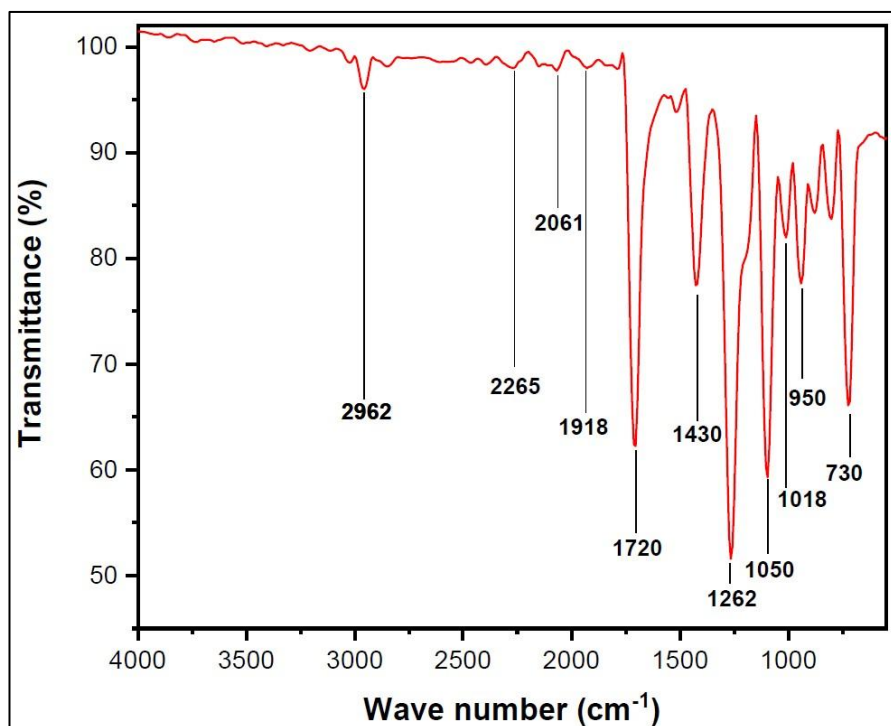


Figure 3.37: FT-IR data of recrystallized DMT

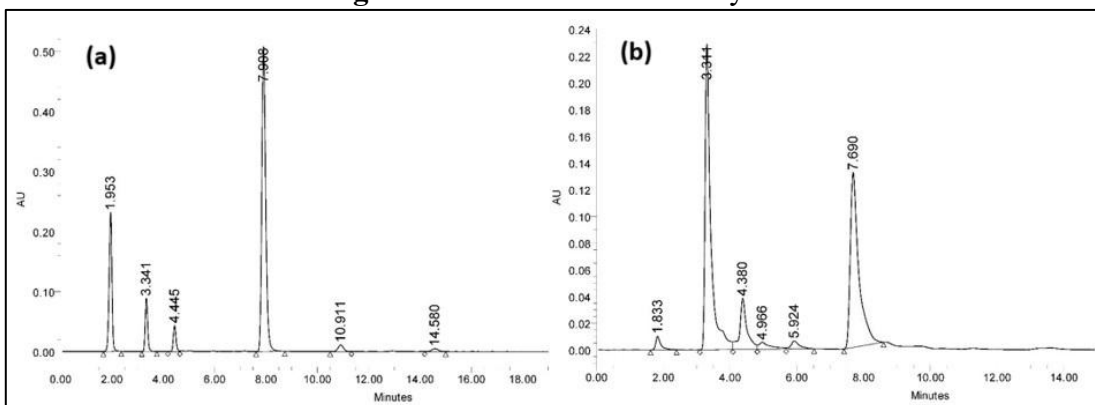


Figure 3.38: (a) HPLC data of the crude product using a reduced methanol loading, (b) HPLC data of the crude product after 2 hrs reaction time

3.4.1.2. Optimization of Reaction Conditions

Catalyst Loading

The effect of OPA concentration was examined by varying catalyst loadings from 10 to 70 mg under otherwise constant conditions. A catalyst loading of 30 mg (6 wt%) yielded the highest conversion, producing 79% DMT and 73% EG within 1

hour (**Table 3.17**). Increasing the catalyst amount beyond this threshold resulted in diminished yields, likely due to excessive basicity promoting reverse reactions such as re-polymerization of monomers into oligomers. This equilibrium behavior reflects findings from Wang et al. (2009) and emphasizes the necessity of optimal catalyst dosage for maximum depolymerization efficiency (H. Wang et al., 2009).

Scheme 3.4: Methanolysis of PET

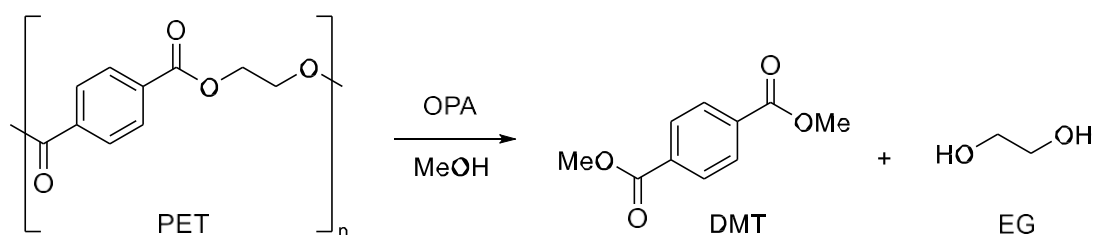


Table 3.17: Optimization of methanolysis of PET using OPA^a

Sl. No.	Catalyst loading (mg)	MeOH loading (mL)	Reaction time (h)	Reaction temp. (°C)	DMT Yield (%) ^b	EG Yield (%) ^c
1	-	5	48	200	0.8	-
2	10	5	1	200	56	53
3	20	5	1	200	62	62
4	30	5	1	200	79	73
5	50	5	1	200	73	67
6	70	5	1	200	66	66
7	30	3	1	200	68	69
8	30	8	1	200	73	71
9	30	10	1	200	69	70
10	30	5	0.5	200	69	67
11	30	5	1.5	200	71	69
12	30	5	2	200	68	62
13	30	5	3	190	65	56
14	30	5	1	210	77	74
15	30	5	1	220	75	76

^a PET (500 mg). ^b Recrystallized product. ^c Isolated yield

Methanol Volume

Varying the methanol volume from 3 to 10 mL revealed that 5 mL was optimal. Lower methanol concentrations (e.g., 3 mL) resulted in lower monomer

yield and greater formation of BHET and HEMT (**Figure 3.38a**), while excess methanol diluted the effective catalyst concentration, reducing contact efficiency. Thus, a methanol-to-PET molar ratio of ~49 equivalents was ideal for maintaining high conversion and selectivity.

Reaction Time and Temperature

The time course study indicated that PET depolymerization progressed rapidly within the first 30 minutes, achieving 69% DMT yield, with a maximum of 73% at 60 minutes. Prolonged reaction times beyond 90 minutes led to increased secondary product formation, confirming the reversible nature of the transesterification process (**Table 3.17; Figure 3.38b**).

Temperature optimization showed that 200 °C was the most favorable, ensuring rapid ester bond cleavage and high DMT yield. At 190 °C, longer times were required (3 h for 65% yield), while increasing temperature to 210-220 °C initially enhanced yield but subsequently promoted undesired side reactions, likely due to thermal degradation and recombination events (Kurokawa et al., 2003).

3.4.2.3. Methanolysis of Colored PET Bottles

To evaluate real-world applicability, methanolysis was extended to colored PET bottles under optimized conditions (30 mg OPA, 5 mL MeOH, 1 h, 200 °C). Slightly reduced yields were observed for red (67%), light-yellow (58%), and green (74%) PET (**Table 3.18**), likely due to acidic pigment additives, which may neutralize basic active sites on OPA (Fukushima, Coulembier, Lecuyer, Almegren, Alabdulrahman, Alsewailem, McNeil, et al., 2011). Nevertheless, the crystallized DMT remained structurally consistent with that from clear PET, as verified by UV-Vis spectra (**Figure 3.39**), and color impurities were effectively removed via activated charcoal treatment.

Table 3.18: Methanolysis of Colored PET Bottles using OPA

Sl. No.	PET Color	Catalyst Loading	MeOH (mL)	Time (h)	Temp. (°C)	Temp. (°C)
1	Clear	30	5	1	200	
2	Red	30	5	1	200	200
3	Light-Yellow	30	5	1	200	200
4	Green	30	5	1	200	200

3.4.2.4. Catalyst Reusability

The heterogeneous nature of OPA allowed for easy catalyst recovery via filtration, followed by ethanol washing and drying at 80 °C. The catalyst was reused for four cycles with minor loss in yield, from 79% (first cycle) to 71% (fourth cycle) (**Table 3.19**). However, a gradual increase in reaction time (from 1.0 to 3.5 hours) was observed, indicating loss of catalytic activity over cycles.

This deactivation is attributed to the leaching of basic active sites, especially potassium and calcium oxides, as supported by EDX analysis in previous catalyst studies. Maintaining activity over multiple cycles may therefore require regeneration protocols or dopant reinforcement.

Table 3.19: Reusability of the Catalyst

Sl. No.	No. Cycle	Catalyst Loading	MeOH (mL)	Time (h)	Temp. (°C)	DMT
1	First	30	5	1	200	Yield %
2	Second	30	5	1.5	200	78
3	Third	30	5	2.5	200	73
4	Fourth	30	5	3.5	200	71

3.4.2.5. Proposed Mechanism

From the in-depth analysis of the OPA catalyst, it is believed that the oxides and carbonates of K, Ca, Mg, Mn, Fe, etc., present in the catalyst are the active sites for PET depolymerization. And, PET transesterification process is strongly assumed to be of cation-anion collaborative effect and the proposed reaction mechanism is shown in **Scheme 3.5**. It is also believed that methanolysis of PET proceeds through three steps: i) shortening of the PET chain to about 1/3, ii) depolymerization into the oligomers, and iii) formation of the monomers using the catalyst.

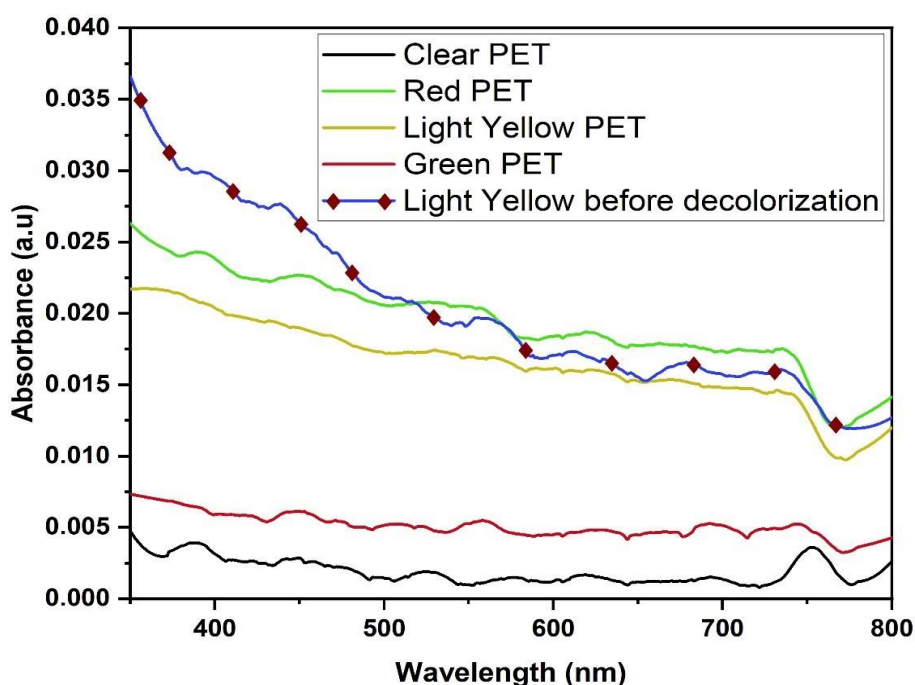
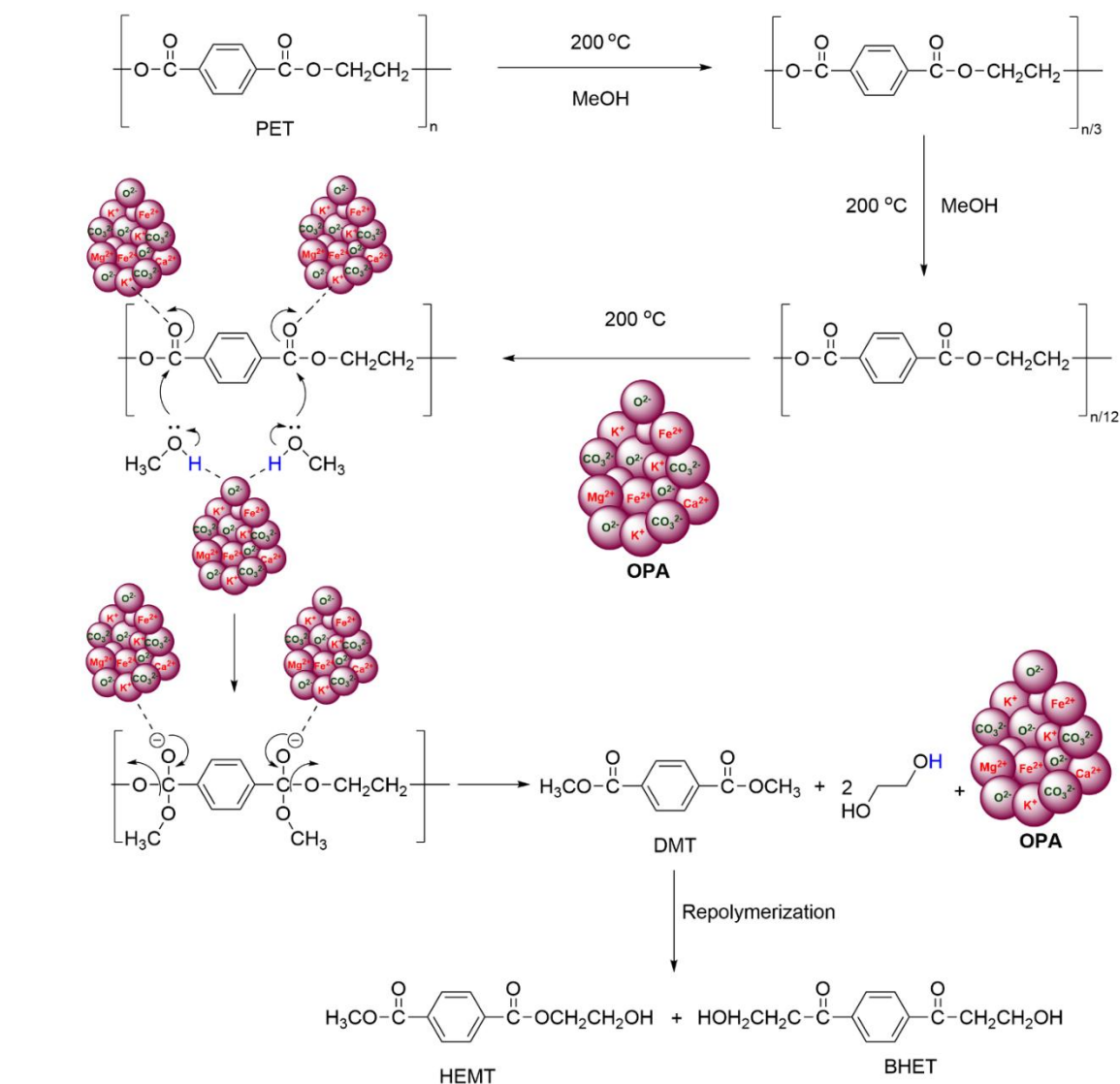


Figure 3.39: UV-Vis Spectra of DMT monomer obtained from clear, red, light-yellow and green PET bottles. The samples were dissolved in chloroform (5 mg/ml).



Scheme 3.5: Proposed mechanistic pathway for methanolysis of PET waste using OPA

As OPA is composed of various metals in the forms of their oxides and carbonates, these metal cations act as Lewis acid which protonate the oxygen of the carbonyl in the ester groups, enhancing the polarity as well as electrophilicity at the carbonyl carbon. The subsequent abstraction of hydrogen from methanol by carbonates or oxides of OPA facilitates a nucleophilic attack from the oxygen of methanol. This results in the cleavage of the ester linkage with a succeeding formation of a new C–O bond, yielding DMT and EG as depolymerized products. However, as the reaction proceeds further, DMT and EG re-amalgamated to form 2-

hydroxyethyl methyl terephthalate (HEMT) and bis-(2-hydroxyethyl) terephthalate (BHET) in a reversible process.

3.4.2. Methanolysis of Polyethylene Terephthalate (PET) Using Bamboo Leaf Ash (BLA)

The methanolysis of polyethylene terephthalate (PET) presents a viable chemical recycling strategy for converting post-consumer plastic waste into valuable monomers under controlled thermal conditions. In this study, Bamboo Leaf Ash (BLA) a sustainable, low-cost, biomass-derived solid base catalyst was employed to catalyze the depolymerization of PET into dimethyl terephthalate (DMT) and ethylene glycol (EG). BLA was selected for its high content of basic metal oxides (CaO, K₂O, MgO, Fe₂O₃), mesoporous architecture, and abundant surface basicity, as confirmed by EDX, SEM/TEM, and complementary characterization techniques discussed in previous section (**Chapter 2 section 3.1.2**). These features collectively provide a synergistic platform for efficient ester bond cleavage and transesterification reactions.

3.4.2.1. Product Characterization and Analysis

Depolymerization was carried out at 200 °C in a Teflon-lined autoclave, using 480 mg of PET flakes, 5 to 10 mL of methanol, and 100 mg of BLA. Following reaction completion and recrystallization from hot methanol, the product mixture was analyzed by high-performance liquid chromatography (HPLC), which revealed the formation of DMT and EG as primary products, alongside minor quantities of BHET and 2-hydroxyethyl methyl terephthalate (HEMT). These compounds were confirmed by comparative retention times against commercial standards: EG (2.177 min), BHET (3.259 min), HEMT (4.273 min), and DMT (7.354 min).

The ¹H NMR spectrum of purified DMT exhibited characteristic singlets at δ = 8.099 ppm (aromatic protons) and δ = 3.948 ppm (methyl esters), while ¹³C NMR displayed peaks at δ = 166.85, 134.48, 130.13, and 53.01 ppm, corroborating its structure (**Figures 3.41**). Additionally, FTIR spectra (**Figure 3.42**) confirmed the presence of ester functionalities, with intense bands at 1703 cm⁻¹ (C=O stretch), 1262 and 1087 cm⁻¹ (C–O stretches), and a methyl C–H stretch at 2952 cm⁻¹. Collectively,

these data confirm the successful cleavage of PET into high-purity DMT under basic catalytic conditions.

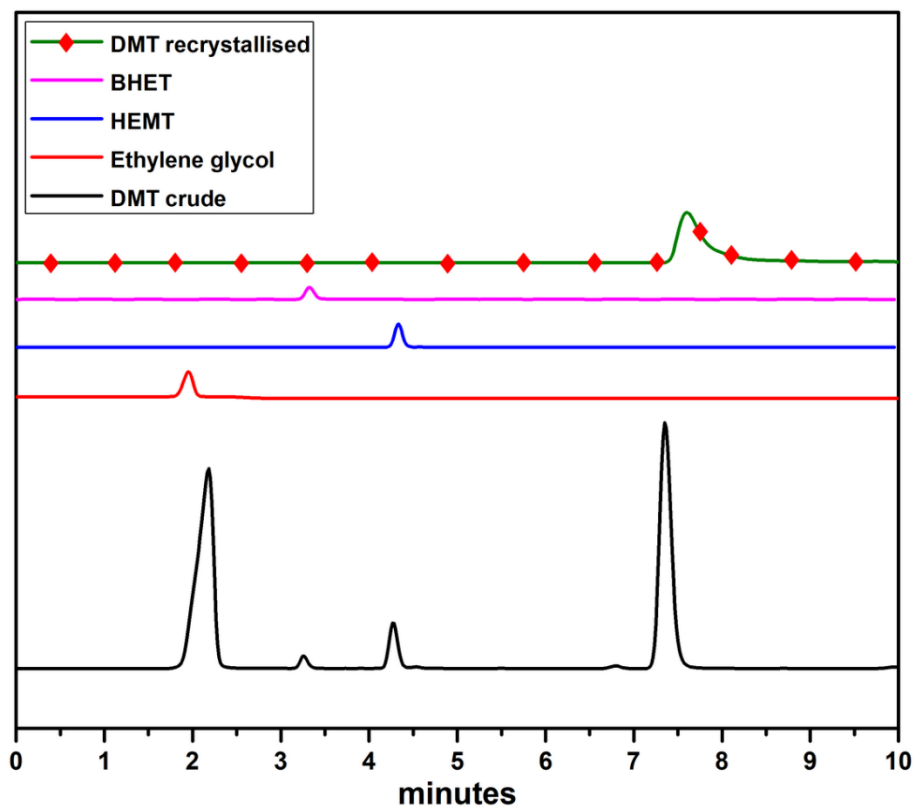


Figure 3.40: HPLC data of recrystallized DMT, commercially BHET, commercially HEMT, commercial EG and the crude product

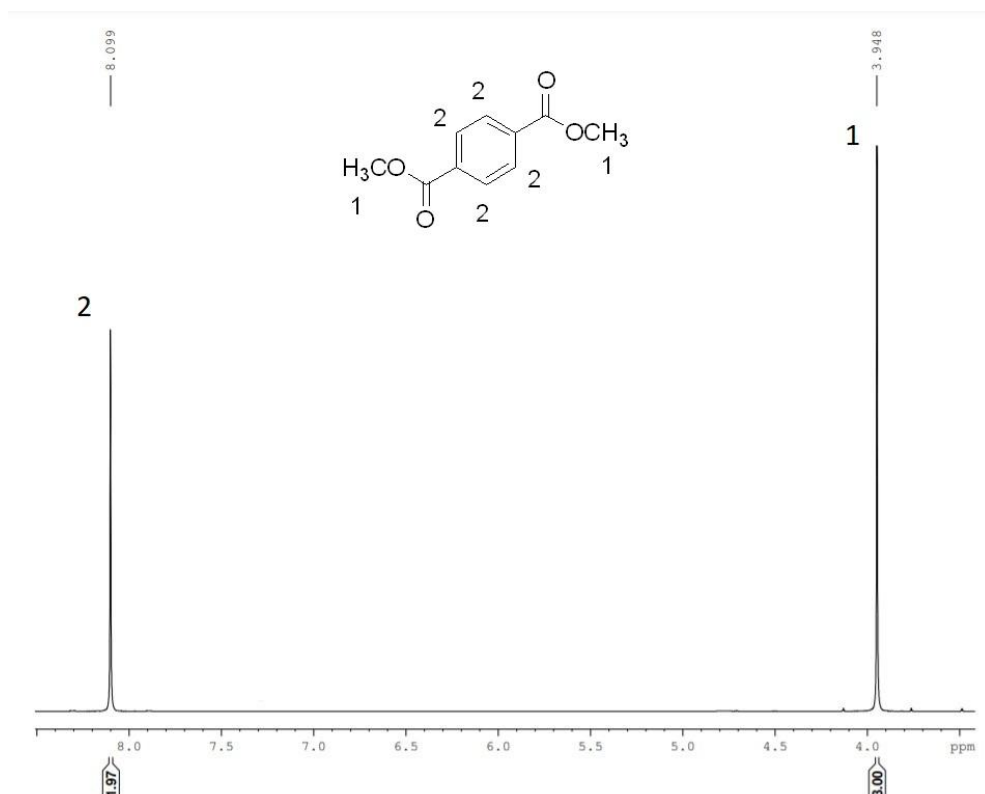


Figure 3.41: ^1H NMR spectra of recrystallized DMT

3.4.2.2. Optimization of Reaction Parameters

Effect of Catalyst Loading

Catalyst loading was found to be a key determinant of PET conversion efficiency. As shown in **Figure 3.43a**, increasing BLA dosage up to 100 mg improved DMT yield substantially, achieving a maximum of 73% within 2 hours. However, further increases beyond this threshold (e.g., 120 mg) led to no significant gain in monomer yield, and instead promoted formation of side-products such as BHET and HEMT (**Figure 3.43a**), likely due to equilibrium limitations and oligomer reformation. These findings align with previously reported mechanistic insights into PET depolymerization via methanolysis (Kurokawa et al., 2003), highlighting the importance of precise catalyst dosing to avoid adverse backward reactions.

Effect of Reaction Time and Temperature

Time-course experiments (**Figure 3.43b**) revealed that extending the reaction from 1 to 2 hours significantly improved DMT yield, while further prolongation

beyond 2 hours caused a mild decline in product output, likely due to thermodynamically favored repolymerization of DMT into oligomers, as evidenced by increased peak areas of BHET and HEMT in HPLC analysis (**Figure 3.44b**).

Temperature played a critical role in dictating both the reaction rate and product selectivity. As shown in **Figure 3.45a**, 200 °C was optimal for complete PET depolymerization within 2 hours. At 180 °C, incomplete depolymerization persisted even after 4 hours, whereas temperatures above 200 °C (e.g., 220 °C) induced excessive thermal activity that favored formation of oligomeric byproducts at the expense of monomer selectivity.

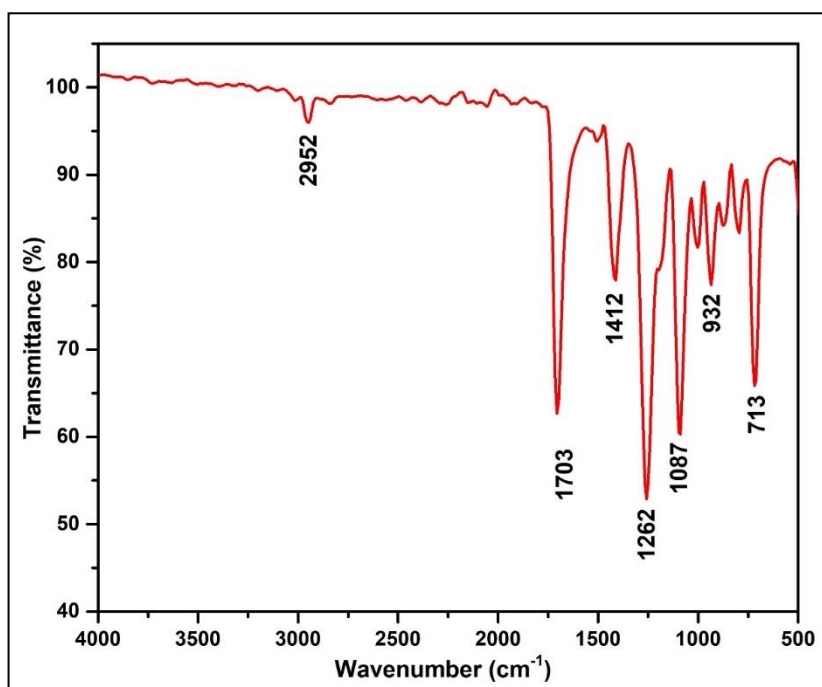


Figure 3.42: IR data of recrystallized DMT

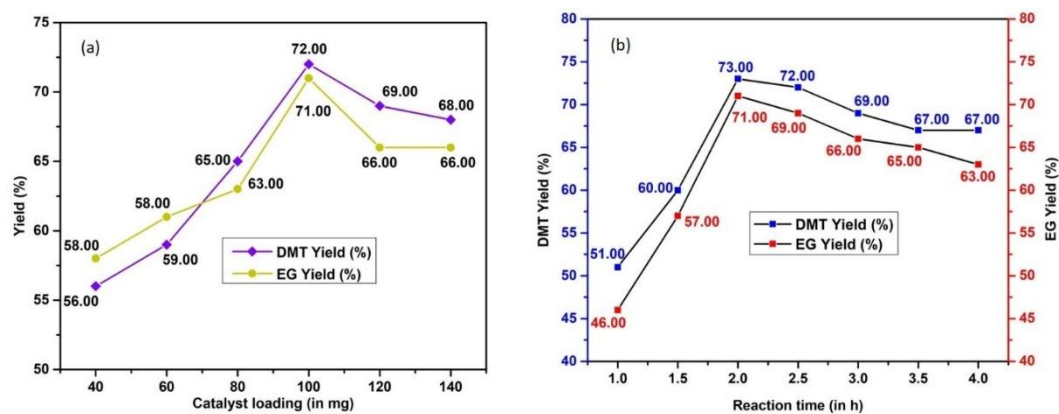


Figure 3.43: (a) Influence of catalyst charging on methanolysis of PET. Reactions were carried out with 480 mg of PET, 5 mL of methanol and varied amount of catalyst at 200 °C for 2 hrs. (b) Influence of time on DMT yield. Reaction condition of 200 °C, 480 mg of PET, 100 mg of BLA and 5 mL of methanol.

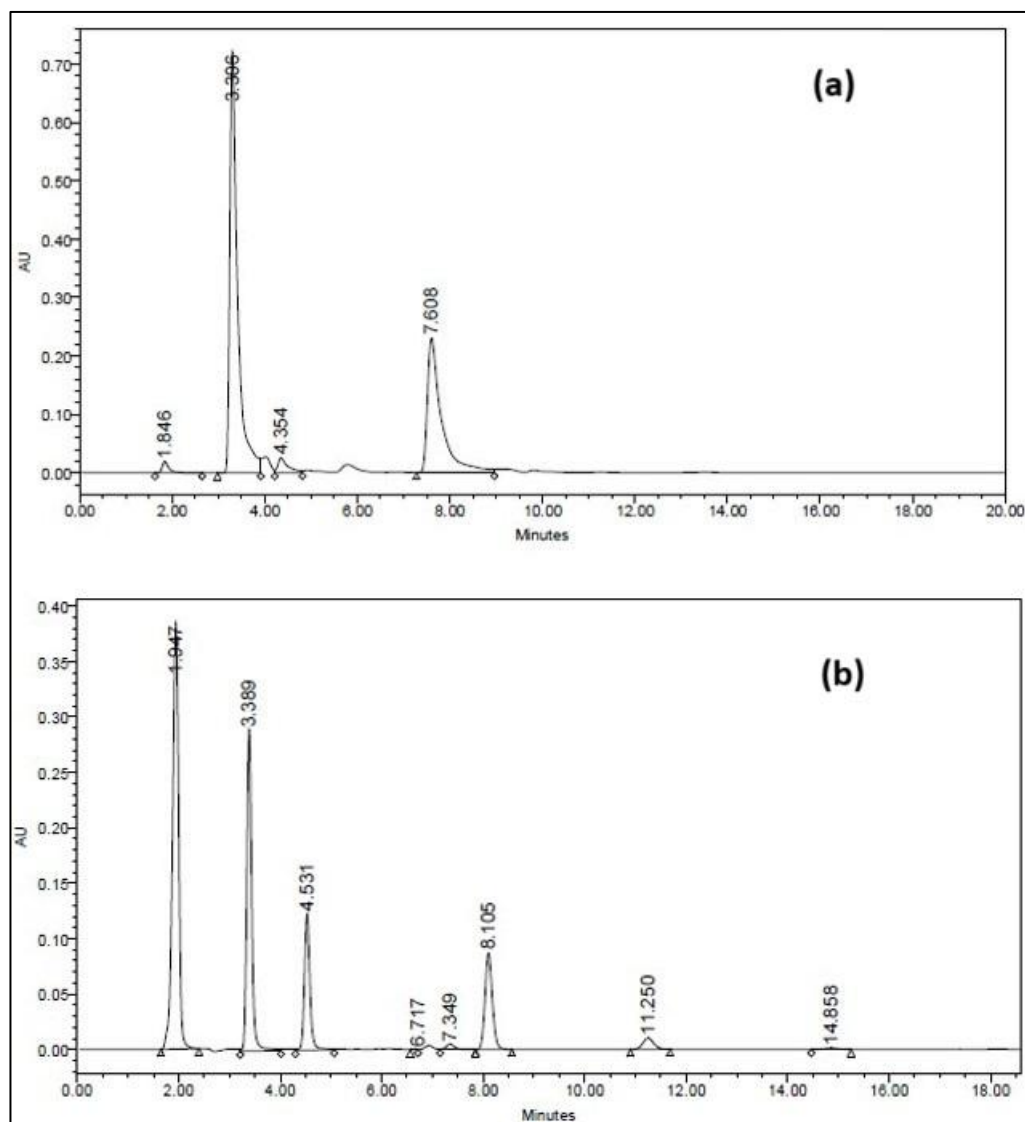


Figure 4.44: (a) HPLC data of the crude product with 120 mg of BLA loading, (b) HPLC data of the crude product after 3 hrs of reaction time.

Effect of Methanol Concentration

The methanol-to-PET ratio was systematically varied from 2 to 12 mL (**Figure 3.45b**). An increase in methanol volume to 10 mL led to enhanced depolymerization, likely due to improved mass transfer and solvation of oligomers. However, further increases in methanol concentration resulted in slight declines in DMT yield, possibly due to dilution of catalyst concentration in the reaction medium, and increased equilibrium reversal. These results highlight the necessity of optimizing reagent stoichiometry for maximal process efficiency.

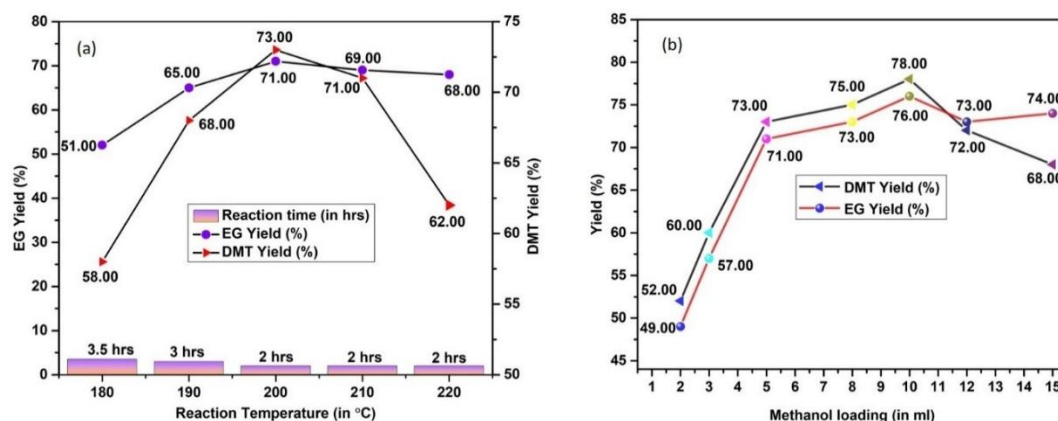


Figure 3.45: (a) Influence of temperature on methanolysis of PET. Reactions with 480 mg of PET, 100 mg of BLA, 5 mL of methanol at 200 °C. (b) Influence of methanol concentration on methanolysis of PET. Reactions with 480 mg of PET, 100 mg of BLA and varied amounts of methanol concentration for 2 hrs at 200 °C.

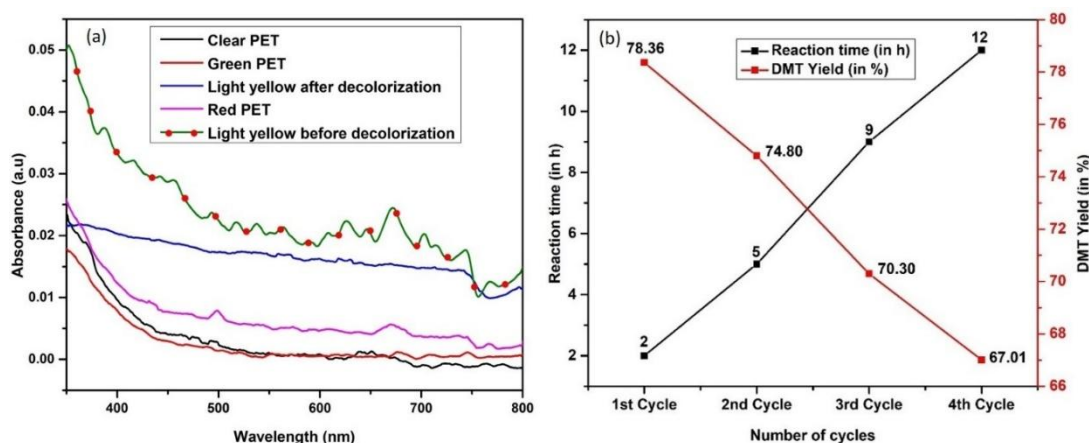


Figure 3.46: (a) UV-vis spectra of DMT monomer derived from clear, green, light-yellow (before and after decolorization) and red PET bottles. (b) Reusability of BLA on degradation of PET. Reaction condition: 480 mg PET, 100 mg BLA, 10 mL methanol, 200 °C.

3.4.2.3. Application to Colored PET Waste

To evaluate catalyst robustness, the optimized methanolysis conditions were applied to colored PET bottles (red, green, and light-yellow). Despite the presence of acidic pigment additives, which are known to interfere with base-catalyzed reactions, BLA achieved high selectivity for DMT. Yields ranged from 58% (light-yellow) to 74% (green) (**Table 3.20**), slightly lower than those observed with clear PET.

Table 3.20: Recycling of color bottles^a

Sl. No.	Color PET bottle	DMT yield (%) ^b	EG yield (%) ^c
1	Red	67	71
2	Light-yellow	58	69
3	Green	74	70

^aReaction conditions: 480 mg of PET, 100 mg of BLA, 10 mL methanol, 200 °C, 2 hrs. ^bYield of recrystallized product. ^cPercent recovery yield.

However, these colorants were effectively removed during recrystallization and decolorized further with activated charcoal, resulting in optically pure DMT, as confirmed by UV-Vis absorbance spectra (**Figure 3.46a**). These findings demonstrate the practical applicability of BLA in treating complex PET waste streams with minimal compromise on product quality.

3.4.2.4. Catalyst Reusability and Structural Evaluation

Reusability is a vital metric for assessing the industrial feasibility of heterogeneous catalysts. BLA was subjected to four consecutive reaction cycles under optimized conditions (**Figure 3.46b**). A gradual decrease in DMT yield from 73% to 67% was observed over these cycles, along with extended reaction times. This decline is likely due to leaching of catalytically active metal species, as confirmed by EDX analysis (**Figure 3.47, Table 3.21**), which showed marked depletion of Ca, Mg, K, and Fe.

Table 3.21: EDX data for elemental composition of Recovered BLA.

SI No.	Elements	Weight %	Atomic %
1	O	53.28	67.22
2	Al	1.19	0.89
3	Si	40.62	29.20
4	P	1.06	0.69
6	S	0.52	0.33
7	Ca	3.33	0.33

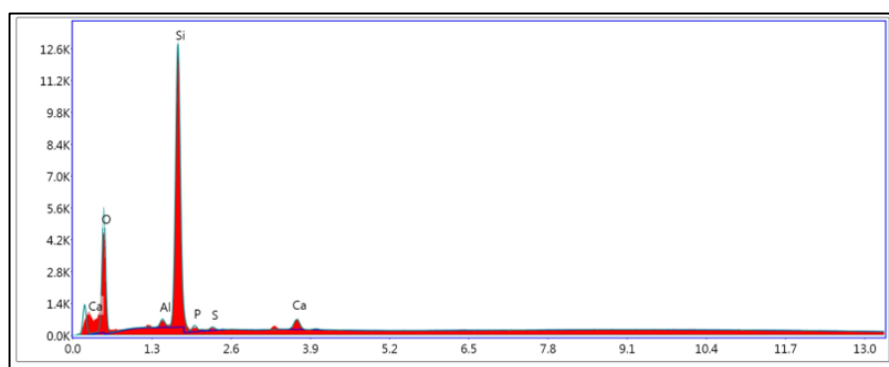


Figure 3.47: EDX data of recovered BLA catalyst

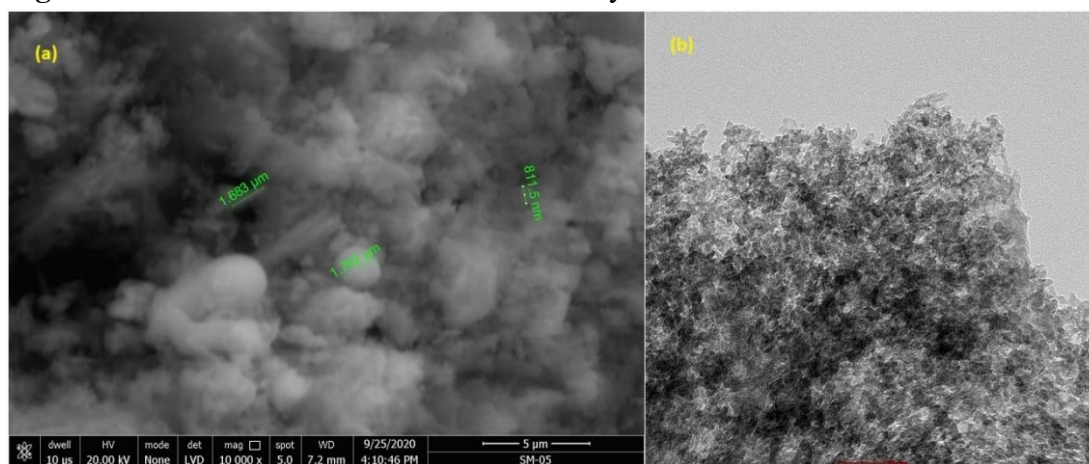


Figure 3.48: (a) SEM images of recovered BLA catalyst after four catalytic cycles, (b) TEM images of recovered catalyst after four catalytic cycles.

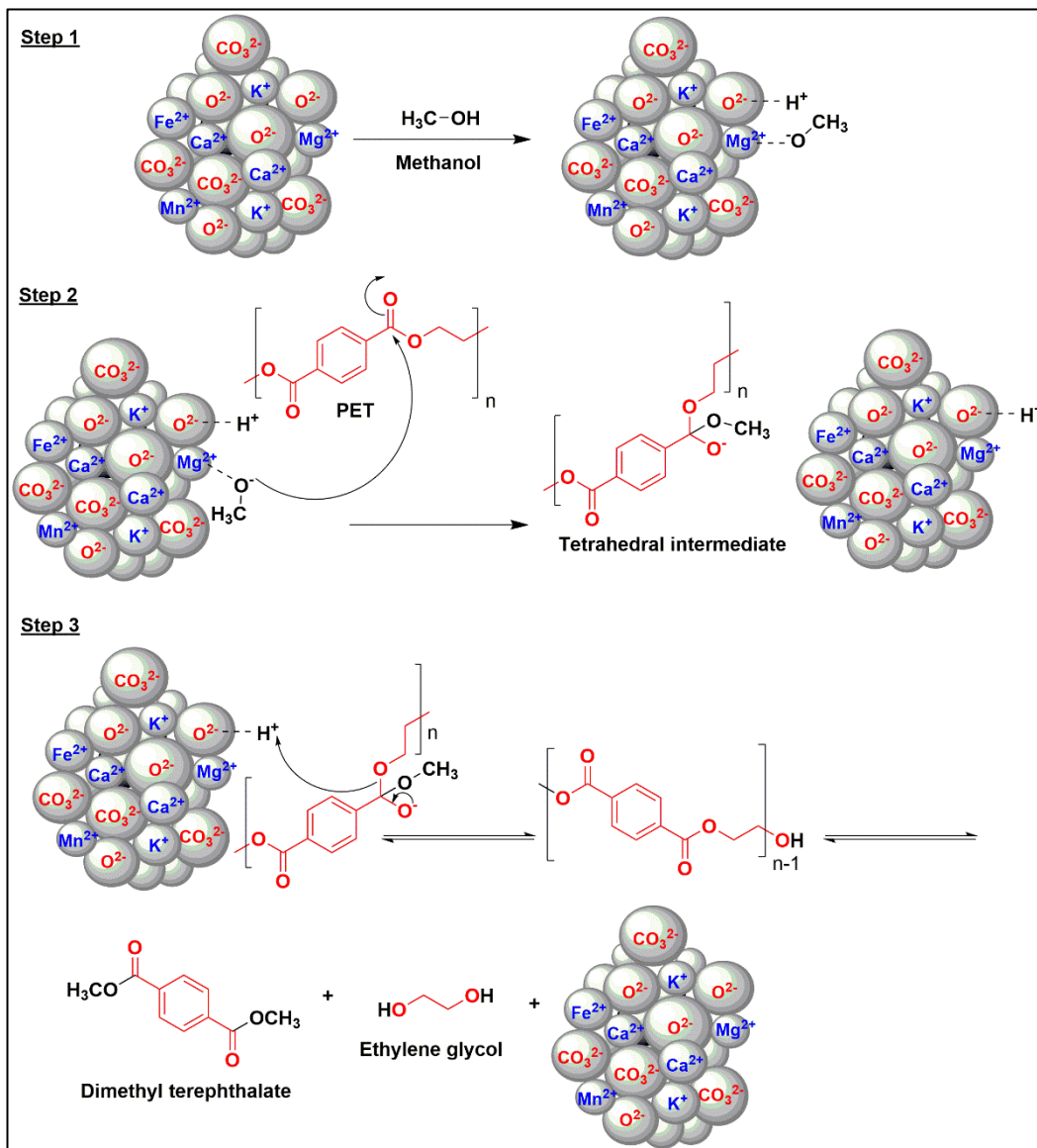
Despite elemental losses, SEM and TEM analyses (**Figures 3.48 (a) and (b)**) confirmed the retention of BLA's agglomerated mesoporous morphology, suggesting that structural integrity was largely preserved. However, the reduction in basic oxide content directly correlates with diminished surface basicity, and hence, reduced catalytic performance. These results suggest that while BLA exhibits reasonable reusability, its long-term stability may benefit from periodic regeneration or modification strategies.

3.4.2.5. Proposed Mechanistic Pathway

The framework of the possible reaction mechanism for methanolysis of PET using BLA as a catalyst is given in **Scheme 3.6**. It is generally accepted that for any reaction involving exchange of ester functionality, the solid-based catalyst should exhibit several basic sites, high surface area as well as large pore diameter to provide an effective transition from start to finish. In this commentary, based on the data available from characterization of the catalyst and experimental results, we consider that the occurrence of several elements like Ca, K, Fe, Mg etc., available in order of their oxides and carbonates have introduced an effective strategy for the degradation of PET waste granules.

Earlier studies have also reported that decomposition of PET waste through transesterification reaction was subjected to Lewis acid-base synergistic effect. Hence, for each successful conversion, a nucleophilic methoxide ion was generated with the abstraction of a proton from -OH group of methanol by the anionic sites (such as O^{2-} , $(CO_3)^{2-}$) present within the catalyst. Subsequently, the methoxide ion interacts with the cationic sites (Mn^{2+} , K^{2+} , Ca^{2+} , Mg^{2+} etc.,) of the catalyst, which initially assembled nucleophilic attack on electron deficient carbonyl of esters group to form a tetrahedral intermediate. As the reaction proceeds further, a rearrangement reaction takes place where the esters bond gets cleaved, and the polymeric substrates experienced a new C–O bond formation between the carbonyl carbon of PET polyester and oxygen from methanol. As a result, the PET chain cleaved, decreasing the chain length to form oligomers and finally into a dimethyl terephthalate (DMT) monomer as the major product. Besides DMT, coupling of the acyl $-OCH_2CH_2-$

group with proton adsorbed by the catalyst results in the formation of ethylene glycol in the reaction mixture.



Scheme 3.6: Plausible reaction pathway for methanolysis of PET using BLA

3.4.3. Methanolysis of PET Using Orange Peel Ash-Derived Magnetic Nanoparticles (OPA@Fe₃O₄)

Building upon the promising results of glycolysis, the methanolysis of polyethylene terephthalate (PET) was investigated using a biomass-derived magnetic nanocatalyst; orange peel ash-functionalized Fe₃O₄ nanoparticles (OPA@Fe₃O₄). The integration of basic metal oxides (such as K₂O and CaO) within the magnetic support framework provides dual functionality: strong Lewis/basic catalytic sites and facile magnetic recovery. The catalytic efficiency of OPA@Fe₃O₄ in PET methanolysis was evaluated through reaction optimization, product characterization, and mechanistic interpretation, establishing its suitability for high-yield, sustainable depolymerization of PET waste.

3.4.3.1. Product Characterization

The formation of DMT was confirmed by performing ¹H NMR and ¹³C NMR analysis as shown in **Figure 3.49**. In its ¹H NMR data, the recrystallized product showed one singlet at $\delta = 8.10$ ppm from two aromatic protons and another singlet at $\delta = 3.94$ ppm due to methoxy protons while its ¹³C NMR data exhibited peaks at $\delta = 166.27, 133.90, 129.55$ and 52.43 ppm, validating the formation of the DMT monomer (**Figure 3.49a & 3.49b**). Investigation of the FTIR spectra of the recrystallized product (Figure 3.49) displayed an absorption band at 1720 cm^{-1} which reveals the presence of carbonyl groups of ester functionality. Also, the occurrence of strong absorption bands at 1262 and 1050 cm^{-1} can be assigned to the ester C–O and C–O–C stretching vibrations. And the observation of peaks at 1430 cm^{-1} and 2965 cm^{-1} indicates the presence of aromatic C–H and methyl group, respectively.

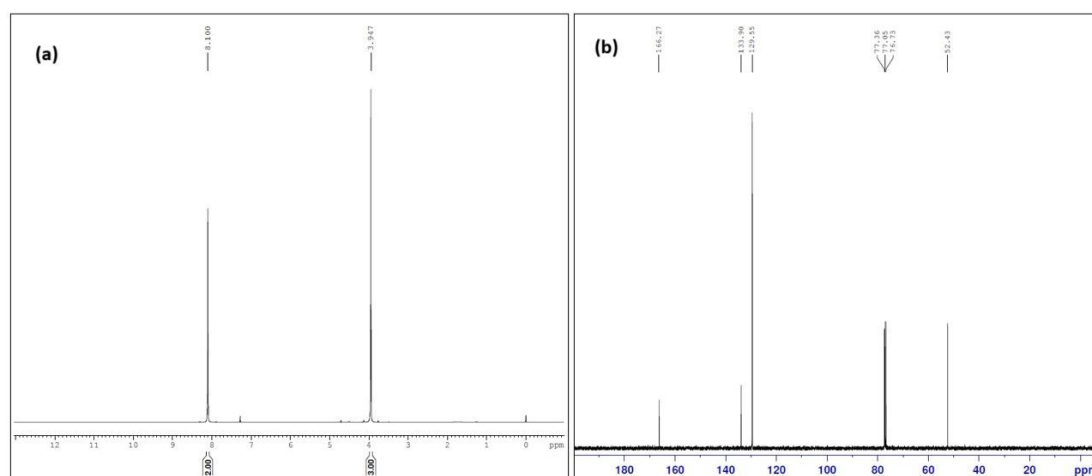


Figure 3.49: (a) ^1H NMR data of recrystallized DMT, (b) ^{13}C NMR data of recrystallized DMT

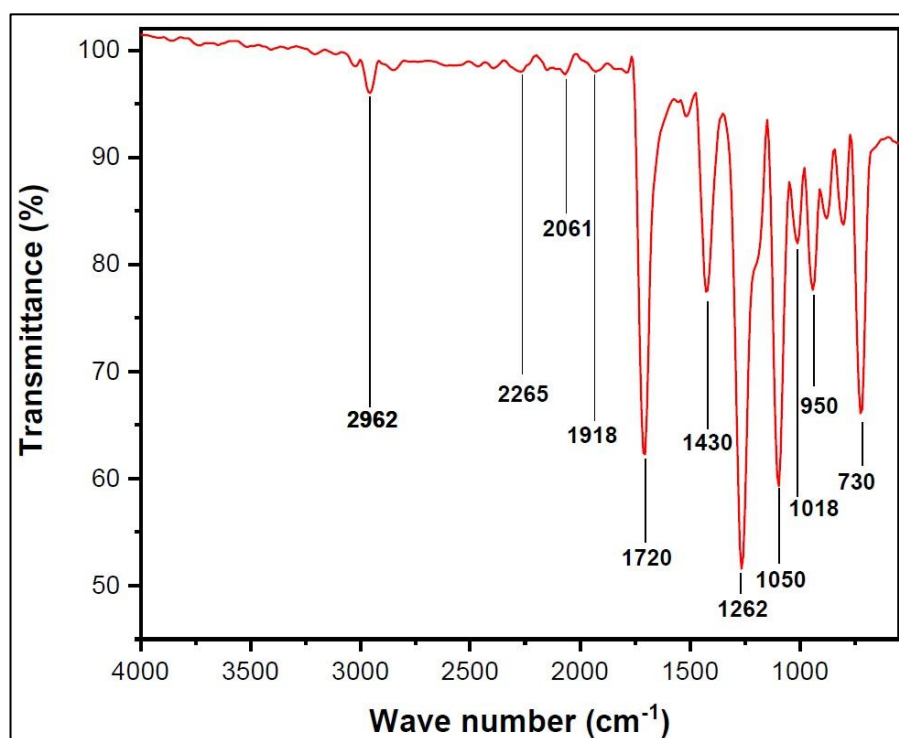


Figure 3.50: FTIR data of recrystallized DMT

Analysis of the crude product using High Performance Liquid Chromatography (HPLC) revealed the formation of EG, BHET, HEMT and DMT at a retention time of 1.953, 3.341, 4.445 and 7.908, respectively (**Figure 3.51**). Investigation of commercially available EG, BHET, HEMT and DMT using HPLC was used to confirm the above observations.

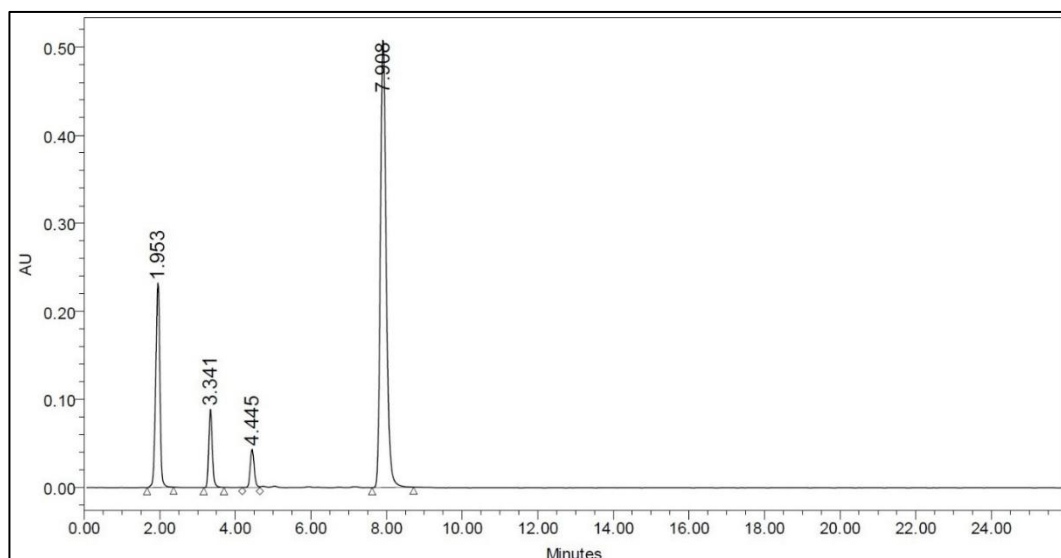


Figure 3.51: HPLC analysis of the crude product

3.4.3.2. Optimization of Methanolysis Conditions

Despite the outstanding physicochemical identity of the nano-sized catalyst, the production of DMT was also clearly affected by various operating reaction variables, such as duration of reaction, catalyst loading and methanol to PET concentration. Studies showed that DMT yield increases with increasing the reaction time, reaching a maximum at 1 hr with 79% yield, under a catalyst loading of 10 wt% and 5 mL of methanol at 200 °C (**Table 3.22**). However, prolonging the reaction time after 1 h gradually decreases the percentage yield which may be due to the development of the reversible reaction.

Table 3.22: Optimization of reaction time for methanolysis of PET^a

Sl. No.	Reaction time (in h)	DMT yield (%)	EG yield (%)
1	0.5	74 ± 1.01	71 ± 1.86
2	0.75	75 ± 0.88	76 ± 1.08
3	1	79 ± 0.72	77 ± 1.30
4	1.5	77 ± 0.82	79 ± 1.40
5	2	76 ± 1.05	78 ± 0.65

^aReaction condition: 2.5 mmol of PET flakes, 5 mL of methanol, 10 wt% of catalyst, at 200 °C; yield is expressed in mean ± standard error mean.

The influence of the catalyst loading on PET to DMT production was also investigated while keeping different reaction parameters such as reagent loading, reaction time and temperature constant at 5 mL, 1 h and 200 °C, respectively (**Table 3.23**). Consequently, the best yield of 83% could be achieved when the catalyst loading was limited to 4 wt%. But, a further increment in the catalyst loading eventually decomposes the percentage yield after crossing the equilibrium condition. This can be explained due to the fact that after reaching the optimum value, transesterification reaction creates a chemical equilibrium between the reactants and product, which induces the equilibrium to shift towards the left side, thereby reducing the overall yield of the product.

Table 3.23: Optimization of the catalyst loading for methanolysis of PET^a

Sl. No.	Catalyst loading (in wt %)	DMT yield (%)	EG yield (%)
1	1	71 ± 0.56	67 ± 1.41
2	2	75 ± 1.22	77 ± 1.72
3	3	78 ± 1.06	79 ± 1.96
4	4	83 ± 0.65	82 ± 1.67
5	5	81 ± 1.00	80 ± 1.24
6	6	80 ± 0.59	80 ± 1.67
7	8	79 ± 0.77	78 ± 1.58
8	10	79 ± 0.92	77 ± 1.81

^aReaction condition: 2.5 mmol of PET flakes, 5 mL of methanol, 1 h, at 200 °C; yield is expressed in mean ± standard error mean.

Besides these, one of the principal factors determining the formation of the desired DMT monomer is methanol to PET ratio. As shown in **Table 3.24**, when methanol concentration was increased from 3 to 5mL, DMT yield also jumped from 77% to 83%. However, further increase in methanol concentration beyond 5 mL doesn't have any remarkable effects on the product formation; instead, we observe a slight decreased in the percentage of yield. So, after this examination, the optimum condition for methanolysis of PET granules using biomass waste-derived magnetic

OPA@Fe₃O₄ was established at 2.5 mmol of PET flakes, 49 molar equivalents of methanol (5 mL), a temperature of 200 °C and 1 hr reaction time.

Table 3.24: Optimization of methanol to PET ratio^a

Sl. No.	Methanol loading (in mL)	DMT yield (%)	EG yield (%)
1	2	69 ± 1.18	71 ± 1.43
2	3	77 ± 1.12	75 ± 1.78
3	4	80 ± 1.13	78 ± 2.00
5	5	83 ± 0.61	82 ± 1.82
6	6	81 ± 1.33	79 ± 1.98
7	8	78 ± 0.88	76 ± 1.95
8	10	75 ± 1.49	73 ± 1.58

^aReaction condition: 2.5 mmol of PET flakes, 4 wt% catalyst loading, 1 hr, at 200 °C; yield is expressed in mean ± standard error mean.

3.4.3.3. Reusability of the Catalyst

The efficacy of recovered magnetic OPA@Fe₃O₄ was also screened for the conversion of PET to DMT under the optimized controlled environment. After completion, the residual nano-sized catalyst recovered using an external magnet was washed thoroughly with hot methanol. The recovered catalyst was dried at 80 °C for 12 hrs and then examined for the next ten consecutive cycles (**Table 3.25**). It was observed that there is a gradual decrease in the production yield after each run, but the catalyst was able to maintain an acceptable DMT yield even after ten cycles, achieving more than 70% DMT from the last runs. Reduced DMT production after each successive cycle may be subjected to leaching of active sites or loss of surface area of the solid base catalyst, which basically reduces its stability and reactivity.

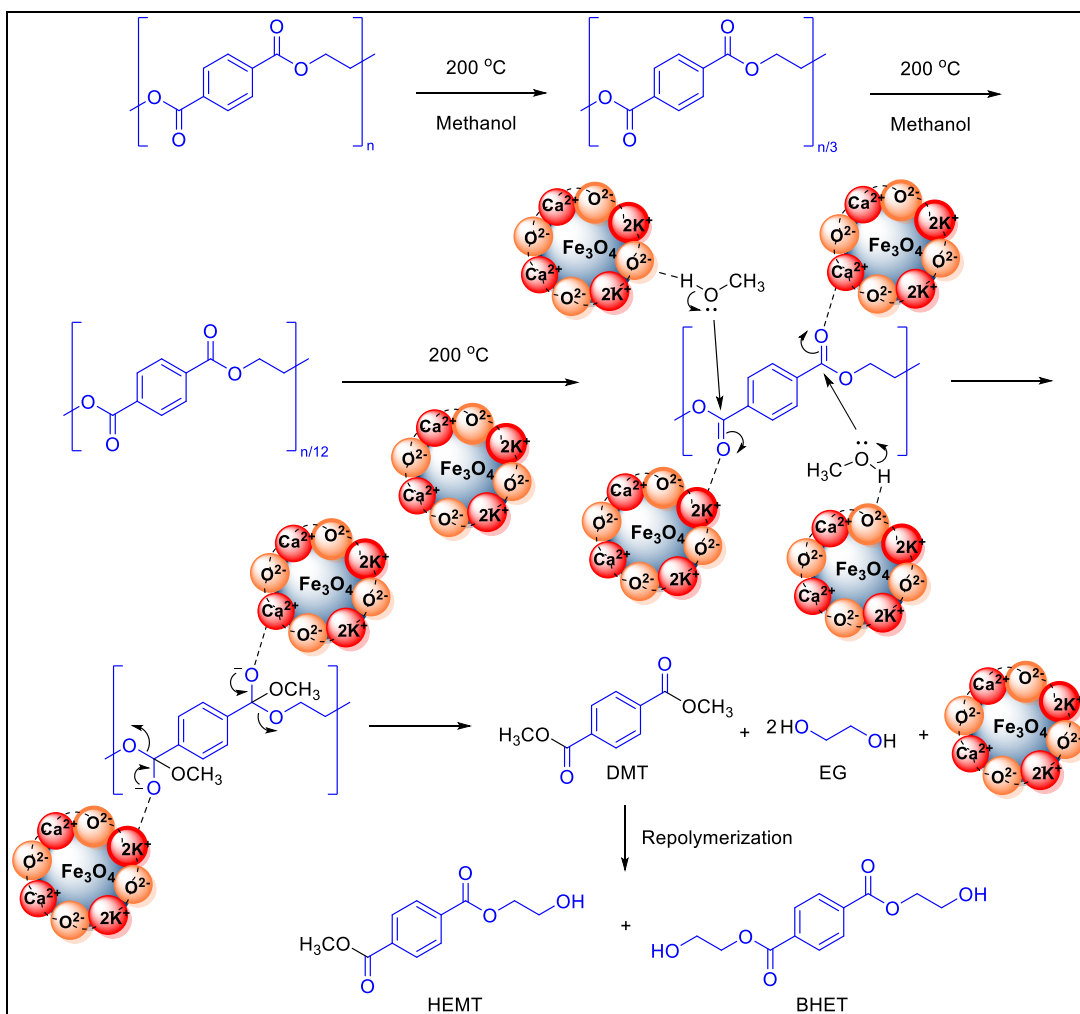
Table 3.25: Reusability of OPA@Fe₃O₄ catalyst for methanolysis of PET^a

Sl. No.	No. of cycles	Time (in hr)	DMT yield (%)	EG yield (%)
1	First	1	83 ± 0.86	82 ± 1.89
2	Second	1.25	81 ± 0.74	79 ± 1.61
3	Third	1.5	80 ± 0.61	77 ± 0.67
4	Fourth	1.75	79 ± 1.01	76 ± 1.95
5	Fifth	2	77 ± 0.77	74 ± 1.52
6	Sixth	2.5	77 ± 1.17	73 ± 1.23
7	Seventh	3	76 ± 0.82	75 ± 1.67
8	Eight	3.5	75 ± 0.69	74 ± 1.98
9	Ninth	4	74 ± 1.09	75 ± 1.63
10	Tenth	5	71 ± 0.73	74 ± 1.86

^aYield is expressed in mean ± standard error mean.

3.4.3.4. Proposed Reaction Mechanism

The proposed reaction mechanism for methanolysis of PET is shown in **Scheme 3.7** and is assumed to materialize through cation-anion combinatorial influence. And the oxides and carbonates of K and Ca present in the catalyst are believed to be the active sites for this transformation. Initially, high temperature and pressure and the presence of methanol inside the reactor vessel prompted the PET chain to be shortened by about 1/3. The shortened PET chain then gets fragmented into the oligomers which was finally disintegrated into the monomers using the catalyst. The metal cations in the catalyst act as Lewis's acid, which protonates the carbonyl oxygen of the ester functionality to intensify electrophilicity at the carbonyl carbon. Concurrently, the oxides of K and Ca abstract proton from methanol, promoting a nucleophilic attack from the oxygen atom of methanol to the electron rich carbonyl group. With the formation of a new C–O bond, the ester linkage breaks, subsequently forming DMT and EG as the final products. However, the process is reversible and as the reaction proceeds further, DMT and EG recombine to form BHET and HEMT as side products.



Scheme 3.7: Proposed mechanistic pathway for methanolysis of PET

3.5. Aldol reaction

The efficacy of orange peel ash (OPA) - a sustainable, biomass-derived solid base catalyst – was evaluated in promoting aldol reactions under environmentally benign conditions. Given its rich composition in basic oxides such as K_2O , CaO , and Fe_2O_3 , confirmed through XRF and EDX analyses, and its mesoporous structure observed via SEM and BET analysis, OPA was anticipated to serve as an effective base catalyst for carbon–carbon bond formation. Accordingly, the reaction of 4-nitrobenzaldehyde and acetone was employed as a model reaction under aqueous conditions at room temperature to assess the catalytic performance.

The reaction proceeded smoothly, yielding 4-hydroxy-4-(4- nitrophenyl)butan-2-one in 96% isolated yield within 5 minutes, without detectable side products. The high yield, rapid conversion, and clean product profile underscore OPA's potent catalytic ability for facilitating aldol-type carbon–carbon coupling under green conditions.

3.5.1. Catalytic Efficiency: Comparative Study with Biomass-Derived Ash Catalysts

To benchmark the catalytic performance of OPA, various biomass-derived solid base catalysts – including ashes from bamboo leaf (BLA), banana peel (BPA), sugarcane bagasse (BA), corn husk (CHA), mango peel (MPA), and cucumber peel (CPA) - were synthesized under identical conditions and tested under the same aldol reaction parameters.

Table 3.26: Aldol reaction using different biomass-waste derived catalysts^a

Sl. No.	Catalyst	Time	Yield of 3 (%) ^b
1	Orange peel ash (OPA)	5 min	96
2	Bamboo leaf ash (BLA)	2 h	67
3	Banana peel ash (BPA)	1.5 h	88
4	Sugarcane Bagasse ash (BA)	1.5 h	71
5	Corn husk ash (CHA)	45 min	79
6	Mango peel ash (MPA)	15 min	91
7	Cucumber peel ash (CPA)	10 min	93
8	None	24 h	-

^a Aldehyde (1 mmol), acetone (2 mmol), room temperature; ^b Isolated yield

OPA outperformed all other catalysts, achieving the fastest reaction and highest yield. This exceptional reactivity is attributed to its high surface basicity (H_{L} < 12.2–15.0), porous morphology, and synergistic interactions among multiple oxides. In contrast, BLA and BA, despite their comparable oxide composition exhibited significantly slower conversion rates, likely due to differences in active surface area, basic site strength, and oxide dispersion.

3.5.2. Optimization of the Reaction Conditions

First, the effect of catalyst loading on the reaction was assessed with a catalytic loading of 5, 10, 20, 30 and 40 mg mmol⁻¹ of the substrate. When 5 mg of the catalyst was added, the reaction was completed within 30 minutes but gave a lower yield of the aldol product (**Table 3.27 entry 1**). As the amount of the catalyst increases, the contact surface for the reaction also increases which eventually upsurges the conversion and yield of the product. The most satisfactory result was obtained when 20 mg of the catalyst was used but a slight decrease in the isolated yield was observed with the use of higher amount of OPA (**Table 3.27 entry 2-5**). This may be due to the fact that after reaching the optimal catalyst loading, the slurry becomes more viscous and it hampers the dispersal of the reactants, thus slowing down the reaction and reducing the overall yield at the same time.

Scheme 3.8: Aldol reaction

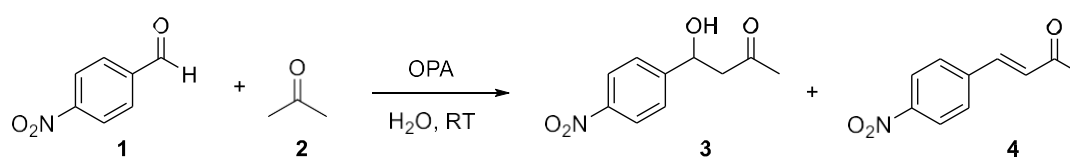


Table 3.27: Optimization of aldol reaction using OPA^a

Sl. No.	Catalysts (mg)	Solvents	Time (min)	Acetone (equiv.)	Product Yield (%) ^b	
					3	4
1	5	H ₂ O	30	2	88	Nil
2	10	H ₂ O	10	2	92	Nil
3	20	H ₂ O	5	2	96	Nil
4	30	H ₂ O	5	2	93	Nil
5	40	H ₂ O	5	2	87	Trace
6	20	-	90	2	-	-
7	20	CH ₂ Cl ₂	90	2	-	-
8	20	CHCl ₃	90	2	-	-
9	20	EtOH	90	2	Trace	-
10	20	CH ₃ CN	90	2	Trace	-

11	20	DMF	20	2	83	-
12	20	DMSO	20	2	89	-
13 ^c	20	H ₂ O	5	2	67	21
14 ^d	20	H ₂ O	5	2	95	-
15	20	H ₂ O	5	1	36	-
16	20	H ₂ O	5	1.5	57	-
17	20	H ₂ O	5	3	92	-
18	20	H ₂ O	10	2	69	12

^a Aldehyde (1 mmol). ^b Isolated yield. ^c 2 mL of H₂O was used. ^d 8 mL of H₂O was used.

Next, several solvents with different polarities were examined to study their influence in the reaction. The reaction was also performed under neat condition and these results are summarized in **Table 3.27, entries 6-12**. No apparent formation of the desired product was observed under solvent free condition. Similar outcomes were perceived when DCM and chloroform were used as a solvent. Even after prolonged reaction time, only trace amount of the final product was obtained with ethanol and acetonitrile. Use of polar aprotic solvents such as DMF and DMSO exponentially increased the rate and yield of the reaction. However, the ideal result was obtained when water was used as a solvent. This result demonstrated that the presence of water as a solvent is essential to achieve the best result with our catalyst.

It was also noticed that the amount of solvent loading plays a significant role in the outcome of the reaction. With 2 mL of water, the dehydration product formed instantly even after only 5 minutes of reaction time (**Table 3.27, entry 13**). But, increasing the solvent amount beyond 5 mL does not show any noticeable improvement in the yield (**Table 3.27, entry 14**).

We further investigated the impact of acetone equivalents on the yield of the reaction. With 1 equivalent of acetone, the reaction gave only 36% isolated yield which was increased to 57% with 1.5 equivalents (**Table 3.27, entries 15 and 16**). No substantial enhancement was observed by increasing the amount of acetone beyond 2 equivalents (**Table 3.27, entry 17**). While keeping other parameters

constant, we then increased the reaction time to investigate its effect on the reaction. After 10 minutes of reaction time, formation of the condensation product was experienced with a substantial decrease in the aldol reaction product (**Table 3.27, entry 18**).

3.5.3. Substrate Scope and Limitations

With the optimized condition in hand, we then explored the scope and limitation of this reaction with a variety of aromatic aldehydes and ketones (**Table 3.28, entries 1-18**). All the reactions were completed within 5 to 120 minutes giving good to excellent yields, but there is a distinct dissimilarity based upon the electron withdrawing/electron donating nature of the aldehydes on the rate of the reaction. Electron withdrawing aldehydes generally favor faster reactions while electron rich aldehydes usually took longer reaction time. But, interestingly, when the nitro (NO₂) group is at the ortho position, the reaction rate decreases substantially giving a lower yield of the product (**Table 3.28, entry 3**). This may be due to the intramolecular hydrogen bond formed between aldehydic hydrogen and oxygen atom from the nitro group, which diminished the reactivity of the aldehyde. And, an elevated temperature of 55 °C was required for the aldol acceptors having *p*-CH₃- and *p*-OCH₃- substituents, when cyclohexanone was used as a substrate (**Table 3.28, entries 9 and 10**). With acetone, all the reactions proceeded effortlessly at room temperature but the use of acetophenone as an aldol donor slightly lengthen the reaction time even with electron deficient aldehydes (**Table 3.28, entries 17 and 18**).

Scheme 3.9: Aldol reaction using different substrates

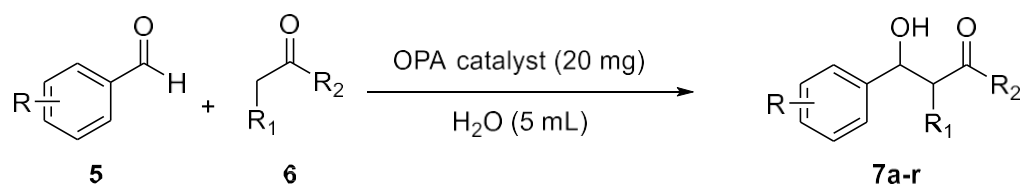


Table 3.28: Aldol reaction catalyzed by OPA^{a, b}

Sl. No.	Substrate (R)	Ketones	Product	Time	Yield (%) ^b
1	<i>p</i> -NO ₂	Cyclohexanone	7a	10 mins	96
2	<i>m</i> -NO ₂	Cyclohexanone	7b	15 mins	90
3	<i>o</i> -NO ₂	Cyclohexanone	7c	1 hr	72
4	<i>p</i> -Cl	Cyclohexanone	7d	15 mins	95
5	<i>m</i> -Cl	Cyclohexanone	7e	15 mins	93
6	<i>o</i> -Cl	Cyclohexanone	7f	20 mins	81
7	<i>p</i> -Br	Cyclohexanone	7g	30 mins	90
8	H	Cyclohexanone	7h	20 mins	70
9 ^c	<i>p</i> -CH ₃	Cyclohexanone	7i	30 mins	88
10 ^c	<i>p</i> -OCH ₃	Cyclohexanone	7j	1 hr	88
11	<i>p</i> -NO ₂	Acetone	7k	5 mins	91
12	<i>m</i> -NO ₂	Acetone	7l	30 mins	87
13	<i>p</i> -Cl	Acetone	7m	10 mins	80
14	H	Acetone	7n	45 mins	76
15	<i>p</i> -CH ₃	Acetone	7o	1 hr	90
16	<i>p</i> -OCH ₃	Acetone	7p	2 hrs	91
17	<i>p</i> -NO ₂	Acetophenone	7q	45 mins	87
18	<i>m</i> -NO ₂	Acetophenone	7r	2 hrs	80

^a Aldehyde (1 mmol), ketone (2 mmol). ^b Isolated yields. ^c Reaction was carried out at 55 °C.

3.5.4. Catalyst Reusability and Structural Stability

The reusability of OPA was assessed through four successive reaction cycles using 4-nitrobenzaldehyde and cyclohexanone (**Table 3.29**). Post-reaction, the catalyst was recovered by filtration, washed, and dried before reuse.

A slight decrease in efficiency and increase in reaction time were observed, primarily attributed to active site leaching. Elemental analysis via EDX (**Table 3.30** and **Figure 3.52**) revealed a significant decrease in potassium content (from 21% to

0.48%), which likely contributed to the diminished basic strength over cycles (Mariscal et al., 2007) .

Scheme 3.10: Aldol reaction between 4-nitro benzaldehyde and cyclohexanone

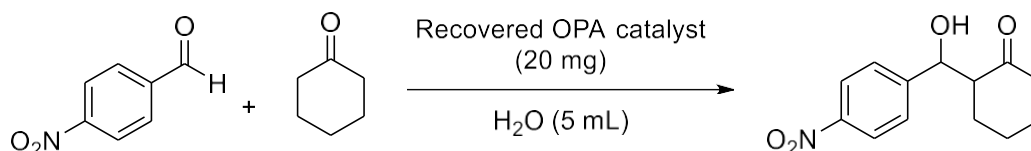


Table 3.29: Reusability of OPA towards Aldol reaction

Catalytic Cycle	Reaction Time (min)	Yield (%) ^b
1 st Cycle	10	96
2 nd Cycle	14	94
3 rd Cycle	20	92
4 th Cycle	30	92

^a Aldehyde (1 mmol), ketone (2 mmol). ^b Isolated yield

SEM and TEM analyses (**Figures 3.53**) showed preservation of the mesoporous, agglomerated morphology post-reaction. While surface texture remained intact, slight structural compaction and pore collapse may have occurred, potentially reducing surface accessibility.

Table 3.29: EDX analysis of spent OPA after 4th Cycle.

SI No.	Elements	Weight %	Atomic %
1	O	53.13	72.16
2	Mg	1.85	1.65
3	Al	0.27	0.22
4	Si	2.71	2.10
5	P	6.18	4.34
6	S	1.53	1.04
7	K	0.98	0.54
8	Ca	32.51	17.62
9	Fe	0.84	0.33

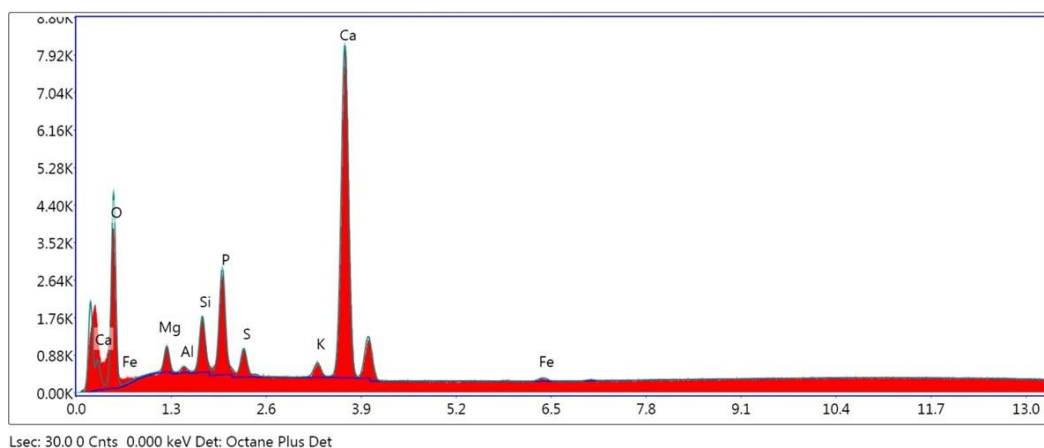


Figure 3.52: EDX spectra of Recovered OPA after 4th cycle

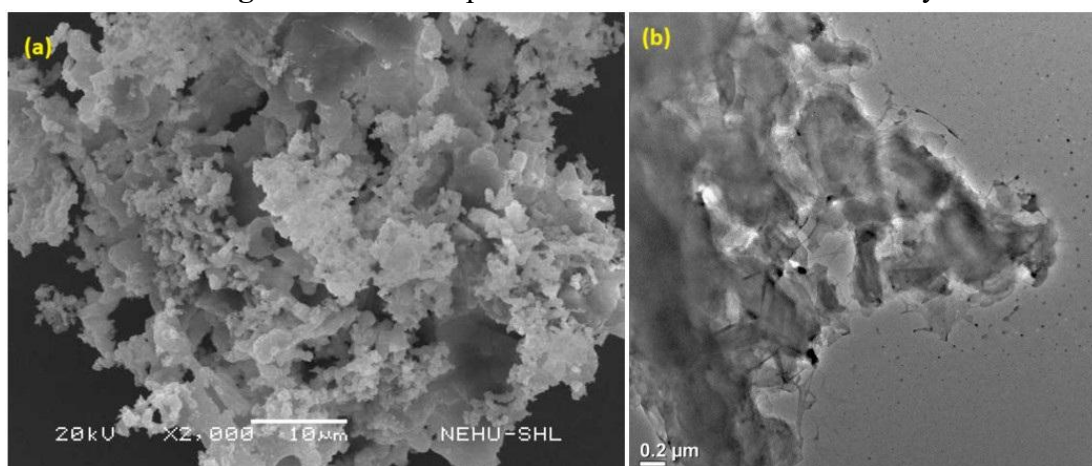
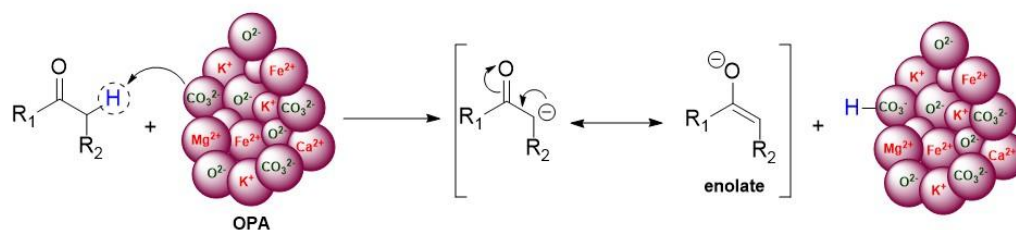
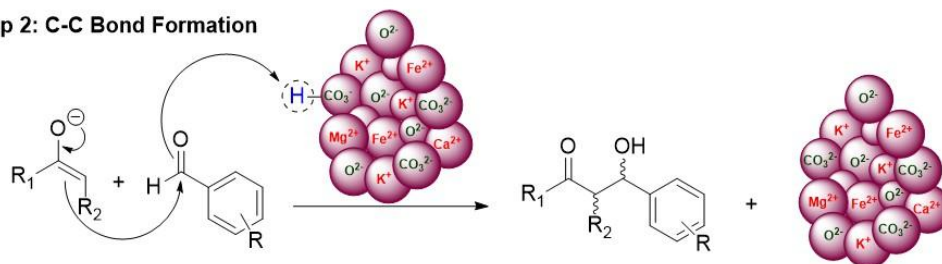


Figure 3.53: (a) SEM image of recovered OPA catalyst, (b) TEM image of recovered OPA catalyst

Step 1: Generation of Carbanion and formation of enolate



Step 2: C-C Bond Formation



Scheme 3.8: Proposed reaction mechanism of aldol reaction with OPA catalyst

3.5.5. Proposed Reaction Mechanism

The high activity of the catalyst towards aldol reaction was attributed to the high basic strength of the catalyst which was found to contain K_2O , CaO , K_2CO_3 , $CaCO_3$, etc among others, in its analyses. The basic strength of the catalyst was also investigated using Hammett indicator method as reported in the literature and it shows a basicity value between $9.8 < H_- < 15.0$. Based on this, we postulated a mechanistic pathway through the general base catalyzed aldol reaction involving an enolate mechanism (Scheme 3.8). The mesoporous nature of the catalyst and its large surface area may have also played an important part in the catalytic activation.

3.6. Comparative Analysis of PET Glycolysis Using OPA, BLA, and OPA@Fe₃O₄

3.6.1. Overview and Experimental Consistency

To evaluate and compare the catalytic efficiency of three distinct bio-derived materials – orange peel ash (OPA), bamboo leaf ash (BLA), and orange extract-coated magnetic nanoparticles (OPA@Fe₃O₄); all glycolysis reactions were conducted under standardized conditions, using 480 mg (2.5 mmol) PET, ethylene glycol (EG) in excess (optimized per catalyst), and reaction temperatures maintained at 190 °C, unless otherwise noted. Each catalyst underwent independent structural and compositional characterization, and their glycolytic performance was correlated with these physicochemical features and their synthesis method.

3.6.2. Effect of Catalyst Composition and Synthesis Route

Table 3.31: Preparation Method and physico-chemical properties of the catalysts

Catalyst	Synthesis Method	Key Active Components	Notable Characteristics
OPA	Direct combustion of orange peel at 600 °C	CaO (32.87%), K ₂ O (30.87%)	High basicity, low surface area (4.97 m ² /g)
BLA	Calcination of bamboo leaves at 700 °C	SiO ₂ (76.02%), CaO (4.78%), K ₂ O (2.88%)	Mesoporous (21.85 m ² /g), thermally stable
OPA@Fe₃O₄	Green synthesis using orange peel extract and Fe salts under basic reduction	Fe ₃ O ₄ (55.79%), K ₂ O (26.17%), SO ₃ (8.86%)	Nanoscale, high surface area (31.23 m ² /g), magnetic core

The thermal combustion of OPA and BLA resulted in bulk ash materials containing alkaline and alkaline-earth metal oxides, responsible for their Brønsted

basicity. In contrast, OPA@Fe₃O₄ were synthesized via a solution-based reduction route involving plant extracts, which not only capped and stabilized the iron oxide nanoparticles but also imparted surface functionality. This difference in synthesis impacted their surface area, dispersion, and active site availability, directly influencing their glycolytic behavior.

3.6.3. Catalytic Efficiency and Product Yield

Table 3.32: Optimized reaction conditions of PET Glycolysis

Parameter	OPA	BLA	OPA@Fe ₃ O ₄
Optimal Catalyst Loading	50 mg (10 wt%)	100 mg (20 wt%)	30 mg (6 wt%)
Optimal EG Loading	16 equivalents	16 equivalents	16 equivalents
Reaction Time	1.5 h	3.5 h	1.5 h
Maximum BHET Yield (%)	79	84	91

OPA displayed rapid PET conversion due to its high concentration of basic oxides (CaO, K₂O), enabling fast nucleophilic activation of EG and ester bond cleavage. However, its low surface area limited the overall yield compared to BLA and OPA@Fe₃O₄. BLA, while slower, yielded the highest purity BHET under optimal conditions, attributed to its mesoporous structure and silica-supported active sites, which moderated the reaction and reduced side product formation. OPA@Fe₃O₄ exhibited superior yield (89%) and fastest reaction time (1 h), likely due to their highly dispersed surface-active Fe₃O₄ and K₂O, combined with nanoscale size, which enhanced contact with PET chains and accelerated depolymerization.

3.6.4. BHET Purity and Characterization Outcomes

All three catalysts produced BHET with comparable spectroscopic signatures, as confirmed by:

- i. HPLC: Retention times ~ 3.38 min,
- ii. ^1H NMR: Signals at $\delta = 8.09, 5.00, 4.30, 3.70$ ppm,
- iii. ^{13}C NMR: Carbonyl and methylene peaks at $\delta = 165, 133, 129, 66, 59$ ppm,
- iv. FTIR: O–H ($\sim 3440\text{ cm}^{-1}$), C=O ($\sim 1700\text{ cm}^{-1}$), C–O ($\sim 1260\text{ cm}^{-1}$).

However, OPA@Fe₃O₄ yielded a BHET product with fewer oligomeric impurities, reflected in sharper HPLC peaks and cleaner NMR profiles, suggesting better selectivity.

3.6.5. Reusability and Catalyst Stability

Table 3.33: Catalysts' stability for PET glycolysis

Cycle	BHET Yield (%) OPA	BHET Yield (%) BLA	BHET Yield (%) OPA@Fe ₃ O ₄
1 st	79	83	91
Final	62 (5 th cycle)	65 (4 th cycle)	80 (10 th)

OPA suffered from substantial potassium leaching (K decreased from 21.32% to 0.48%), as confirmed by EDX. BLA also experienced depletion of key oxides (Ca, K, Fe), though its mesoporous structure remained intact over four cycles. OPA@Fe₃O₄ retained morphology and compositional integrity better, likely due to stabilization of Fe₃O₄ by plant-based capping agents, contributing to improved recyclability.

3.6.6. Colored PET Recycling

Table 3.34: Catalysts' efficacy on glycolysis of colored PET

Catalysts	Red PET BHET Yield %	Green PET BHET Yield %	Light-yellow PET BHET Yield %
OPA	70	66	69
BLA	75	68	75
OPA@Fe ₃ O ₄	89	85	88

All catalysts effectively depolymerized colored PET bottles under the same conditions. The addition of activated carbon post-crystallization eliminated residual pigments. OPA@Fe₃O₄ consistently outperformed the others in colored PET conversion, suggesting better accessibility and adsorption of pigmented additives, although exact surface-pigment interactions were not evaluated.

3.6.7. Mechanistic Comparison

Table 3.35: Proposed reaction mechanism of Catalysts for the glycolysis of PET

Catalyst	Proposed Mechanism Summary
OPA	Base-catalyzed EG activation by CaO and K ₂ O → ester bond cleavage via nucleophilic attack → rapid PET depolymerization
BLA	Surface oxide sites (Ca, K, Mg, Mn, Fe) generate 2-hydroxyethanolate → PET swelling → nucleophilic attack → stepwise PET breakdown to BHET
OPA@Fe₃O₄	Similar base-catalyzed pathway (K ₂ O, Fe ₃ O ₄) → no redox mechanism proposed/tested → enhanced reactivity due to nanostructure and surface dispersion

Mechanistic Implications:

All three catalysts operate via base-promoted transesterification, with EG activated by metal oxides to form nucleophilic intermediates. OPA's high surface

basicity enables faster reaction but also increases dimer formation. While BLA's balanced oxide matrix ensures higher selectivity and slower reactivity. OPA@Fe₃O₄'s nanoscale surface architecture accelerates reaction without compromising BHET purity, and extends operational lifetime.

3.7. Comparison of the prepared catalysts for PET glycolysis with other reported catalyst

The present study was carried out in an attempt to find a greener route for PET glycolysis and to reduce the overall cost by using biomass-waste derived recyclable catalyst. Several other catalysts were reported earlier to catalyze the depolymerization of PET waste to BHET monomer and are compared with OPA, BLA and OPA@Fe₃O₄ catalyst (**Table 3.37**). Traditionally, glycolysis was carried out in the presence of metal acetates (Zn, Pb, Mn, Co) as catalysts giving moderate to excellent yield. Zeolites, ionic liquids, nanoparticles and organocatalysts also showed high activity towards PET depolymerization. But, the main drawbacks of these catalysts are their high cost, complex preparation procedure and some difficulty in handling as their preparations require use of harmful chemicals. For example, depolymerization using organocatalysts affords BHET monomer in excellent yield but they are usually expensive which ultimately reduced its applicability at the industrial scale. The preparation of ionic liquids and nanoparticles requires several steps and, sometimes corrosive chemicals have to be employed for their production. In contrast, the preparation and handling of the present catalysts were very simple and as it is waste-origin, hence cost-free. Furthermore, our approach of resolving plastic waste problems with bio-waste is a merit in itself, opening a new waste-valorization technique and affording a window for converting synthetic polymeric waste to reusable resources in an eco-friendly procedure.

Table 3.36: Comparison of the prepared catalysts with other reported catalyst

Catalyst	EG loading (molar equiv.)	Catalyst loading	Time (in h)	Temp. (°C)	Yield (%)	Reference
Titanium (IV)-phosphate ester	2.76	0.3 wt %	2.5	190-200	97.5	(Troev et al., 2003)
Zeolites	18.6	1 wt. %	8	196	65	(Shukla et al., 2008)
Zn(OAc) ₂	7.6	1 wt. %	1	196	70	(López-Fonseca et al., 2010)
Na ₂ CO ₃	7.6	0.13 wt. %	1	196	80	(López-Fonseca et al., 2011)
[Bmim]OH	10	5 wt %	2	190	71.2	(Yue et al., 2011)
SO ₄ ²⁻ /Co-Zn-O	17	0.3 wt. %	3	180	75	(Zhu et al., 2012)
[deim][Zn(OAc) ₃]	20.6	16.66 wt. %	2.5	180	70.94	(Zhou et al., 2012)
Calcined Mg-Al hydrotalcites	15.49	1 wt. %	0.83	196	81.3	(F. Chen et al., 2013)
Tetragonal ZnMn ₂ O ₄	17.2	1 wt. %	1	260	92.2	(Imran et al., 2013)
[amim][ZnCl ₃]	12.39	10 wt %	1.25	175	80.7	(Q. Wang et al., 2013)
Calcined Zn/Al Hydrotalcites	15.49	1 wt. %	1.25	196	79	(F. Chen et al., 2014)
Cu(OAc) ₂ -[Bmim][OAc] and Zn(OAc) ₂ -[Bmim][OAc]	20.64	33.33 wt. %	3	190	53.95 and 45.6	(Al-Sabagh, Yehia, Eissa, Moustafa, Eshaq, Rabie, & Elmetwally, 2014a)

[Bmim][OAc]	20.64	33.33 wt. %	3	190	58.2	(Al-Sabagh, Yehia, Eissa, Moustafa, Eshaq, Rabie, & Elmetwally, 2014b)
γ -Fe ₂ O ₃	11.36	0.05 wt. %	1	300	>90	(Bartolome et al., 2013)
Ti(OCH ₂ CH ₂ O) ₃ Na ₂	12	1.4 wt. %	3	190	85	(S. Wang et al., 2015)
[bmim] ₂ [CoCl ₄]	12.39	20 wt %	4	170	77.8	(Q. Wang et al., 2015)
(Mg–Zn)–Al LDH	30.98	1 wt %	3	196	75	(Eshaq & Elmetwally, 2016)
Fe ₃ O ₄ -boosted MWCNT	30.98	5 wt %	2	190	100	(Al-Sabagh, Yehia, Harding, et al., 2016)
γ -Fe ₂ O ₃ /N-doped graphene hybrid material	42.96	10 wt. %	3	195	>99	(Nabid et al., 2017)
TBD:MSA (1:1)	20	50 wt. %	2	180	91	(Jehanno, Flores, et al., 2018)
Ultrasmall cobalt nanoparticle	85	1.5 wt. %	3	180	96	(Veregue et al., 2018b)
Perkalite F100	5	0.5 wt %	2	240	80	(Guo et al., 2018)
CaO(SrO, BaO)/MCF	20	0.05 mol%	3	190	80	(Zhao et al., 2018)
SiO ₂ @Fe ₃ O ₄	34	15 wt. %	24	190	100	(Cano et al., 2020)
Choline acetate ([Ch][OAc])	12.39	5 wt. %	4	180	85.2	(Y. Liu et al., 2020)
1,3-	30.981	15 wt. %	1	185	60	(L. Wang et al.,

Dimethylimidazolium-2-Carboxylate						2020)
Mixed oxide (Co/RZnO)	8	1 wt. %	2	196	80	(Fuentes et al., 2020)
Mixed Lewis acidic ionic liquids	34	1 wt. %	2	190	87.1	(Shuangjun et al., 2021)
MnO ₂ /HGO nanosheets	56.01	0.01 wt %	0.166	200	100	(S. Bin Jin et al., 2021)
Orange peel ash (OPA) (Present work)	16	10 wt. %	1.5	190	79	(Lalmangaihual et al., 2021)
Bamboo Leaf ash (BLA) (Present work)	16	20.83 wt. %	3.5	190	83.15	(Z. Laldinpui et al., 2021)
OPA@Fe ₃ O ₄ (Present work)	16	4 wt. %	1.5	190	89	(Lalmangaihual et al., 2023)

3.8. Comparative Analysis of PET Methanolysis Using OPA, BLA, and OPA@Fe₃O₄

3.8.1. Effect of Catalyst Properties and Preparation Method

Table 3.37: Physico-chemical properties of the prepared catalysts

Catalyst	Synthesis Method	Major Oxide Components (XRF)	BET Surface Area (m ² /g)	Thermal Stability
OPA	Direct combustion of orange peel at 600 °C	CaO (32.87%), K ₂ O (30.87%)	4.97	Stable up to 600 °C
BLA	Calcination of bamboo leaves at 700 °C	SiO ₂ (76.02%), CaO (4.78%), K ₂ O (2.88%)	21.28	Stable up to 600 °C
OPA@Fe₃O₄	Green synthesis using orange extract with FeCl ₃ :Fe ₂ SO ₄ and NH ₃ (co-precipitation)	Fe ₃ O ₄ (55.79%), K ₂ O (26.17%), SO ₃ (8.86%)	31.23	Stable up to 500-600 °C

OPA and BLA were synthesized by controlled thermal treatment of agro-waste, yielding basic oxide-rich ash with modest surface areas. OPA@Fe₃O₄, synthesized via a green co-precipitation route using orange peel extract, resulted in nanoscale iron oxide particles coated with bioactive compounds, significantly enhancing surface area, active site density, and particle dispersion. The higher surface area and nanoscale morphology of OPA@Fe₃O₄ played a pivotal role in boosting catalytic efficiency during PET methanolysis.

3.8.2. Catalytic Performance in PET Methanolysis

Table 3.38: Catalysts' optimized reaction conditions of PET Methanolysis

Parameter	Optimal Catalyst Loading	Reaction Time	Max DMT Yield (%)
OPA	30 mg (6 wt%)	1 h	79
BLA	100 mg (20 wt%)	2 h	78
OPA@Fe ₃ O ₄	20 mg (4 wt%)	1 h	83

OPA, owing to its high CaO and K₂O content, demonstrated a strong base-catalyzed activity, rapidly promoting ester bond cleavage and resulting in a 79% DMT yield within 1 hour. BLA, although thermally robust, displayed slower catalytic behavior, requiring 2 hours to yield 78% DMT, likely due to its lower base strength and high SiO₂ content, which is catalytically inert. OPA@Fe₃O₄ outperformed both ash-based catalysts, achieving 83% DMT yield with the lowest catalyst loading (20 mg) and shortest reaction time (1 h). This superior activity is attributed to: high surface area (31.23 m²/g), nanoscale size (10-20 nm), uniform dispersion of Fe₃O₄ and basic K₂O, and enhanced contact between PET and catalytic surface due to porous structure and high surface energy. These results underscore the impact of preparation strategy and surface accessibility in determining catalyst efficiency.

3.8.3. Product Purity and Analytical Consistency

The DMT monomer obtained from each system was analyzed via HPLC, FTIR, and NMR, and was found to match commercial DMT in spectral fingerprint and purity.

FTIR showed consistent peaks across all samples:

C=O stretching at ~1720 cm⁻¹, confirming ester linkage, aromatic C=C at ~1600 cm⁻¹, and C–O–CH₃ at ~1250 cm⁻¹.

HPLC retention times for DMT were identical, indicating high-purity recovery in each case, with OPA@Fe₃O₄ showing slightly sharper peak resolution, suggesting cleaner product separation. Despite differences in reaction kinetics, all three catalysts successfully facilitated the methanolytic conversion of PET to high- purity DMT, making them suitable for monomer recovery applications. However, the OPA@Fe₃O₄ system exhibited the cleanest product profile, likely due to rapid depolymerization and minimal side product formation.

3.8.4. Catalyst Reusability

Table 3.39: Catalysts' reusability for PET methanolysis

Catalyst	Maximum Number of Effective Cycles	Final DMT Yield (%)
OPA	4	71
BLA	4	67
OPA@Fe₃O₄	10	71

Optimized reaction conditions of PET Glycolysis

All catalysts demonstrated moderate reusability. Ash-based systems (OPA and BLA) experienced gradual activity loss, primarily due to leaching of surface K⁺ and Ca²⁺ during washing and reaction (as shown in EDX data). OPA showed a ~8% yield loss by the fourth cycle, while BLA suffered more rapid decline due to its lower active oxide content and elemental depletion.

In contrast, OPA@Fe₃O₄ maintained catalytic activity for ten cycles, attributed to the robust iron oxide core, better structural integrity, and possible capping effect from the orange extract, which minimized nanoparticle aggregation and leaching.

3.8.5. Summary of Key Findings

Table 3.40: Key findings from methanolysis using the prepared solid catalysts

Parameter	OPA	BLA	OPA@Fe ₃ O ₄
Base Strength	High (K ₂ O, CaO)	Moderate (low oxide content)	Moderate–High (K ₂ O, Fe ₃ O ₄)
Surface Area	Low (4.97 m ² /g)	Moderate (21.85 m ² /g)	High (31.23 m ² /g)
Max DMT Yield (%)	79	78	83
Reaction Time	1 h	2 h	1 h
Reusability (Effective Cycles)	4	4	10
Product Purity	High	High	Very High
Synthesis Simplicity	Very easy	Easy	Moderate (requires extract handling and precipitation)

3.9. Comparison of the prepared catalysts for methanolysis of PET with other reported catalyst

Several methodologies have been reported for the methanolysis of PET, as summarized in **Table 3.42**. However, many of these approaches suffer from significant drawbacks, including the requirement for high temperatures, prolonged reaction times, tedious product purification, the use of co-solvents to improve efficiency, and high catalyst loadings. To address and overcome these limitations, a more cost-effective and environmentally sustainable strategy was developed using a biomass-derived heterogeneous catalyst synthesized from waste materials. The prepared catalysts offer several distinct advantages: they are inexpensive, eco-

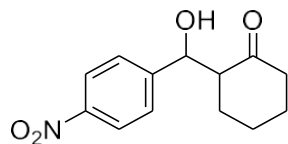
friendly, easy to synthesize and handle, and exhibit excellent reusability and high selectivity toward dimethyl terephthalate (DMT) formation. Additionally, the catalyst enables straightforward separation and recovery, making it a promising candidate for scalable and sustainable PET methanolysis.

Table 3.42: Comparison of the efficacy of the prepared catalyst with some reported procedure

Catalyst	Catalyst (in wt.%)	Temperature (in ° C)	Pressure (in atm)	Time	MeOH (mol. eq.)	Yield (in %)	Reference
-	-	300	-	30 mins	71.27	55	(Sako et al., 1997)
-	-	310	99.4	30 mins	83.98	98	(B. K. Kim et al., 2001)
-	-	270	108.562	40 mins	28.5	96	(Yang et al., 2002)
[Al(O ⁱ Pr) ₃]	10	200	-	2 h	95.00	67.30	(Kurokawa et al., 2003)
KOH	69	100	-	30 mins	16.78	96	(Nikje & Nazari, 2006)
Zn (OAc) ₂	1	180	-	55 mins	9.5	—	(Siddiqui et al., 2012)
K ₂ CO ₃	14.35	25	-	24 h	50.00	93.50	(Pham & Cho, 2021)
BLA (Present work)	20	200	-	2 h	98.8	78	(Z. T. Laldinpui et al., 2021)
OPA (Present work)	6	200	-	1 h	49	79	(Z. T. Laldinpui et al., 2021)
OPA@Fe ₃ O ₄ (Present work)	4	200	-	1 h	49	83	(Lalmangaihzuala et al., 2023)

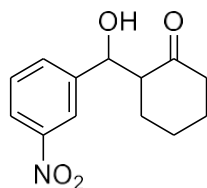
3.10. NMR Spectral data of the aldol products

2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one (1a, white solid):



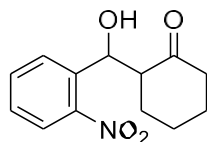
^1H NMR (400 MHz, CDCl_3): δ 8.22 - 7.47 (m, 4H), 5.48 (d, $J = 2.4$ Hz, 1H for *syn*), 4.90 (d, $J = 8.4$ Hz, 1H for *anti*), 2.48 - 1.54 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 214.95, 214.26, 149.30, 148.58, 128.11, 126.85, 123.81, 123.70, 74.28, 70.38, 57.43, 57.04, 42.91, 42.85, 31.00, 28.08, 27.87, 26.16, 25.02, 24.94. . (**1a**, white solid) (96% yield, room temperature RT, 15 min).

2-(hydroxy(3-nitrophenyl)methyl)cyclohexan-1-one (1b, oily liquid):



^1H NMR (400 MHz, CDCl_3): δ 8.21 - 7.51 (m, 4H), 5.48 (d, $J = 2.0$ Hz, 1H for *syn*), 4.89 (d, $J = 8.4$ Hz, 1H for *anti*), 2.62 - 1.55 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 215.06, 214.33, 148.55, 144.06, 143.51, 133.42, 132.18, 129.53, 129.38, 123.10, 122.32, 122.26, 121.11, 74.28, 70.15, 57.37, 57.00, 42.89, 42.84, 30.98, 28.09, 27.86, 26.15, 24.99, 24.90. (**1b**, oily liquid) (72% yield, RT, 1 h).

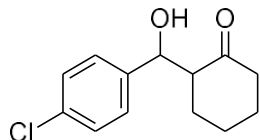
2-(hydroxy(2-nitrophenyl)methyl)cyclohexan-1-one (1c, oily liquid):



^1H NMR (400 MHz, CDCl_3): δ 8.11 - 7.42 (m, 4H), 5.96 (d, $J = 2.0$ Hz, 1H for *syn*), 5.47 (d, $J = 8.4$ Hz, 1H for *anti*), 2.46 - 1.55 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 214.28, 188.34, 137.22, 134.28, 133.92, 133.37, 129.88, 129.86, 128.17, 124.89,

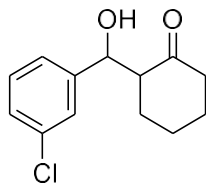
124.74, 66.93, 55.08, 42.80, 28.23, 26.76, 25.10. **1c**, oily liquid, (95% yield, RT, 15 min).

2-((4-chlorophenyl)(hydroxy)methyl)cyclohexan-1-one (1d, white solid):



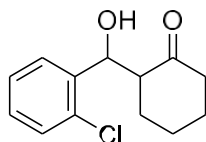
^1H NMR (400 MHz, CDCl_3): δ 7.41 - 7.10 (m, 4H), 5.27 (s, 1H for *syn*), 4.69-4.66 (dd, $J_1 = 2.8$ Hz, $J_2 = 2.4$ Hz, 1H for *anti*), 3.91 (d, $J = 2.8$ Hz, 1H for OH), 2.50-1.03 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 213.96, 213.32, 142.97, 141.25, 131.43, 131.36, 127.98, 127.54, 121.72, 121.12, 74.13, 70.32, 57.43, 57.12, 42.67, 30.85, 28.12, 27.86, 26.14, 25.24, 24.97. **1d**, white solid, (95% yield, RT, 15 min).

2-((3-chlorophenyl)(hydroxy)methyl)cyclohexan-1-one (1e, white solid):



^1H NMR (400 MHz, CDCl_3): δ 7.25 - 7.08 (m, 4H), 5.28 (s, 1H for *syn*), 4.68 - 4.66 (d, $J = 8.8$ Hz, 1H for *anti*), 3.96 (s, 1H for OH), 2.52 - 1.46 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 215.41, 143.31, 134.58, 129.83, 129.67, 128.28, 127.38, 126.25, 125.53, 124.10, 74.50, 70.31, 57.50, 57.20, 42.89, 31.01, 28.13, 27.95, 26.16, 25.05, 24.93. **1e**, white solid, (93%, 15 min).

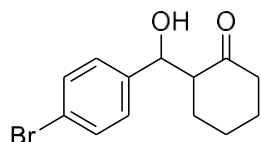
2-((2-chlorophenyl)(hydroxy)methyl)cyclohexan-1-one (1f, white solid):



^1H NMR (400 MHz, CDCl_3): δ 7.55 - 7.18 (m, 4H), 5.71 (2, 1H for *syn*), 5.36 - 5.33 (dd, $J_1 = 3.6$ Hz, $J_2 = 4.0$ Hz, 1H for *anti*), 4.05 (d, $J = 3.6$, 1H for OH), 2.69 - 1.53 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 215.27, 214.79, 139.10, 138.58, 132.97,

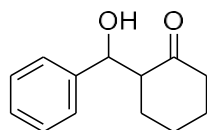
130.86, 129.22, 128.75, 128.54, 128.26, 128.20, 127.26, 126.61, 70.45, 67.72, 57.60, 53.57, 42.73, 42.67, 30.40, 27.95, 27.82, 25.97, 24.92, 24.86. **1f**, white solid, (81%, 20 min).

2-((4-bromophenyl)(hydroxy)methyl)cyclohexan-1-one (1g, white solid):



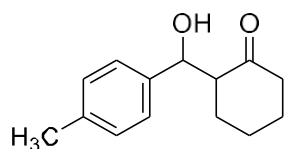
^1H NMR (400 MHz, CDCl_3): δ 7.48 - 7.17 (m, 4H), 5.33 (d, $J = 2.4$ Hz, 1H for *syn*), 4.75 (d, $J = 8.8$ Hz, 1H for *anti*), 2.55 - 1.52 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 215.27, 214.57, 140.53, 140.02, 131.49, 131.26, 128.75, 127.55, 121.72, 120.77, 74.19, 70.15, 57.33, 56.99, 42.67, 30.76, 27.93, 27.73, 25.96, 24.85, 24.71. **1g**, white solid, (90% yield, RT, 30 min).

2-(hydroxy(phenyl)methyl)cyclohexan-1-one (1h, white solid):



^1H NMR (400 MHz, CDCl_3): δ 7.34 - 7.26 (m, 5H), 5.39 (d, $J = 2.4$ Hz, 1H for *syn*), 4.78 (d, $J = 8.8$ Hz, 1H for *anti*), 2.47 - 1.52 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 215.78, 215.04, 141.72, 141.17, 128.63, 128.40, 128.15, 127.28, 127.23, 126.01, 75.38, 70.89, 57.67, 57.44, 42.93, 31.10, 28.19, 28.05, 26.26, 25.13, 24.98. **1h**, white solid, (70% yield, RT, 20 min).

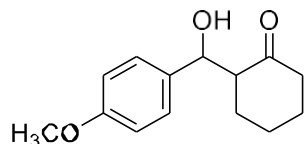
2-(hydroxy(p-tolyl)methyl)cyclohexan-1-one (1i, white solid):



^1H NMR (400 MHz, CDCl_3): δ 7.25-7.13 (m, 4H), 5.34 (d, $J = 1.6$ Hz, 1H for *syn*), 4.75 (d, $J = 8.8$ Hz, 1H for *anti*), 2.60 - 1.52 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3): δ 215.85, 215.07, 138.74, 138.22, 137.80, 136.79, 129.29, 129.08, 127.17, 125.94,

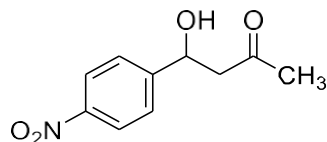
74.80, 70.82, 57.68, 57.49, 42.91, 31.12, 28.19, 28.06, 26.35, 25.13, 24.90, 21.38, 21.30. **1i**, white solid, (88% yield, 55°C, 30 min).

2-(hydroxy(4-methoxyphenyl)methyl)cyclohexan-1-one (1j, light yellow solid):



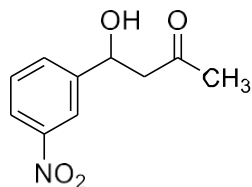
^1H NMR (400 MHz, CDCl_3): δ 7.86 - 7.82 (m, 4H), 5.32 (d, $J = 2.4$ Hz, 1H for syn), 4.74 (d, $J = 8.8$ Hz, 1H for anti), 3.89 (s, 3H, for syn-isomer), 3.80 (s, 3H, for anti-isomer), 2.59 - 1.25 (m, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 215.87, 215.11, 191.05, 159.52, 158.86, 133.86, 133.40, 132.23, 128.39, 127.16, 114.56, 114.03, 113.82, 74.51, 70.65, 57.74, 57.51, 55.50, 42.91, 42.89, 31.08, 28.20, 28.03, 26.43, 25.11, 24.96. **1j**, light yellow solid, (88% yield, 55°C, 1 h).

4-hydroxy-4-(4-nitrophenyl)butan-2-one (1k, light yellow solid):



^1H NMR (400 MHz, CDCl_3): δ 8.27 - 7.09 (m, 4H), 5.17 - 5.07 (dd, $J = 2.4, 2.4$ Hz, 1H), 3.02 - 1.73 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 197.74, 148.88, 140.91, 140.31, 130.62, 129.04, 128.72, 124.45, 123.99, 50.80, 44.64, 28.27. **1k**, light yellow solid, (91% yield, RT, 5 min).

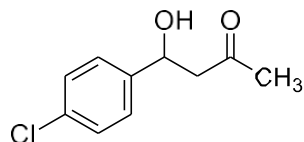
4-hydroxy-4-(3-nitrophenyl)butan-2-one (1l, light pinkish white solid):



^1H NMR (400 MHz, CDCl_3): δ 8.41 - 7.53 (m, 4H), 5.19 - 5.07 (dd, $J = 2.4, 2.4$ Hz, 1H), 3.00 - 1.69 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 197.76, 151.23, 140.41,

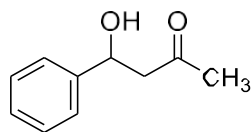
136.54, 133.97, 130.28, 129.64, 124.94, 122.84, 51.98, 28.31. **1l**, light pinkish white solid, (87% yield, RT, 30 min).

4-(4-chlorophenyl)-4-hydroxybutan-2-one (1m, white solid):



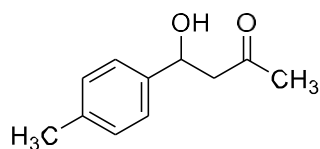
^1H NMR (400 MHz, CDCl_3): δ 7.32 - 7.23 (m, 4H), 5.14 - 5.10 (dd, $J=3.6$, 3.6 Hz, 1H), 2.98 - 2.14 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 198.08, 141.88, 136.47, 132.96, 129.40, 129.28, 127.50, 51.28, 27.67. **1m**, white solid, (80% yield, RT, 10 min).

4-hydroxy-4-phenylbutan-2-one (1n, colourless liquid):



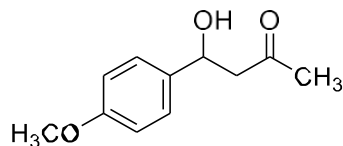
^1H NMR (400 MHz, CDCl_3): δ 7.33 - 7.23 (m, 5H), 5.13 - 5.10 (dd, $J=3.6$, 3.6 Hz, 1H), 2.99 - 2.15 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 209.17, 143.03, 128.66, 127.79, 125.78, 69.99, 52.16, 30.88. **1n**, colourless liquid, (76% yield, RT, 45 min).

4-hydroxy-4-(p-tolyl)butan-2-one (1o, light yellow liquid):



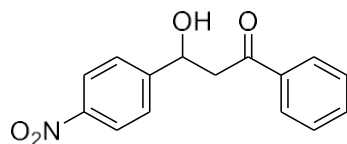
^1H NMR (400 MHz, CDCl_3): δ 7.62 - 7.18 (m, 4H), 5.51 - 5.48 (dd, $J=2.4$, 2.4 Hz, 1H), 3.00 - 2.64 (m, 6H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 209.38, 140.35, 131.34, 129.54, 128.79, 127.45, 127.29, 50.23. **1o**, light yellow liquid, (90% yield, RT, 1 h).

4-hydroxy-4-(4-methoxyphenyl)butan-2-one (1p, white solid):



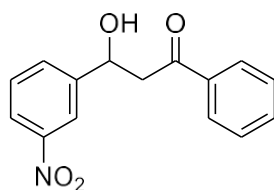
^1H NMR (400 MHz, CDCl_3): δ 7.51 - 7.691 (m, 4H), 5.53 - 5.46 (dd, $J = 2.4$, 2.4 Hz, 1H), 3.84 (s, 3H), 3.01 - 2.35 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 198.63, 161.87, 143.49, 130.19, 127.33, 125.28, 114.69, 55.63, 27.61. **1p**, white solid, (91% yield, RT, 2 h).

3-hydroxy-3-(4-nitrophenyl)-1-phenylpropan-1-one (1q, white solid):



^1H NMR (400 MHz, CDCl_3): δ 8.24 - 7.26 (m, 9H), 5.47 - 5.44 (dd, $J = 3.7$, 3.2 Hz, 1H), 3.44 - 3.31 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.73, 150.45, 147.62, 136.43, 134.25, 129.07, 128.39, 126.80, 124.04, 69.47, 47.20. **1q**, white solid, (87% yield, RT, 45 min).

3-hydroxy-3-(3-nitrophenyl)-1-phenylpropan-1-one (1r, light yellow solid):



^1H NMR (400 MHz, CDCl_3): δ 8.32 - 7.46 (m, 9H), 5.46 - 5.44 (dd, $J = 3.2$, 3.6 Hz, 1H), 3.46 - 3.33 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.80, 148.68, 145.34, 136.45, 134.20, 132.17, 129.74, 129.04, 128.39, 122.81, 121.11. **1r**, light yellow solid, (80% yield, RT, 2 h).

Figure S1: ^1H NMR data of 2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one (1a)

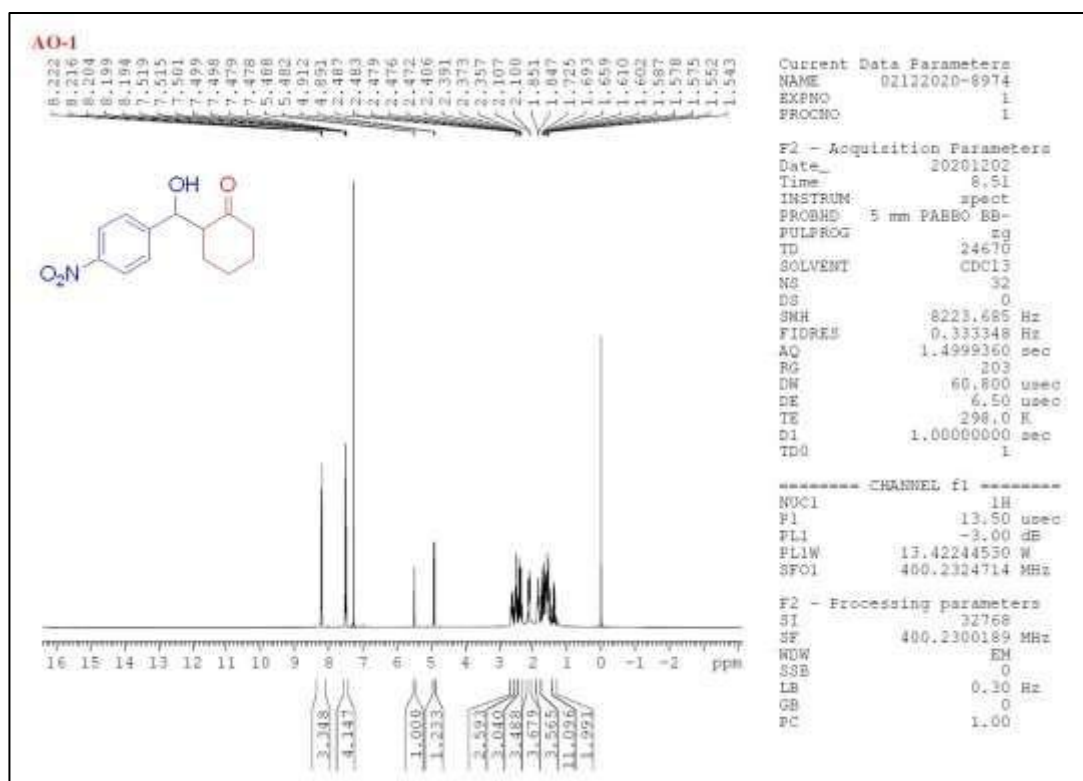


Figure S2: ^{13}C NMR data of 2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one (1a)

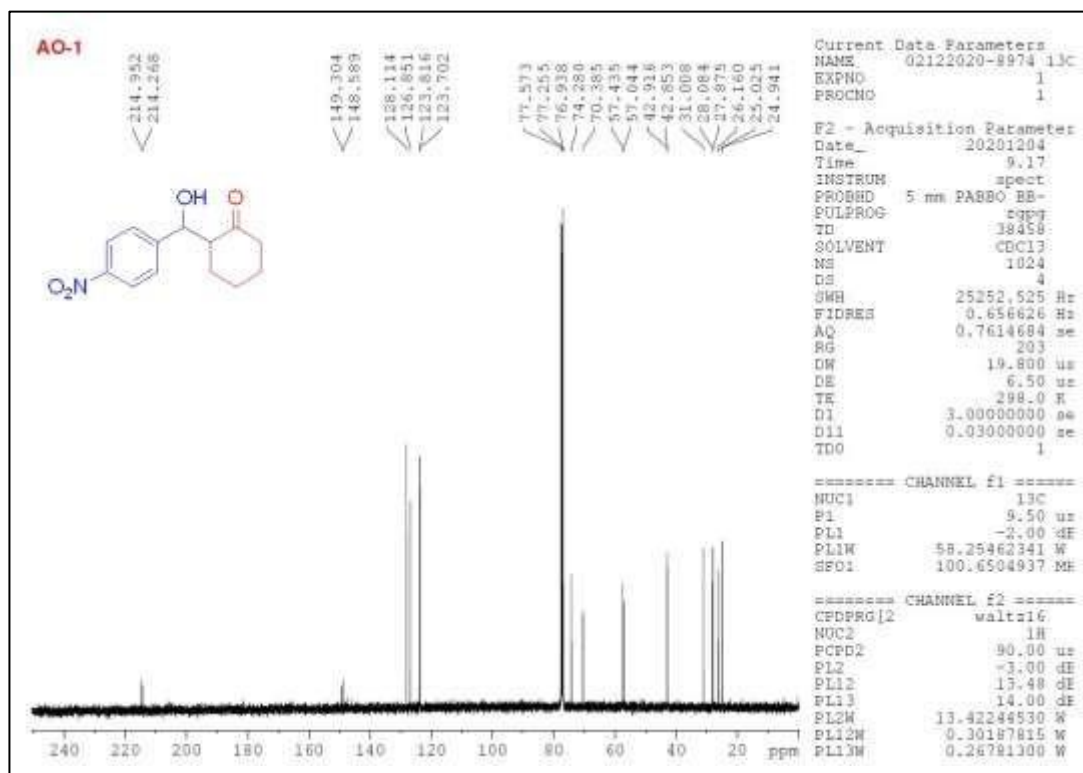


Figure S3: ^1H NMR data of 2-(hydroxy(3-nitrophenyl)methyl)cyclohexan-1-one (1b)

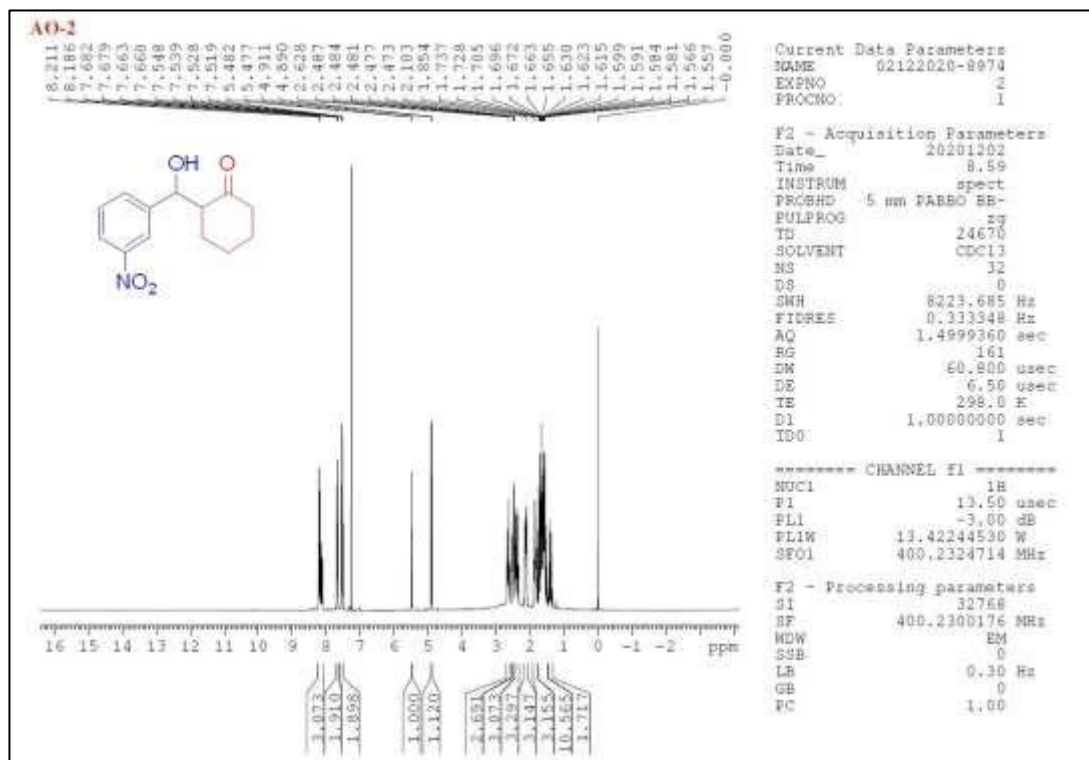


Figure S4: ^{13}C NMR data of 2-(hydroxy(3-nitrophenyl)methyl)cyclohexan-1-one (1b)

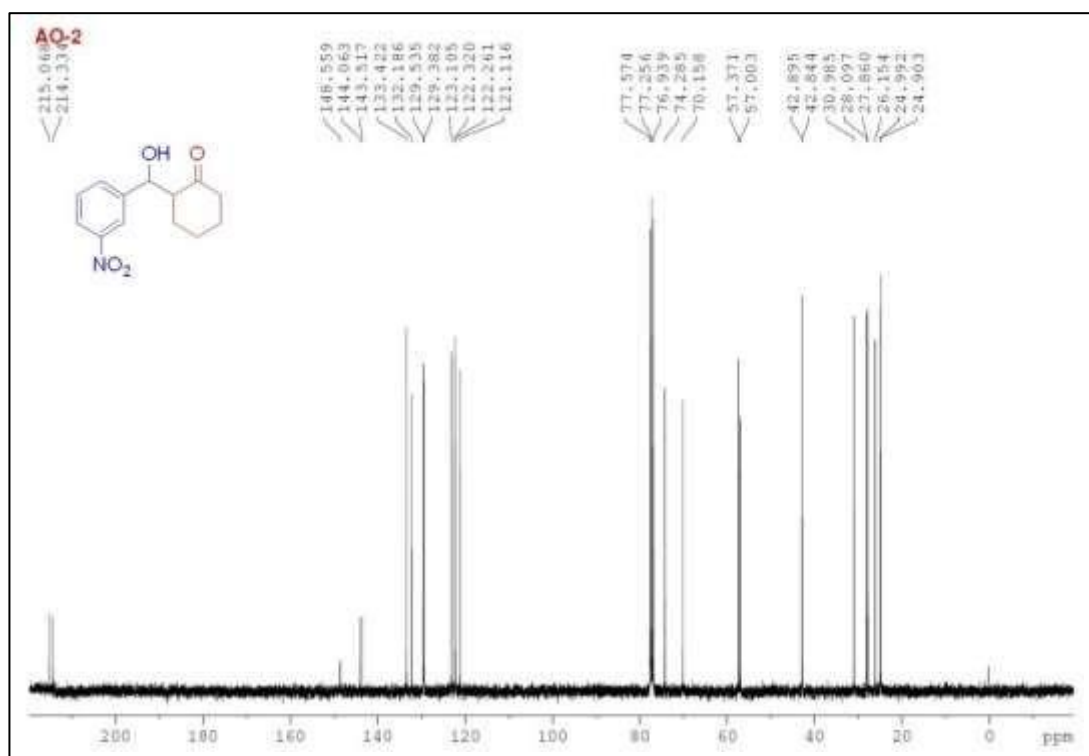


Figure S23: ^1H NMR data of 2-((4-chlorophenyl)(hydroxy)methyl)cyclohexan-1-one (7d)

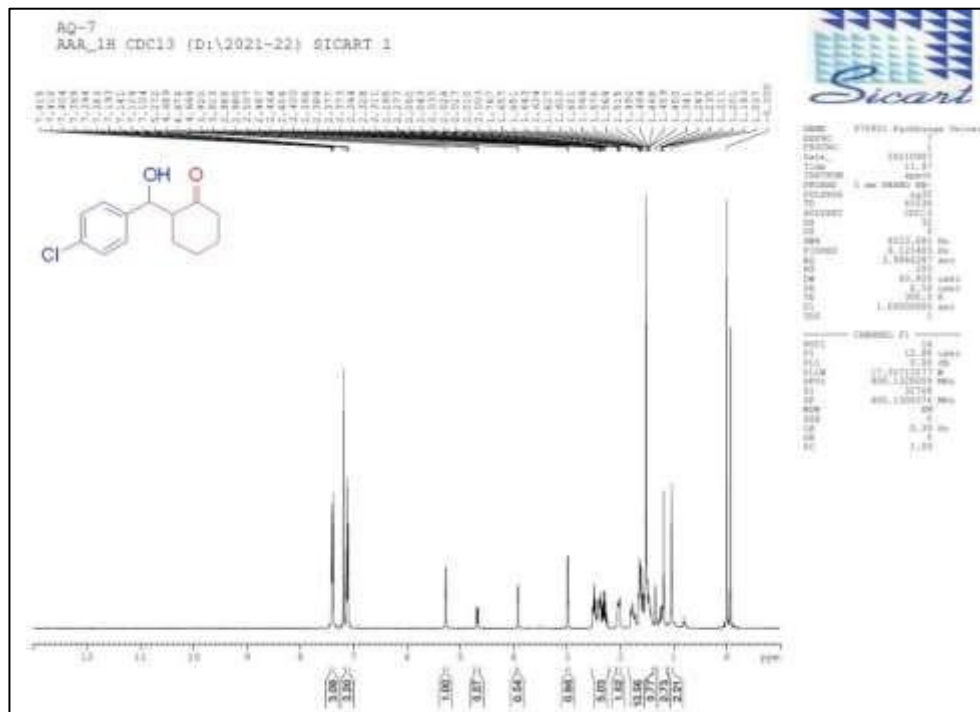
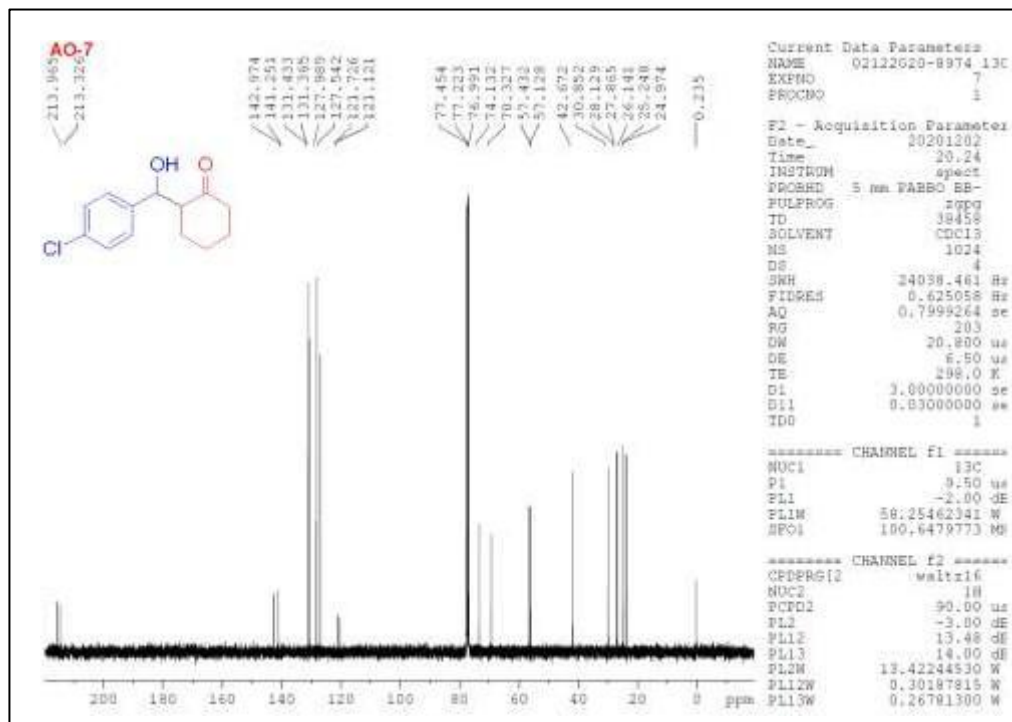


Figure S24: ^{13}C NMR data of 2-((4-chlorophenyl)(hydroxy)methyl)cyclohexan-1-one (7d)



CHAPTER 4

CONCLUSION

CONCLUSION

This study has successfully demonstrated the valorization of agro-waste biomass: specifically orange peel and bamboo leaf, into efficient, low-cost heterogeneous catalysts for sustainable chemical transformations. Through controlled thermal and green synthetic routes, three catalytic systems were developed: Orange Peel Ash (OPA), Bamboo Leaf Ash (BLA), and a magnetically recoverable nanocatalyst, OPA@Fe₃O₄. The preparation strategies emphasized simplicity, eco-friendliness, and scalability, aligning with the core principles of green chemistry.

A comprehensive suite of physicochemical characterization techniques was employed to probe the structure–activity relationships of the catalysts. X-ray diffraction (XRD) revealed the presence of catalytically active crystalline phases such as CaO, K₂O, Fe₃O₄, and silicates, with OPA@Fe₃O₄ showing pronounced polycrystallinity. FTIR spectroscopy confirmed the existence of metal–oxygen and carbonate functionalities, while XPS analysis verified the presence of surface-active basic species like K₂O, K₂CO₃, CaO, and Fe–O, which are crucial for base-catalyzed mechanisms. SEM and TEM images illustrated distinct morphologies: OPA exhibited a cloud-like agglomerated structure with moderate porosity; BLA showed globular micro-aggregates with higher roughness and porosity; and OPA@Fe₃O₄ displayed well-dispersed rod-like nanostructures in the 10 to 20 nm range. BET surface area analysis further confirmed the hierarchy in surface accessibility: OPA (4.97 m²/g) < BLA (21.85 m²/g) < OPA@Fe₃O₄ (31.23 m²/g), with all three showing mesoporosity favorable for diffusion-controlled catalysis. Thermogravimetric analysis (TGA) demonstrated excellent thermal stabilities up to 600 °C for all the catalysts, with BLA maintaining partial integrity even beyond 800 °C due to its robust silica core. EDX and XRF confirmed the abundance of basic metal oxides (CaO, K₂O, Fe₃O₄), validating their catalytic potential.

In the domain of chemical PET recycling, both glycolysis and methanolysis were effectively catalyzed using these materials. OPA demonstrated strong base activity due to its high K₂O and CaO content, resulting in rapid depolymerization but was limited by lower surface area and moderate recyclability. BLA, with its silica-

rich matrix and mesoporosity, facilitated selective depolymerization with moderate reaction rates and good thermal robustness. OPA@Fe₃O₄, however, exhibited superior performance in both reactions achieving the highest yields of BHET (91%) and DMT (83%) with enhanced selectivity, low catalyst loading, and reusability up to 10 cycles. Its nanoscale morphology, magnetic separability, high surface area, and hybrid oxide composition endowed it with excellent diffusion dynamics and prolonged catalytic lifespan.

In aldol condensation reactions, OPA was found to be an exceptional base catalyst, catalyzing C–C bond formation under aqueous, room-temperature conditions. Its performance surpassed other biomass-derived ashes (Bamboo Leaf Ash, Bagasse Ash, Banana Peel Ash, etc.), affording up to 96% product yield in 5 minutes. The high activity was directly attributed to its strong surface basicity, porous microstructure, and synergistic interaction of multiple oxides. The catalyst also displayed good substrate tolerance, successfully catalyzing aldol reactions with both electron-donating and electron-withdrawing aromatic aldehydes, and maintained activity over four cycles with minimal structural deterioration, as confirmed by SEM and EDX.

Importantly, this work offers a comparative analysis between biomass-derived catalysts and conventional systems (metal acetates, ionic liquids, organocatalysts, and nanoparticles). While synthetic systems often achieve high yields, they suffer from high cost, complex preparation, poor recyclability, and environmental concerns. In contrast, the presented catalysts are not only inexpensive, scalable, and environmentally benign, but also exhibit competitive or superior catalytic performance, particularly in green reaction settings.

This investigation provides compelling evidence for the catalytic valorization of biomass waste. The integration of structure-property-activity correlations and reaction optimization establishes a robust platform for biomass-derived catalyst development. By enabling both plastic waste remediation and agro-waste utilization, this work contributes meaningfully to the goals of circular chemistry, green catalysis,

and sustainable materials design. The successful application of OPA, BLA, and OPA@Fe₃O₄ in diverse reactions underlines the potential of waste-derived materials as next-generation heterogeneous catalysts for eco-efficient synthesis.

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HSLC	2011	Mizoram Board of School Education	English, Mizo, Social Science, Sciences, Mathematics	75	Distinction
HSSLC	2013	Mizoram Board of School Education	English, Mizo, Biology, Physics, Chemistry	73	First
B. Sc. (Chemistry)	2016	Mizoram University	Chemistry, Zoology, Geology	82	First
M. Sc. (Chemistry)	2018	North-Eastern Hill University (NEHU)	Chemistry	66	First

List of Publications:

1. Lalthanpuui, P.B., **Laldinpuui, Z.T.**, Lalmangaihzuala, S., Vanlaldinpuia, K., Lalruatfela, B., Lalnunfela, C., Lalawmpuii, R., Lalhriatpuui, T.C., Lahlenmawia, H. and Lalchhandama, K., (2020). Chemical profiling of alkylamides from the "herbal Botox", *Acemella oleracea*, cultivated in Mizoram and their pharmacological potentials. *J. Environ. Biol.*, **41(4)**, 845-850.
2. Lalmangaihzuala, S., **Laldinpuui, Z.**, Lalmuanpuia, C., and Vanlaldinpuia, K., (2020). Glycolysis of poly (ethylene terephthalate) using biomass-waste derived recyclable heterogeneous catalyst. *Polymers*, **13(1)**, 37.
3. **Laldinpuui, Z.**, Lalmangaihzuala, S., Pachuau, Z., & Vanlaldinpuia, K., (2021). Depolymerization of poly (ethylene terephthalate) waste with biomass-waste derived recyclable heterogeneous catalyst. *Waste Manag.*, **126**, 1-10.
4. **Laldinpuui, Z. T.**, Lalmuanpuia, C., Lalmangaihzuala, S., Khiangte, V., Pachuau, Z., and Vanlaldinpuia, K., (2021). Biomass waste-derived recyclable heterogeneous catalyst for aqueous aldol reaction and depolymerization of PET waste. *New J. Chem.*, **45(41)**, 19542-19552.
5. **Laldinpuui, Z. T.**, Khiangte, V., Lalmangaihzuala, S., Lalmuanpuia, C., Pachuau, Z., Lalhriatpuia, C., and Vanlaldinpuia, K., (2022). Methanolysis of PET waste using heterogeneous catalyst of bio-waste origin. *J. Polym. Environ.*, **1-15**.
6. Khiangte, V., Lalmangaihzuala, S., **Laldinpuui, Z. T.**, Nunnemi, L., Muthukumaran, R. B., and Vanlaldinpuia, K., (2023). Novel dragon fruit peel ash-derived solid catalyst for biodiesel production and PET waste recycling. *Bioresour. Technol. Rep.*, **101663**.
7. . Lalmangaihzuala, S., **Laldinpuui, Z. T.**, Khiangte, V., Lallawmzuali, G., and Vanlaldinpuia, K., (2023). Orange peel ash coated Fe₃O₄ nanoparticles as a magnetically retrievable catalyst for glycolysis and methanolysis of PET waste. *Adv. Powder Technol.*, **34(7)**, 104076.
8. Lalmangaihzuala, S., Khiangte, V., **Laldinpuui, Z.**, Nunnemi, L., Malsawmsanga, J., Lallawmzuali, G., Liana, T., Lalhriatpuia, C., Pachuau, Z., and anlaldinpuia, K., (2023). Synthesis of D-Fructose-Based Bifunctional

Primary Amine-Thiourea Organocatalysts and their Applications in Asymmetric Reactions. *Chemistry*, 5(4), 2362-2375.

Seminar/Conference:

1. Presented “**Assessment of the antioxidant activity and anticancer property of *Picria felterrae* in human colon cancer cells (HCT116)**” at International Conference on Recent Advances in Animal Sciences (ICRASS) on 6th to 8th November, 2019 which was organized by Department of Zoology, Pachhunga University College, Aizawl, Mizoram, India.
2. Presented “**Orange peel derived magnetic nanoparticles for chemical recycling of Poly(ethylene) terephthalate**” in the 2nd Annual Convention of North East (India) Academy of Science and Technology (NEAST) & International Seminar on Recent Advances in Science and Technology (ISRAST) during 16th–18th November 2020 (Virtual) organized by NEAST, Mizoram University, Aizawl-796004, Mizoram (India).
3. Presented “**Upcycling of Plastic Waste Using Biomass-derived Catalysts**” at the 4th Mizoram Science Congress on 24th to 25th, November, 2022 which was organized by Mizoram Science, Technology, and Innovation Council (MISTIC) in collaboration with Mizo Academy of Sciences (MAS), Mizoram Science Society (MSS), Science Teachers’ Association, Mizoram (STAM), Geological Society of Mizoram (GSM), Mizoram Mathematics Society (MMS), Biodiversity and Nature Conservation Network (BIOCON) and Mizoram Information & Technology Society (MITS).
4. Presented “**Chemical recycling of PET waste using biomass derived catalysts**” at the International Conference on Current Trends in Green and Sustainable Chemistry (ICCTGSC-2023) on 11th to 12th May, 2023 which was organized by Department of Chemistry, Pachhunga University College, Aizawl, Mizoram, India.



Depolymerization of poly(ethylene terephthalate) waste with biomass-waste derived recyclable heterogeneous catalyst

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ABSTRACT

Poly(ethylene terephthalate) (PET) is one of the most widely used polymeric materials in chemical industry representing about 13% of the world's production. With the exponentially increasing consumption of plastics combined with its non-biodegradability, the accumulation of plastic waste in the environment rises steeply and its recycling has attracted enormous attention among researchers in recent years. In this present work, we describe bamboo leaf ash (BLA) as a bio-waste derived recyclable heterogeneous catalyst for the depolymerization of waste PET. The prepared catalyst was characterized by FT-IR, XRD, SEM, TEM, EDX, TGA and BET analyses to assess its morphology and composition. Postconsumer PET bottles were shredded and processed with 20 wt% BLA and 16 equivalents of ethylene glycol (EG) at 190 °C for 3.5 h under atmospheric pressure to give recrystallized bis(2-hydroxyethyl) terephthalate (BHET) monomer in 83% yield. The catalyst can be reused for four catalytic cycles and the residual EG was recovered for subsequent catalytic reactions. Excellent activity, cost-free, environmental-friendliness and ease of preparation, handling and reusability of the catalyst with simple work-up procedure are the notable advantages of this protocol.

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1. Introduction

Large scale production of plastics, or synthetic polymers started only in the early 1950s, but it has now become one of the most pervasive materials in the world. According to PlasticsEurope Market Research Group (PEMRG), the global production of plastics in 2014 was 311 million tons which was increased to 359 million tons in 2018 (PlasticEurope, 2019; Webb et al., 2015). It was estimated that by the end of 2015, all the plastics waste ever generated from virgin materials and secondary (recycled) plastics was 6300 million tons out of which around 4900 million tons were castoff through landfills (Geyer et al., 2017). Owing to its high tensile strength, glass-like lucidity and chemical and thermal stability, poly(ethylene terephthalate) or PET is now the third most extensively used thermoplastic polyester (Bartolome et al., 2012a; Sinha et al., 2010; Webb et al., 2013). It is mainly used in fiber manufacturing, packaging and textile industry, the manufacture of films and thermoformed products (Awaja and Pavel, 2005; Kint and Muñoz-Guerra, 1999; Scheirs and Kaminsky, 2006). But, with

a rapid increase in its production and consumption coupled with its sturdiness against degradation, the amount of PET waste increases drastically and its disposal poses a serious global issue (Paszun and Sychaj, 1997; Webb et al., 2013). Consequently, PET waste management has attracted enormous attention for both economic and environmental reasons (Yamada-Onodera et al., 2001; Zheng et al., 2005). There are three main methods of PET waste removal: landfilling, incineration and recycling (Webb et al., 2013). As landfill occupy space and incineration produced undesirable products such as CO₂, recycling is now the most practicable and environmentally friendly method of PET waste handling.

The two main approaches widely used in PET recycling are physical and chemical recycling. Physical recycling is the most common technique employed for PET which includes size reduction and melt filtration to produce new material but results in degradation of the plastic properties. On the other hand, chemical recycling includes depolymerization, purification and then repolymerization to yield high-quality end products (Karayannidis and Achilias, 2007; Karayannidis et al., 2006; Yamada-Onodera et al., 2001; Zhang et al., 2004).

In recent years, chemical recycling processes such as aminolysis, ammonolysis, glycolysis, hydrolysis and methanolysis have

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been developed for the depolymerization of PET (Thomas et al., 2019). The primary aim of these processes is to obtain the monomer or higher oligomers to reproduce PET and/or to synthesize other polymers with superior economic significance (Duarte et al., 2016; Karayannidis et al., 2005; Roy et al., 2013; Shukla et al., 2008, 2009). However, due to the exorbitant charge involved with methanolysis, low purity of terephthalic acid (TPA) monomer obtained from hydrolysis and limited applications of products procured from aminolysis and ammonolysis on a commercial scale, depolymerization of PET through glycolysis is considered as the best method for PET recycling as it results in the formation of BHET monomer, which is the substrate for PET synthesis (George and Kurian, 2014; Khoonkari et al., 2015). Also, it is regarded as the least capital-intensive process (Bartolome et al., 2012b) and a wide range of reagents have been used including ethylene-glycol, diethylene glycol, 1,4-butanediol, propylene glycol, dipropylene glycol, neopentyl glycol, some oligoesters and even its monomer bis(2-hydroxyethyl)terephthalate (BHET) (El Mejjati et al., 2014). Since the process is slow and complete depolymerization could not be achieved without the presence of a catalyst (Campanelli et al., 1994; Chen and Chen, 1999), a wide range of catalysts such as alkalis, metal salts, zeolites, nanoparticles, ionic liquids and organocatalysts were developed and explored to increase the rate and yield of the depolymerized product (Jehanno et al., 2019; Khoonkari et al., 2015). However, these methods usually suffer from difficulty in the purification process, poor selectivity, high environmental and economic cost and high toxicity of the catalysts (Khoonkari et al., 2015). So, to address these shortcomings, the development of new methodologies with more efficient and cost-effective catalysts is still the center of research interest.

Every year, large amounts of lignocellulosic biomass are produced around the world from agriculture products and disposing of these wastes to the landfill becomes a great concern in developed as well as in developing countries (Pathak et al., 2017; Stewart, 2010). Utilization and conversion of these deposits to value-addition products could not only minimize the reliance on fossil fuels but it would also greatly decrease wastes from the environment. Recently, the use of these waste biomass as heterogeneous catalysts for different types of organic transformation has gained momentum due to their eco-friendly and excellent catalytic activity (Abdullah et al., 2017). It has been reported that these bio-wastes derive catalysts can be used for bio-fuel production, C-C bond formation and peptide bond formation (Basumatary et al., 2018; Chakraborty et al., 2016; Konwar et al., 2016; Pathak et al., 2018; Rajkumari et al., 2019). More recently, we have also reported for the first time, the glycolysis of PET waste using orange peel ash (OPA) as a recyclable heterogeneous catalyst (Lalmangaihzualla et al., 2020).

Bamboo is a fast-growing member of the grass family which includes 1250 species and considered as one of the highest yielding natural resources (Scurlock et al., 2000). It has been used for handicrafts, construction materials, paper and textile production and as a food source in different parts of the world. Nonetheless, despite its immense usages, the silica-rich bamboo leaves (~30–50% silica) are considered as waste and its application is very limited (Rangaraj and Venkatachalam, 2017). Ash from bamboo leaves was investigated for the production of pozzolanic material in cement composites (Umoh and Odesola, 2015; Villar-Cociña et al., 2011). Recently, the utilization of ZrO₂ impregnated bamboo leaf ash (BLA) as a heterogeneous catalyst in microwave-assisted biodiesel conversion was also reported (Fatimah et al., 2019). So, in continuation to our interest in the development of greener methodology for PET depolymerization, we have investigated the application of bio-waste, cost effective and eco-friendly bamboo leaf ash (BLA) as a recyclable heterogeneous catalyst for glycolysis of PET to BHET monomer.

2. Experimental section

2.1. Materials and methods

Used PET bottles were procured from the local area. After removing the cap and label, it was washed with distilled water, dried and then cut into about 1 mm × 1 mm flakes. Ethylene glycol, methanol and dichloromethane were purchased from Sigma-Aldrich. Deionized water was obtained from HiMedia. All the chemicals were of analytical grade and used without further purification.

Powder X-ray diffraction (XRD) was performed on Philips, Xpert MPD to examine the crystalline composition. Wavelength dispersive X-ray fluorescence (XRF) of the prepared catalyst was analyzed using PANalytical, Axios mAX. Scanning Electron Microscope (SEM) images and elemental compositions of the catalyst were recorded on JSM-6360, Jeol, and ESEM EDAX XL-30. Transmission Electron Microscope (TEM) image was recorded on JEM-2100, 200 kV instrument. FT-IR spectra was recorded on a Spectrum BX FT-IR, Perkin Elmer ($\nu_{\max}$ in cm⁻¹) using KBr disks. The N₂ adsorption-desorption isotherm was recorded using Quanta chrome Nova-1000 surface area and porosity analyzer. The samples were pre-treated at a degassing temperature of 150 °C for 10 h. The thermogravimetric analysis was performed using Perkin Elmer TGA 4000. The weight loss of the prepared ash catalyst was recorded at a varying temperature ranging from 30 °C to 995 °C, with heating rate at 10.00 °C/min. Nuclear magnetic resonance (¹H NMR and ¹³C NMR) were performed on Bruker, 400 MHz Avance III spectrometer in DMSO *d*₆ (chemical shift in δ with TMS as internal standard). HPLC (High Performance Liquid Chromatography) analysis was carried out with Waters 1525 binary pump using Spherisorb ODS2 5 μ m, 4.6 × 250 mm analytical column and Waters UV detector 2489 set at 254 nm.

2.2. Preparation of the catalyst

Bamboo (*Melocanna baccifera*) leaves were collected from Mizoram, India. It was washed thoroughly with distilled water, dried in sunlight for three days or inside the oven at 60 °C for 24 h, and then burnt in an open air. The black-colored ash originally formed as a result of incomplete combustion was calcined at 700 °C for 4 h. The grey-colored ash was then collected and sifted to 100 BSS (British Standard Sieve) and stored at room temperature.

2.3. Glycolysis of PET waste

A two necked 100 mL round bottom flask fitted with thermometer and reflux condenser was loaded with 480 mg (2.5 mmol) of PET flakes, 2.25 mL of ethylene glycol and 100 mg of BLA. The mixture was immersed in an oil bath and the reaction was carried out at 190 °C in atmospheric pressure. After completion of the reaction (3.5 h), the compound obtained was purified by either of the following two methods (Fukushima et al., 2011).

Method 1: The catalyst was separated quickly via filtration and then washed with 100 mL of hot deionized water. After the mixture was cooled down, the white precipitate insoluble in water was filtered. The filtrate was then concentrated to about 40 mL and stored in a refrigerator at 2 °C for 12 h. The white crystalline product formed in the filtrate was separated, dried and then weighed (83% yield).

Method 2: After filtration, the residue was washed with 15 mL of methanol. The filtrate was collected and the solvent was evaporated under reduced pressure. The crude solid was dissolved in warm CH₂Cl₂ (150 mL) and then washed with water (2 times). The aqueous portion was extracted with 50 mL of CH₂Cl₂, the

organic fractions were combined, dried with Na_2SO_4 , and then evaporated to give BHET as a white powder (56% yield).

The conversion % of PET and yield % of the recrystallized product were calculated using the following equations:

$$\text{Conversion \% of PET} = \frac{\text{weight of initial PET} - \text{undepolymerized PET}}{\text{weight of initial PET}} \times 100 \quad (1)$$

$$\text{Yield \% of BHET} = \frac{\text{weight of BHET monomer}}{\text{theoretical weight of BHET monomer}} \times 100 \quad (2)$$

The water insoluble product % was also calculated from the total amount of solid obtained by using the following equation:

$$\text{Yield of water insoluble part \%} = \frac{\text{water insoluble product}}{\text{BHET} + \text{water insoluble product}} \times 100 \quad (3)$$

3. Results and discussion

3.1. Characterization of the catalyst

The chemical composition of the ash was investigated by XRF analysis and the results are recorded in Table S1 (see [Supplementary material](#) published with this article, page S1). The catalyst was found to contain silica (SiO_2) as the major component with 76.026% followed by SO_3 (6.892%), CaO (4.783%), K_2O (2.876%), Fe_2O_3 (2.341%), MnO (1.888%) and MgO (1.277%). Several other metal oxides such as Na_2O , MgO , Al_2O_3 , P_2O_5 , TiO_2 , etc were also present in less than 1% concentration.

The BLA catalyst was then characterized by FT-IR spectrophotometer in the range of $4000\text{--}500\text{ cm}^{-1}$ to detect the functional group present in it (Fig. 1a). A broad vibration band at 3438 cm^{-1} is indicating the --OH stretching vibration of the absorbed moisture at the surface of the catalyst. The appearances of peaks at 1647 cm^{-1} and 1454 cm^{-1} might be due to the presence of C--O stretching in metal carbonates (Rajkumari et al., 2019). And the stretching vibration of Si--O--Si bond is detected at 1097 cm^{-1} (Fatimah et al., 2019; Tran et al., 2013).

To find out the crystalline structure of the catalyst, XRD analysis was carried out and the results are illustrated in Fig. 1 (b). The strong characteristic peaks of SiO_2 were observed at $2\theta = 20.817$, 26.577 and 50.088° (JCPDS reference file no. 89–1961, 89–8936 and 89–8945). The characteristic peaks at $2\theta = 29.422$, 42.355 and 45.688° (JCPDS reference file no. 86–2334, 02–1088 and 87–1863) revealed the presence of CaO and CaCO_3 . The appearances of peaks at $2\theta = 39.422$ and 40.222° (JCPDS reference file no. 47–1701 and 70–0292) also exhibited the occurrence of K_2O and K_2CO_3 in the catalyst. Apart from these, peaks at $2\theta = 35.750$, 36.840 , 43.135 , 47.422 , 48.355 , 54.755 , 59.822° (JCPDS reference file no. 89–8104, 73–2169, 86–0305, 86–0294, 88–0107, 73–1539) were observed signifying the presence of Fe_2O_3 , SO_3 , Na_2CO_3 , Al_2O_3 and MnO_2 in BLA.

The surface area of BLA was determined by Brunauer-Emmett-Teller (BET) method and the average pore size was calculated using Barrett-Joyner-Halenda (BJH) model. Fig. 1 (c) and (d) displays pore size distribution analysis and N_2 adsorption-desorption isotherm of bamboo leaf ash, correspondingly. The N_2 adsorption-desorption isotherm exhibit H1 hysteresis loop indicating the typical type-IV isotherm which suggested the porous nature of the catalyst. It was found that the pore volume, pore diameter and surface area of the catalyst were 0.127 cc g^{-1} , 13.684 nm and 21.847 m^2

g^{-1} , respectively. EDX studies of the catalyst was also in accord with XRD and XRF data and disclosed the presence of Si, O, Ca, K, Al, Mg, Fe and P among others (Fig. 2a).

TGA analysis was performed under N_2 atmosphere in the range of $30\text{--}1000^\circ\text{C}$ to validate the stability of the catalyst with increasing temperature. The initial weight loss of about 6% was detected up to 200°C which is due to the elimination of water molecules absorbed in the catalyst. The further weight loss observed at high temperature might be due to the decomposition of carbonaceous materials but the overall weight loss is only 13% which demonstrates the thermal stability of BLA even at an elevated temperature (Fig. 2b).

The morphology of BLA was studied with SEM and TEM analysis which revealed a spongy nature of the bamboo leaf ash and appeared as agglomerated structure as shown in Fig. 3. From these observations, we believed that the catalytic activity of BLA is mainly due to the presence of some metals in the form of their oxides and carbonates and the high porosity of the catalyst which offer suitable morphology for adsorption of organic materials for catalytic stimulations.

3.2. Glycolysis of PET using BLA

Glycolysis of PET was performed in a two necked round bottom flask containing EG, PET and BLA at 190°C under atmospheric pressure. The disappearance of PET flakes was used as a visible indicator for the end of the reaction (Fukushima et al., 2011). After completion of the reaction, the crude product was purified by either recrystallization or extraction methods and the pure product was characterized using HPLC, IR, ^1H and ^{13}C NMR. The crude product and water-insoluble part obtained in the recrystallization process were also characterized using HPLC and NMR.

The High-Performance Liquid Chromatography (HPLC) analysis was carried out in a reversed-phase column using a mixture of methanol/water at a volume fraction of 70/30 as a mobile phase at a flow rate of 1 mL/min . The crude product showed three major peaks at the retention time of 1.872, 3.385 and 6.363 min which corresponds to ethylene glycol, BHET monomer and BHET dimer, respectively (Fig. 4b). HPLC analysis of commercially available BHET monomer, ethylene glycol and recrystallized product (Fig. 4a), as well as the water insoluble fraction is in accord with the findings (see [Supplementary material](#) published with this article, Figure S1–S5). Three prominent bands at $\nu = 3441\text{ cm}^{-1}$ (OH), 2950 cm^{-1} (CH_3) and 1693 cm^{-1} (C=O) were observed in its IR spectra and a strong absorption peak at 1260 cm^{-1} was assigned to esters C--O bond (see [Supplementary material](#) published with this article, Fig. S6).

^1H NMR spectra of the recrystallized product using $\text{DMSO-}d_6$ as solvent revealed resonances at $\delta = 8.09$, 5.00 , 4.30 , 3.70 and 2.49 ppm (see [Supplementary material](#) published with this article Fig. S7) and assigned to aromatic protons, hydroxyl protons, methylene protons of COO--CH_2 and $\text{CH}_2\text{--OH}$ and DMSO, respectively. In its ^{13}C NMR, distinctive peaks at $\delta = 165.09$ (carbonyl), 133.63 and 129.43 (aromatic carbons), 66.95 and 58.91 ppm were also detected (see [supplementary material](#) published with this article Fig. S8). The water insoluble fraction was found to be composed mainly of BHET dimer (see [supplementary material](#) published with this article Figs. S9 and S10), but most probably other oligomers and terephthalic esters are also present in it (Fukushima et al., 2011).

3.2.1. Optimization of the catalyst loading

Initially, the conversion of PET waste to its monomer (Scheme 1) was carried out in the presence of 16 equivalent of ethylene glycol and 15 wt% BLA at 190°C and after 3 h, 77% yield of BHET mono-

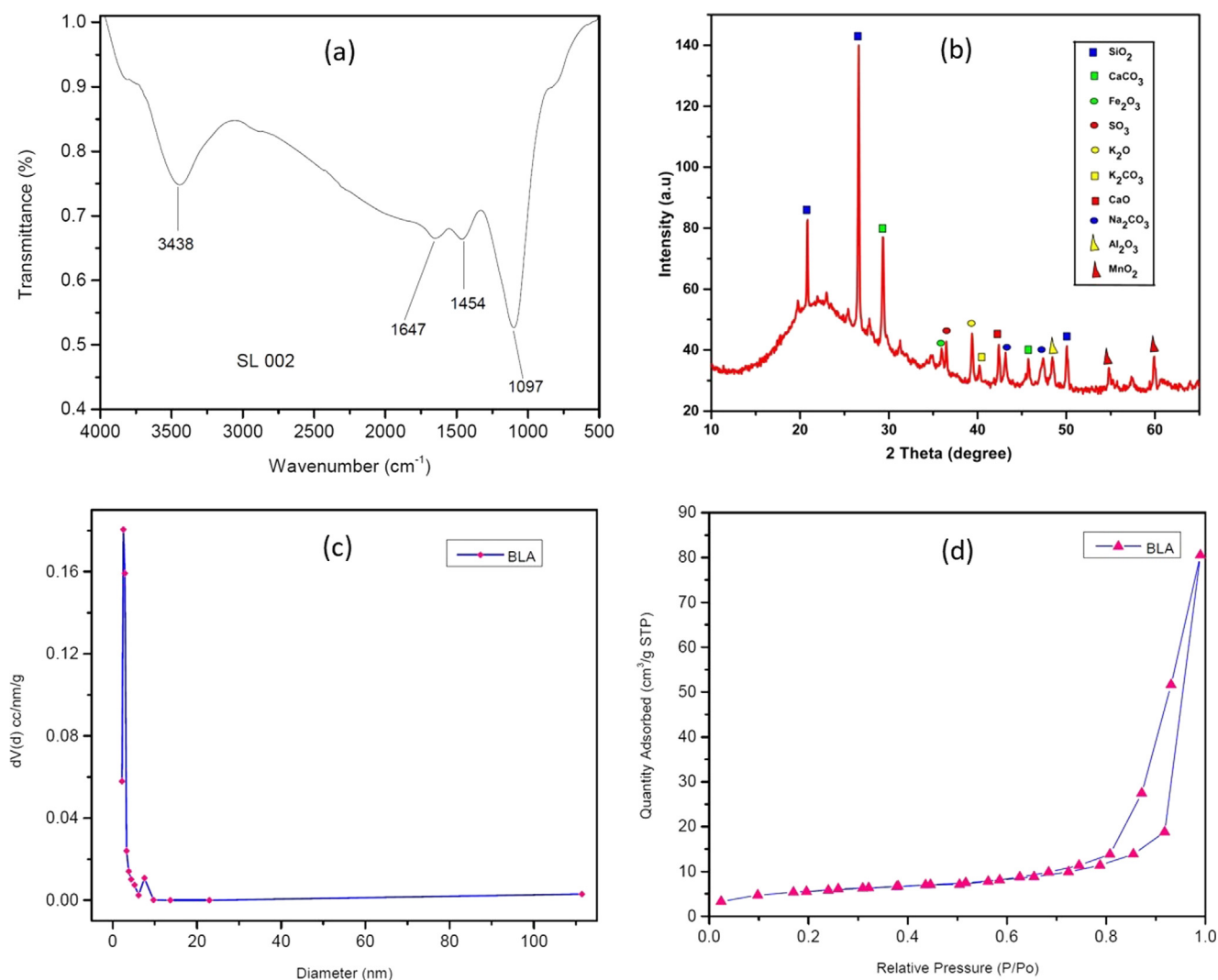


Fig. 1. (a) IR data of BLA, (b) XRD data of BLA, (c) BJH pore size distribution of BLA, and (d) N₂ adsorption-desorption isotherm of BLA.

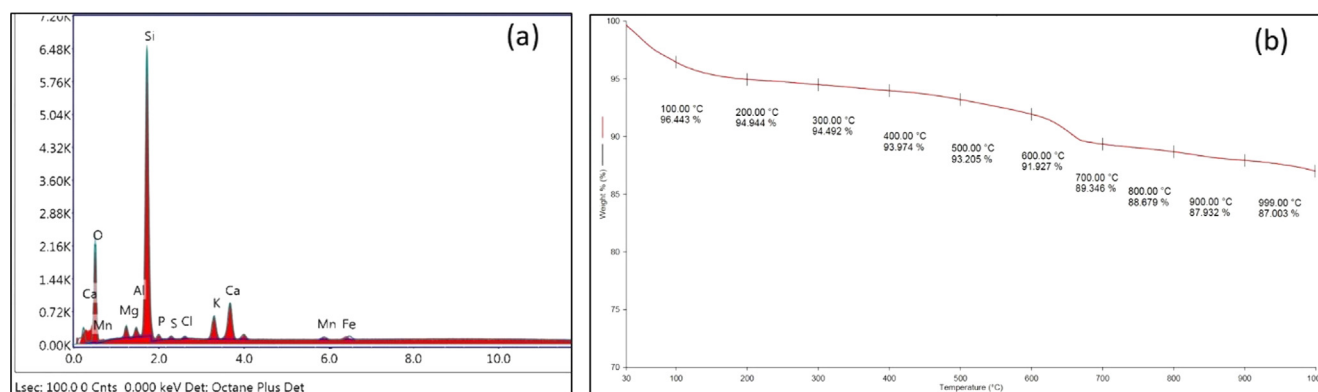


Fig. 2. (a) EDX data of BLA, and (b) TGA thermogram of BLA.

mer was obtained (Table 1, entry 4). When the same reaction was performed in the absence of our catalyst, even after 100 h of reaction time at 190 °C, only 74% PET conversion and 41% BHET yield were achieved (Table 1, entry 2). So, while keeping other parameters such as EG loading and reaction time constant, optimization of the catalysts loading was performed and the result is shown in Table 1. Previous studies have shown that an equilibrium exists

between BHET monomer and oligomers particularly its dimer during glycolysis (Ghaemy and Mossaddegh, 2005; Raheem et al., 2019; Xi et al., 2005). Our results were also on a par with an earlier report that increasing the catalyst loading accelerates the reaction but shortens the equilibration time (Al-Sabagh et al., 2014; Zhou et al., 2012). Table 1, entry 3–5 clearly exhibited this trend as enhancing the amount of catalyst from 10 wt% to 20 wt% led to

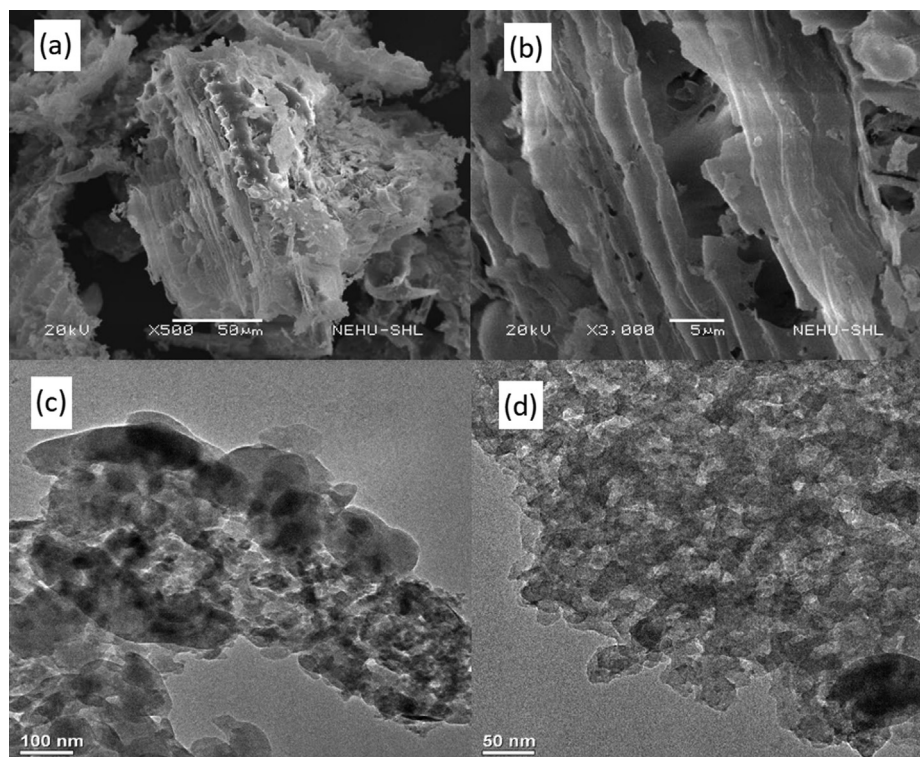


Fig. 3. SEM [a) and b)] and TEM [c) and d)] micrographs of BLA.

the improved formation of BHET monomer with a decreased in the production of water insoluble part. The best result was obtained with 20 wt% of the catalyst giving 79% BHET yield (Table 1, entry 5) and we choose this catalyst loading for further study. However, an additional increase in the catalyst amount led to the reduction of BHET yield (Table 1, entry 6 and 7). This might be attributed to the fact that, after crossing the optimal catalyst loading, the reaction progressed more rapidly to form BHET monomer. As the reaction proceeds further, BHET then repolymerized into its dimer and oligomers, which plummets the BHET yield while increasing the water insoluble product at the same time (Al-Sabagh et al., 2014; Wang et al., 2010).

3.2.2. Optimization of the reagent loading and reaction time

The impact of EG loading and reaction time on glycolysis of PET were examined and the results are shown in Fig. 5a and 5b. It has been observed in the previous reports that the ratio of ethylene glycol to PET influences both the conversion and yield of the product (Ghaemy and Mossaddegh 2005; Xi et al., 2005). This is consistent with our findings and with an increase in the concentration of ethylene glycol, the formation of oligomer decreases, which also contributes to easy recrystallisation and purification (see Supplementary material published with this article, Table S3). Even at a low concentration of EG (6 equiv.), the glycolysis proceeded efficiently, but there is some difficulty in the purification process as the recrystallized products usually contain small amount of the dimer and/or oligomers of BHET. We have also observed that the equilibrium between BHET monomer and dimer was reached after 3.5 h of reaction when the temperature and EG loading were fixed at 190 °C and 16 equivalents, correspondingly. Shorter or longer reaction time results in the increased formation of water-insoluble fraction (see Supplementary material published with this article, Table S2). This selectivity of BHET monomer to initial increase and then decrease with reaction time can be explained on account of their depolymerization and repolymerization pro-

cess. During glycolysis, PET first degrades into its oligomers, then to the dimers and lastly, into its monomer. With increasing glycolysis time, BHET repolymerized into its dimers and then into oligomers, forming chemical equilibrium (Al-Sabagh et al., 2014; Wang et al., 2009). Shorter reaction time results in the incomplete degradation of the oligomers or dimers whereas prolonged reaction time beyond 3.5 h results in the repolymerization of BHET monomer.

3.2.3. Effect of reaction temperature

We further examine the effect of temperature for glycolysis of PET and observed that it exponentially affected the reaction time as well as BHET yield (see Supplementary material published with this article, Table S4). When the reaction was carried out at 190 °C using 2.5 mmol of PET, 100 mg of catalysts and 16 equiv. of EG, depolymerization was completed within 3 h. But the best result was obtained after prolonging the reaction for another 30 min. At 150 °C, depolymerization required 72 h which indicated that this process can be performed even at a reduced temperature. But at 200 °C, there is a slight decrease in BHET yield with an increase in BHET dimer and/or oligomer production (Fig. 6a).

3.2.4. Reusability of the catalyst

Further, the efficacy of the recovered BLA catalyst was investigated for the next subsequent four catalytic cycles under our optimized condition and recovery technique (Fig. 6b). A mixture of PET flakes (480 mg), BLA (100 mg) and EG (2.25 mL) were heated at 190 °C for 3.5 h. After filtration and washing with methanol, the catalyst was dried in an oven at 80 °C for 5 h. It was noticed that there was a loss of about 5 to 10% catalyst by weight which was then compensated with a fresh catalyst. For the second run, depolymerization requires 7.5 h and there was a gradual increase in PET degradation time as well as a slight decreased in BHET yield for the next successive run (see Supplementary material published with this article, Table S5). This might be due to the leaching of the active components of the catalyst during the reaction and purifica-

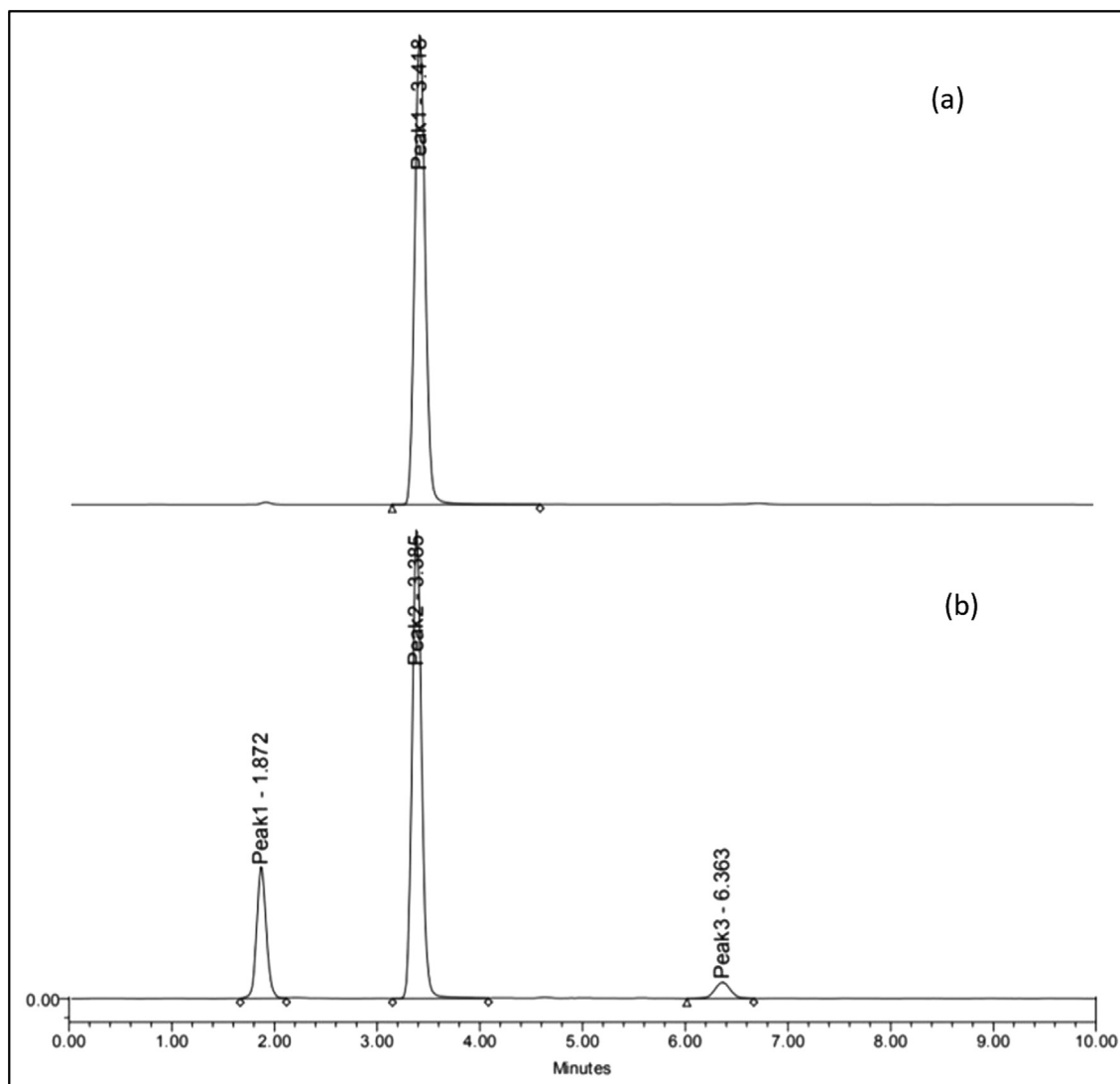
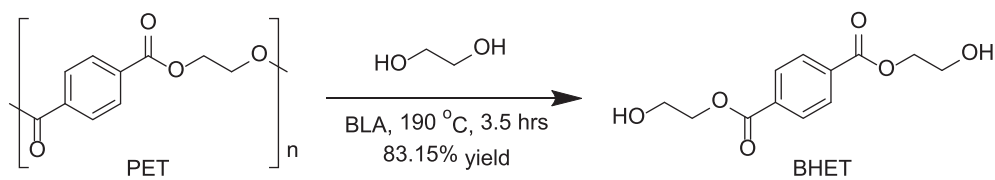


Fig. 4. HPLC data of (a) the recrystallized product and (b) the crude product.



Scheme 1. Depolymerization of PET.

Table 1
Optimization of the catalyst loading.^a

Entry	Catalyst loading (in mg)	Reaction time (in h)	Yield of water insoluble product %	BHET yield %
1	–	24 ^b	less than 1	2
2	–	100 ^c	2	41
3	50	3	7	72
4	70	3	5	77
5	100	3	3	79
6	120	3	4	78
7	140	3	6	76

^a Reaction condition: 480 mg (2.5 mmol) of PET, and 2.25 mL of ethylene glycol at 190 °C.

^b 16% PET conversion.

^c 74% PET conversion.

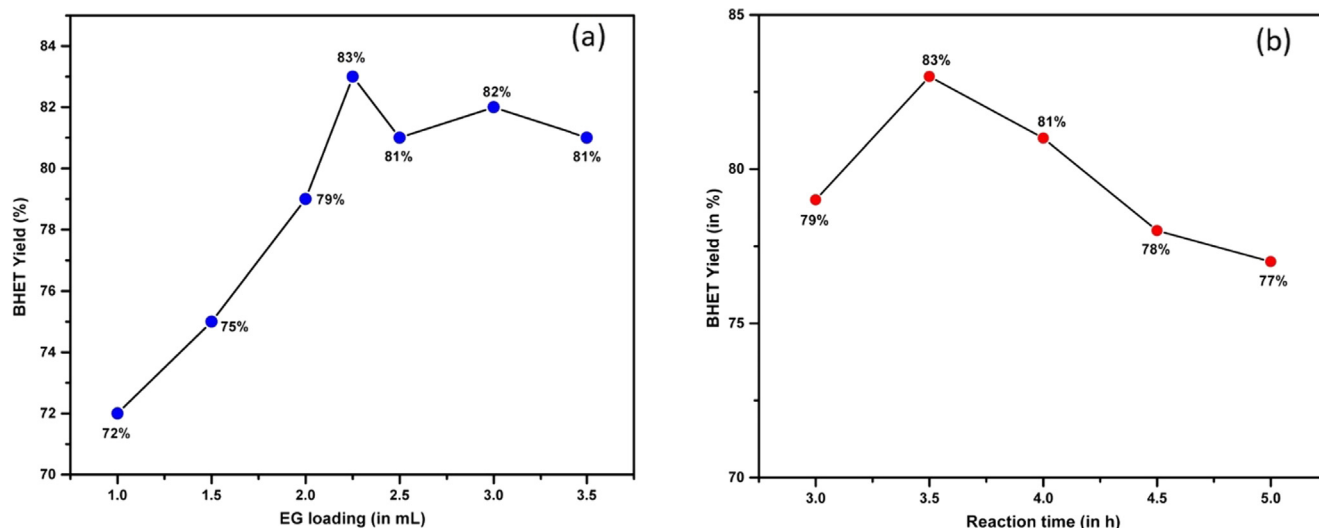


Fig. 5. (a) Effect of EG loading on glycolysis of PET. The reaction was conducted using varied amount of EG, 480 mg of PET and 100 mg of the catalyst at 190 °C, and (b) Degradation time of PET. The reaction was conducted using 480 mg of PET, 100 mg of the catalyst, 2.25 mL of EG at 190 °C.

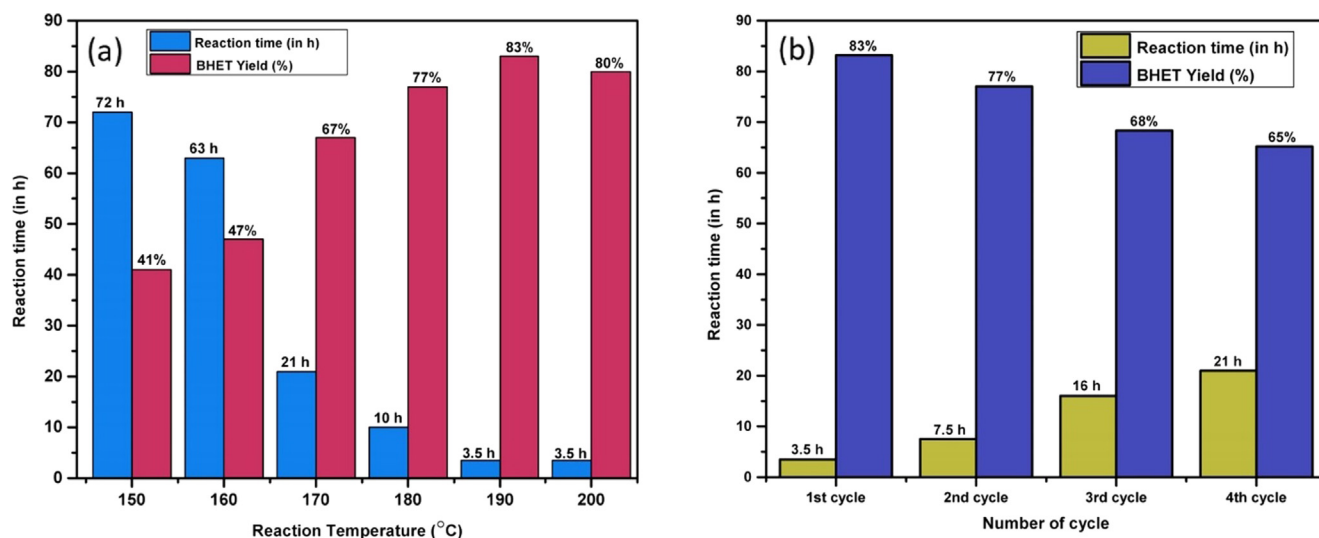


Fig. 6. (a) Effect of reaction temperature on degradation time of PET. Reaction conditions: PET (2.5 mmol), catalyst (100 mg), EG (16 eq), and (b) Reusability of the catalyst in the degradation of PET.

tion processes (Pathak et al., 2018) as shown by EDX analysis after four cycles.

TEM, SEM, and EDX analysis of the recovered catalysts after the 4th cycle were performed to investigate the changes in their morphology and elemental compositions. The reused catalysts after the 4th cycle exhibited an irregular morphological structure with mesoporous characteristic similar to that in the fresh catalyst in its SEM and TEM analyses (see [Supplementary material](#) published with this article, [Figs. S11 and S12](#)). The elemental composition of the recovered catalysts studied via EDX analysis shows a significant loss of Ca concentration from 9.06% to 3.33% in comparison with the fresh catalysts. It also showed a complete loss of potassium (K), magnesium (Mg), manganese (Mn) and iron (Fe) weight % from the original 4.61%, 1.59%, 1.25% and 0.52% to an undetectable trace amount in the recovered ash (see [Supplementary material](#) published with this article, [Figs. S13 and S14](#)). This significant loss in Ca, K, Mg, Mn and Fe concentration might have directly affected the outcome of the reaction with the recovered catalyst (Ahmed et al., 2013; Bartolome et al., 2014; Farahat and Nikles, 2002; Goje and Mishra, 2003; Nikje and Nazari, 2006). On

the other hand, the EDX data clearly indicated that the concentration of Si remains almost the same even after four catalytic cycles. So, to investigate whether SiO₂ has played an important role in the catalysis (Jin et al., 2015; Kundu et al., 2014) of PET depolymerization, a reaction was carried out in the presence of commercially available silica under our optimized protocol. To our surprise, it was found that even after 5 h of stirring at high temperature, no conversion of PET was observed and recrystallized BHET monomer could not be isolated from the reaction.

3.2.5. Recovery of the residual reactant

The unreacted ethylene glycol (EG) was recovered by separating the BHET crystal from the aqueous phase followed by evaporation of the filtrate under vacuum at 60 °C (Jehanno et al., 2018). The recovered EG was then distilled at 120 °C under reduced pressure and then used for subsequent catalytic depolymerization. This process of recovery and reusability of the residual reactant greatly increases the feasibility of the described protocol towards greener methodology.

3.2.6. Recycling of color bottle

We also investigated the glycolysis of red, green and light-yellow postconsumer PET bottles under our optimum condition. All the reactions were completed within 3 h of reaction time, but like before the best results in terms of BHET yield was obtained after 3.5 h. The recrystallized BHET yield % were almost equivalent to those of clear bottles (see [Supplementary material](#) published with this article Table S6) and most of the color were removed during recrystallization and filtration (see [Supplementary material](#) published with this article Fig. S15). The residual pigments, if any, can be removed by adding 50 mg of activated carbon after separation of the water insoluble part followed by filtration (Fukushima et al., 2011).

3.2.7. Comparison of BLA with other reported catalyst

The present study was carried out in an attempt to find a greener route for PET glycolysis and to reduce the overall cost by using biomass-waste derived recyclable catalyst. Several other catalysts were reported earlier to catalyze the depolymerization of PET waste to BHET monomer and are compared with BLA catalyst (see [Supplementary material](#) published with this article, Table S7). Traditionally, glycolysis was carried out in the presence of metal acetates (Zn, Pb, Mn, Co) as catalysts giving moderate to excellent yield. Zeolites, ionic liquids, nanoparticles and organocatalysts also showed high activity towards PET depolymerization. But, the main drawbacks of these catalysts are their high cost, complex preparation procedure and some difficulty in handling as their preparations require use of harmful chemicals. For example, depolymerization using organocatalysts affords BHET monomer in excellent yield but they are usually expensive which ultimately reduced its applicability at the industrial scale. The preparation of ionic liquids and nanoparticles requires several steps and, sometimes corrosive chemicals have to be employed for their production. In contrast, the preparation and handling of the present BLA catalyst were very simple and as it is waste-origin, hence cost-free. Furthermore, our approach of resolving plastic waste problems with bio-waste is a merit in itself, opening a new waste-valorization technique and affording a window for converting synthetic polymeric waste to reusable resources in an eco-friendly procedure.

3.2.8. The proposed reaction mechanism for glycolysis of PET using BLA

Glycolysis of PET proceeds through three stages: breaking into the oligomers, followed by dimer formation and finally, degeneration into the monomer (George and Kurian, 2014). In the current study, PET waste depolymerization was carried out using a recyclable BLA as a heterogeneous catalyst and the proposed mechanistic pathway is illustrated in Scheme S1 (see [Supplementary material](#) published with this article, page S5). Heterogeneous catalysis reaction proceeded through diffusion of the reactants to the surface of the catalysts, where they get adsorbed by forming new bonds. The reacting molecules then interact to give new products which was subsequently followed by desorption of the final products from the surface of the catalyst. With BLA, it is assumed that the oxides and carbonates of Ca, K, Mg, Mn and Fe present in the catalyst are the active sites for PET depolymerization (Changmai et al., 2021). These anionic sites abstract the proton of ethylene glycol to generate a nucleophile, 2-hydroxyethanolate. During the degradation process, the glycol itself diffuses into the PET pellets and caused it to swell up (Wang et al., 2009). The nucleophile which formed earlier then attacks the carbonyl carbon of the ester bond to form a tetrahedral intermediate, the ester bond in the chain cleaved and reduces the PET polyester into lower fractions. As the acyl group breaks, the $-OCH_2CH_2-$ group gets eliminated and abstract a proton from the catalyst, forming $HOCH_2CH_2$ group (Al-Sabagh et al., 2014). The conversion of PET to BHET proceeds

through stepwise reaction, where oligomers, dimers, and monomers are produced successively. As the reaction progressed further, BHET can be repolymerized back to its dimers and then oligomers, thereby generating an equilibrium.

4. Conclusion

In conclusion, we have demonstrated and reported for the first time, the use of bamboo leaf ash (BLA) as an environmentally benign and cost-free bio-waste derived heterogeneous catalyst for the depolymerization of PET flakes through the transesterification reaction. The BHET monomer was obtained under eco-friendly nature in a reasonably high yield. The high surface area, the mesoporous nature of the catalyst and the presence of Ca, K, Mg, Mn and Fe in the form of their oxides and carbonates are believed to be responsible for the PET degradation reaction. Despite its high abundance, we observed that the presence of SiO_2 in bamboo leaves ash might have no catalytic property in this reaction. The catalyst was found to be stable even at an elevated temperature and shows good catalytic activity over four cycles. Additionally, the green nature of the catalyst and the facile synthetic protocol promises a massive potential in the field of plastic waste treatment. In fact, the highlight of this methodology lies in its operational simplicity where large scale second-hand plastic waste treatment can be carried out under favorable conditions.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2021.02.056>.

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PAPER



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Biomass waste-derived recyclable heterogeneous catalyst for aqueous aldol reaction and depolymerization of PET waste†

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In this work, we discuss the valorization of biomass waste-derived orange peel ash (OPA) by exploring its applicability as a heterogeneous catalyst in aqueous aldol reactions and demonstrating its versatility by promoting the methanolysis of poly(ethylene terephthalate) (PET) waste. The catalyst was characterized using Fourier-transform infrared spectroscopy (FT-IR), Brunauer–Emmett–Teller (BET) analysis, X-ray powder diffraction (XRD), X-ray fluorescence (XRF), energy dispersive X-ray (EDX) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and thermal gravimetric analysis (TGA) to decode its chemical composition. The aldol reactions were carried out at ambient temperature in the presence of water as a solvent. PET depolymerization was performed in an autoclave for 1 h using only 6% w/w OPA. The catalyst was recovered and reused in both the reactions for up to four successive cycles with minimal loss in the catalytic activity. The use of OPA as a cost-free, eco-friendly and effective recyclable catalyst enables a greener route for C–C bond formation and PET waste recycling.

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1. Introduction

Environmentally benign heterogeneous catalysts provide an immense advantage due to their excellent catalytic activities as well as their simplicity and efficacy under adverse conditions. They can easily be separated out by simple filtration and also have the potential to be recycled and reused in subsequent cycles of the reaction.¹ While homogeneity seems to deliver a higher activity with a more uniform substrate–catalyst mixture, homogeneous catalysts, however, are associated with problems in their recovery and recycling, which are seen major drawbacks. So, the incorporation of heterogeneity in a homogeneous system with minimal production of waste materials is one such improvement.² Nevertheless, an additional step is still required to prepare this system, which is resource-consuming. Hence, highly accessible heterogeneous catalysts are usually preferred due to their robustness, low operational cost, easier recovery and higher catalytic performance for achieving superstoichiometric conversion.^{3–5} Therefore, solid-based catalysts in liquid-phase reactions have attracted widespread research

attention in recent years to demonstrate their superiority and advantages over their homogeneous counterparts.⁶

Recently, the valorization of biomass wastes using simple processing steps to yield effective heterogeneous catalysts has become an escape route for avoiding the use of expensive solid catalysts, as the primary raw material is available free of cost and a greener synthesis method therefore facilitated.^{7,8} Orange peel ash,⁹ waste shells of mollusk and egg,¹⁰ pineapple peel ash,¹¹ mango peel ash,¹² banana peel ash,¹³ wood ash,¹⁴ fly ash,¹⁵ walnut shell ash,¹⁶ peanut husk ash,¹⁷ pineapple leaf ash,¹⁸ coconut husk ash¹⁹ and banana trunk ash²⁰ have been reported as an efficient biomass waste-derived heterogeneous catalyst for the production of biodiesel. These ash-based heterogeneous catalysts have also been described as catalyzing peptide bond formation, the *aza*-Henry reaction, bis-enol synthesis, biosugar and quercetin production, the Dakin reaction, the Knoevenagel reaction, Suzuki–Miyaura coupling, the Sonogashira reaction and the Henry reaction.^{21–30} More recently, we have also investigated the glycolytic depolymerization of poly(ethylene terephthalate) (PET) waste using biomass waste-derived catalysts.^{31,32} As the worldwide production of agro-waste biomass increases exponentially (about 998 million tons), with a further expected increased rate of 5–10% per annum,⁸ the realistic intervention of a scientific solution for its pragmatic reuse seems to be the need of the hour for decreasing

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that amount of waste that normally takes up landfill site space, which is already at a premium. And with these recent improvements in the value addition of biomass waste, the thought of further extrapolating and valorizing these wastes comes to the mind and so, in continuation of our current interest, we investigated the first example of a biomass waste-derived heterogeneous catalyst for the aldol reaction in water, and its applications were extended to the catalytic depolymerization of PET waste to the dimethylterephthalate (DMT) monomer.

The discovery of the aldol reaction by Charles-Aldolphe Wurtz in 1872 was an important milestone in organic synthesis, and it has advanced to be one of the most versatile and important carbon-carbon bond-forming reactions.^{33–35} It has been used in the large-scale production of several drugs, and aldol structural units are found in many natural products.^{36,37} The reaction is usually carried out using metal oxides, metal hydroxides and metal carbonates, and there have also been reports of metal-supported SiO₂, supported ionic liquids, functionalized nanoparticles, hydrotalcites, zeolites and organic bases used for this transformation.^{38–44} To control the stereochemical outcome, metal enolates, transition metal complexes, enzymes and chiral organocatalysts have also been developed and investigated for the formation of aldol adducts.^{45–49} However, to the best of our knowledge, this is the first report on the use of a biomass waste-derived heterogeneous catalyst for the aldol reaction. And, with the evolution of the concept of “green and sustainable chemistry”, the development of greener methodologies for the efficient construction of C–C bonds is still one of the most sought-after processes for researchers.

With so much diversity in its utilization, plastic production has increased from 335 million tons in 2016 to 348 million tons in 2017, a massive 3.7% increase in just one year.⁵⁰ This increase in plastic production justifies the rise in demand and it automatically enhances the amount of plastic waste production by many fold. But only around 9% of the plastic waste ever generated is recycled and it is estimated that, with the current trend, by 2050, roughly 12 000 Mt of plastic waste will be in the natural environment.⁵¹ And due to its high chemical resistivity, high strength to weight ratio, thermal stability, moldability and low market price, PET has now become an unparalleled food and beverage packaging material.⁵² It is also often used in the textile industry, in the manufacture of video and audio tapes, and in synthetic fibers and plastic insulating films, and it accounts for 13% of the world's plastic production.^{53,54} These post-consumer waste plastics occupy lots of space and their extremely slow natural degradation process can cause land degradation.⁵⁵ Therefore, using landfill for their removal is an undesirable option from an environmental point of view.⁵⁶ Other methods of plastic waste removal, like incineration and pyrolysis, can help to generate energy; however, this is at the expense of the emission of toxic fumes and gases. So, chemical depolymerization of plastic waste is now the best alternative for dealing with its removal from the environment.⁵⁷

The recycling of PET waste may be broadly classified into mechanical and chemical recycling.⁵⁸ While mechanical

recycling often produces poor-quality products, chemical recycling is more versatile and produces the corresponding monomer.^{56,58,59} The chemical recycling of PET can be performed by any of the solvolytic reactions like glycolysis, methanolysis, hydrolysis, ammonolysis and aminolysis, giving rise to various depolymerized products.⁵⁹ Although glycolysis offers a huge advantage for its simplicity and low capital cost,⁶⁰ the reaction products are not discrete chemicals and more than a simple purification technique is needed.^{61,62} While ammonolysis and aminolysis suffer from limited applications of their end products, the low purity of terephthalic acid (TPA) obtained from the hydrolysis of PET is another restrictive factor. By contrast, methanolysis involves the degradation of PET using methanol at high temperature and pressure, yielding dimethyl terephthalate (DMT) and ethylene glycol.⁶³ Even though this process has some criticism for its requirement of higher capital and energy investments compared with the glycolytic method of degradation, the methanolysis of PET waste has revitalized modern-day recycling technique through its high tolerance to impurities, simple purification steps, and easy recovery process of EG and methanol.^{58,64} As a result, numerous studies have been conducted and catalysts such as metal acetates, aluminium isopropoxides, metal hydroxides and carbonates together with supercritical methanol have been explored for promoting an effective degradation pathway.^{65–69}

Orange (*Citrus sinensis*) is one of the most cultivated fruit trees in the world, with a global production of 53.84 million metric tons in 2018–2019.⁷⁰ This leaves a huge amount of orange peel (OP) as waste, which typically ends up in landfill sites. Apart from the aforementioned use of OP waste, there have been some reports of its utilization in the production of solid biofuels and biosorbents, in the adsorptive removal of heavy metals from contaminated water and as a catalyst in heterogeneous synthesis.^{71–74} In this work, we investigated the efficiency of orange peel ash (OPA) as a recyclable heterogeneous catalyst for C–C bond formation and PET waste depolymerization. The easy availability of orange peel, the simple catalytic preparation procedure, the cost-effectiveness and reusability of the catalyst, and the possibility of carrying out the reaction in an aqueous medium are in accord with the principles of green chemistry, which make this protocol an attractive substitute for the recycling of such waste.

2. Experimental

2.1 Materials

Chemicals were purchased from Sigma-Aldrich and used without further purification. Deionized water was obtained from HiMedia. The caps and labels of used PET bottles collected from the local area were removed and the bottles were washed thoroughly with distilled water. After drying, they were shredded into 1 mm square flakes before use.

2.2 Preparation of the OPA catalyst

The peel of oranges was collected from local vendors in Aizawl, Mizoram, India. It was meticulously washed with distilled water

and then dried in an oven at 80 °C for 12 hours. The dried peel was burned in open air. The dark grey-colored ash was collected and then sieved using 100 British Standard Sieve (BSS). The finely divided orange peel ash was stored in a closed container at room temperature and the elemental, morphological and structural composition of the catalyst was determined using FT-IR, BET, XRD, XRF, EDX, SEM, TEM, XPS and TGA analyses.

2.3 Instruments

FT-IR spectra were recorded using a PerkinElmer spectrum BX FT-IR instrument (λ_{max} in cm^{-1}) using KBr disks. The diffraction pattern of the catalyst was determined *via* powder X-ray diffraction (XRD) analysis using a Philips Xpert MPD, and the wavelength dispersive X-ray fluorescence (XRF) of the catalyst was inspected using a PANalytical, Axios mAX instrument. X-ray photoelectron spectroscopy (XPS) analysis was performed on using a Physical Electronics, model no. PHI 5000 VersaProbe III instrument at 40% humidity and room temperature. The thermal stability of the catalyst was determined *via* TGA using PerkinElmer TGA 4000 instrument under a nitrogen atmosphere. The catalyst sample was heated from 30–995 °C at a rate of 10 °C min^{-1} . A Quanta chrome Nova-1000 surface area and porosity analyzer was used to record the N_2 adsorption–desorption isotherm. The samples were pre-heated at a degassing temperature of 150 °C for 10 h. Scanning electron microscopy (SEM) images were obtained using a Jeol JSM-6360 microscope, and an ESEM EDAX XL-30 microscope. Transmission electron microscopy (TEM) images were recorded using a JEM 2100, 200 kV instrument. High performance liquid chromatography (HPLC) analysis was performed using a Waters 1525 binary pump with a Spherisorb ODS2 5 μm , 4.6×250 mm analytical column and a Waters UV detector 2489 measuring at 254 nm. Nuclear magnetic resonance (^1H NMR and ^{13}C NMR) analysis was carried out using a Bruker, 400 MHz Avance III spectrometer in DMSO-d_6 (chemical shift in δ with TMS as the internal standard).

2.4 General procedure for the aldol reactions

In a 25 mL round-bottom flask charged with a mixture of ketone (2 mmol), 20 mg of the catalyst and 5 mL of water, aldehyde (1 mmol) was added to it and the reaction mixture was stirred at room temperature. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, ethyl acetate was added to dissolve the compound followed by filtration to remove the catalyst. The organic layer was separated and the aqueous layer was washed with ethyl acetate (2×30 mL). The organic layers were combined and washed with water (2×50 mL), dried over Na_2SO_4 and evaporated to obtain the product. The product obtained was analyzed *via* NMR and FT-IR spectroscopy without further purification, where acetone was used as a substrate. Using cyclohexanone and acetophenone, the crude products were purified *via* column chromatography.

2.5 Methanolysis of PET bottles

A Shilpent Teflon Lined Hydrothermal Autoclave (50 mL) was charged with 500 mg of PET flakes (2.60 mmol), 100 mg of OPA catalyst and 5 mL of methanol. The autoclave was immersed in

an oil bath preheated at 200 °C and the reaction was carried out at a constant temperature for 1 h. After completion, it was allowed to cool down and 40 mL hot methanol was added before filtration. The filtrate was cooled to room temperature and then placed in a refrigerator for 2 h where dimethyl terephthalate (DMT) crystals formed from the solution. The filtrate was distilled under reduced pressure to recover methanol followed by isolation of ethylene glycol. The obtained DMT was characterized using IR, NMR and HPLC analyses and the percentage yield was calculated using the following equation:

$$\text{Yield of DMT monomer (\%)} = \frac{W_{\text{DMT}}/MW_{\text{DMT}}}{W_{\text{PET,I}}/MW_{\text{PET}}} \times 100\%$$

where W_{DMT} , $W_{\text{PET,I}}$, MW_{DMT} , and MW_{PET} refer to the weight of DMT, the weight of initial PET, the molecular weight of DMT (194 g mol^{-1}) and the molecular weight of the PET repeating unit (192 g mol^{-1}), respectively.

3. Results and discussion

3.1 Characterization of the catalyst

Initially, the crystalline composition of the catalyst was studied using XRD analysis (Fig. 1a), where the presence of various carbonates and oxides of metals was observed. The strong characteristic peaks of CaCO_3 , K_2O and SO_3 were observed at $2\theta = 29.651$, 48.509 , 25.514 , 34.274 and 28.202 (JCPDS reference file no. 86-2334, 86-2334, 77-2176, 26-1327 and 72-1664). Beside these, several peaks were observed at $2\theta = 32.023$, 36.031 , 37.028 , 43.176 , 39.497 and 40.884 (JCPDS reference file no. 02-1088, 89-7047, 75-1525, 75-1525, 71-1466 and 89-3436) corresponding to K_2O , SO_3 , CaO , Fe_2O_3 , K_2CO_3 and MgO , respectively.

FTIR analysis of the prepared ash catalyst was then performed to detect the functional groups (Fig. 1b). The bands at 3412 and 2958 cm^{-1} represent the stretching frequency of the O–H bond, which arises from the adsorption of water molecules from the atmosphere.⁷⁵ The peaks at 1440 , 1048 , and 874 cm^{-1} correspond to the presence of carbonate stretching and bending vibrations.⁷⁶ The peaks at 811 cm^{-1} and 688 cm^{-1} were attributed to the presence of K–O and Ca–O functionalities.⁷⁷

The surface area of the catalyst was also studied using the Brunauer–Emmett–Teller (BET) method, and the average pore size distribution was calculated using Barrett–Joyner–Halenda (BJH) model. These methods highlight the external area and pore volume of the ash catalyst, delivering notable information regarding the surface porosity of the material. The surface area, pore diameter and pore volume of the catalyst were found to be 4.974 $\text{m}^2 \text{g}^{-1}$, 25.22 Å, and 0.022 $\text{cm}^3 \text{g}^{-1}$, respectively (Fig. 1d). The N_2 adsorption–desorption isotherm showed a typical type-IV isotherm of the catalyst, which is characteristic of a mesoporous material (Fig. 1c). One of the underlying reasons behind the high catalytic activity of the catalyst may be ascribed to its high surface area and mesoporous nature.

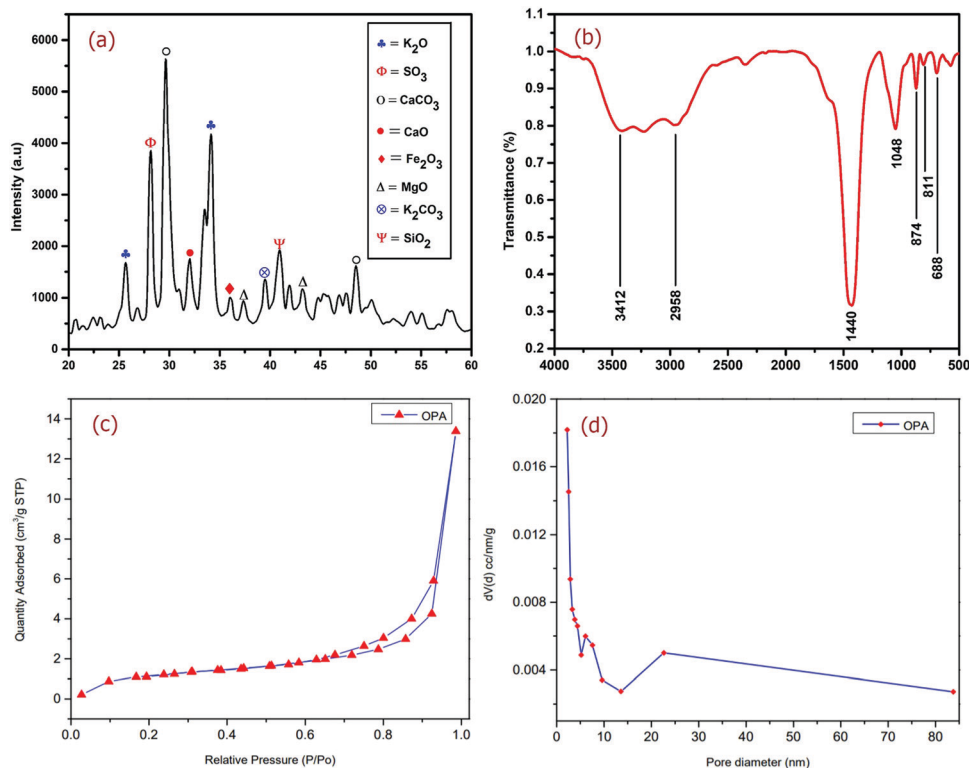


Fig. 1 (a) XRD data of OPA, (b) FT-IR spectrum of OPA, (c) nitrogen adsorption–desorption isotherm, and (d) BJH pore size distribution of OPA.

XRF analysis was carried out to determine the elemental composition of the prepared catalyst and the catalyst was found to contain 31.32% of calcium oxide (CaO) and 29.38% of potassium oxide (K_2O) as the major components of the catalyst (see Table S1, ESI†). In addition, oxides of silicon, sulphur, phosphorus, aluminium, alkali metals, alkaline earth metals, and transition metals were present in small amounts, as shown in Table S1 (ESI†). And our results are consistent with the report by Changmai and co-workers.⁹ From our investigation, the OPA catalyst was found to be highly basic in nature, which may have stimulated the catalyst to promote various base-catalyzed reactions.

The elemental composition of the catalyst was analyzed using EDX spectroscopy to validate the existence of carbon, oxygen, and other elements (see Fig. S1, ESI†). The EDX spectrum indicated the presence of oxygen, potassium, calcium and carbon with weight percentages of 51.73, 21.32, 13.73 and 6.86, respectively. Our EDX analysis results thus firmly backed our XRF and XRD data.

The surface elemental composition and bonding state of the fresh OPA catalyst were also investigated using X-ray photoelectron spectroscopy (XPS) and the wide-scan spectrum shows that the principal elements in the outer part of the catalyst's surface to be C, O, Ca and K (Fig. 2). Deconvolution of the C 1s spectrum reveals four peaks of 292.78 eV, 290.08 eV, 286.59 eV and 282.47 eV binding energies, respectively (Fig. 2b). The C–C and C=O bonds of metal carbonate peaks can be ascribed for the OPA catalyst with binding energies of

286.59 eV and 292.78 eV. The metal oxides in the ash are equated by a single peak with a binding energy of 528.66 eV in the deconvoluted spectrum of O 1s (Fig. 2c). Furthermore, the K 2p spectrum displays two peaks at 292.75 eV and 290.08 eV, allocated to the K_2O and K_2CO_3 binding energies after deconvolution (Fig. 2d).¹³ Similarly, two peaks at 347.65 eV and 344.05 eV were displayed in the Ca 2p spectrum, respectively, confirming the existence of $CaCO_3$ and CaO (Fig. 2e).⁹

The exterior morphology of the ash content was also analyzed *via* SEM and TEM (Fig. 3). It shows a spongy character and a well-defined microporous and mesoporous structure on the exterior surface of the OPA catalyst. This mesoporosity of the catalyst may have increased the external surface area, exposing more active sites, which ultimately increases the catalytic activity of the OPA.

To investigate the thermal stability of the prepared ash catalyst, thermal gravimetric analysis (TGA) was conducted, and the TGA thermogram revealed weight loss in three stages (see Fig. S2, ESI†). The initial weight loss (~5%) at a temperature below 190 °C can be attributed to vaporization of the intercalated water. The additional weight loss of the OPA catalyst at higher temperatures can be ascribed to the oxidation of the carbonaceous materials present in the catalyst.⁷⁸

3.2 Aldol reaction using OPA and water

The aldol reaction was performed with water as the solvent and the reaction of 4-nitrobenzaldehyde with acetone was used as a model system for the initial screening. The reaction was carried

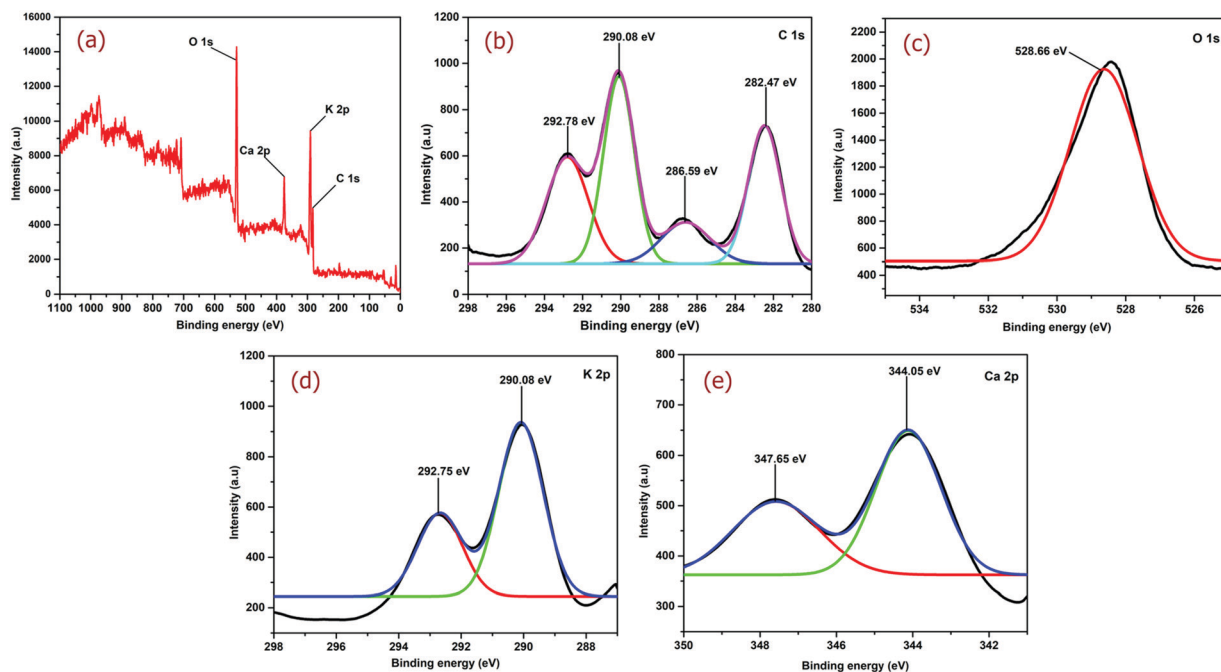


Fig. 2 XPS analysis of OPA catalyst.

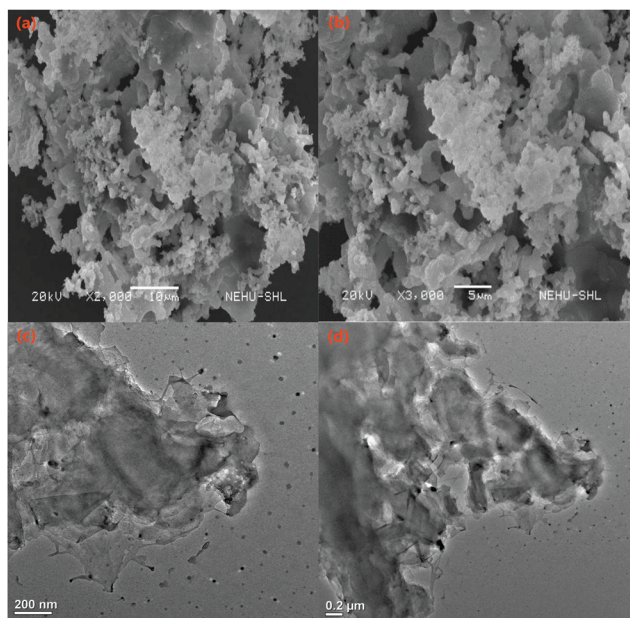


Fig. 3 SEM (a) and (b) images of OPA, and TEM (c) and (d) images of OPA.

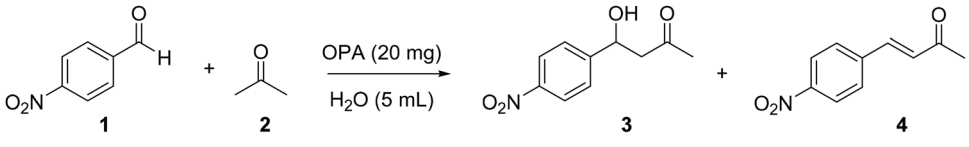
out using 20 mg of OPA as the catalyst and it was completed within 5 min at room temperature. Extraction followed by column chromatography gave 4-hydroxy-4-(4-nitrophenyl)-butan-2-one as the isolated product in 96% yield with no ostensible formation of the condensation product. The reaction of acetone and 4-nitrobenzaldehyde was also carried out in the presence of other biomass waste-derived heterogeneous catalysts to assess their unique catalytic properties, and the results are depicted in Table 1. The results revealed that among the

catalysts given in Table 1, OPA was found to be the most efficient catalyst, affording the aldol product within 5 min. Cucumber peel ash (CPA) and mango peel ash also afford the aldol addition product in 93% and 91% yield, respectively, but other heterogeneous catalysts showed a rather low catalytic efficacy for the reaction. In the absence of the catalyst, no aldol product formation was observed. To optimize the reaction conditions for the selective formation of the aldol adduct, different reaction parameters were examined, and the result is listed in Table 2.

First, the effect of catalyst loading on the reaction was assessed with a catalytic loading of 5, 10, 20, 30 and 40 mg mmol⁻¹ of the substrate. When 5 mg of the catalyst was added, the reaction was completed within 30 min but gave a lower yield of the aldol product (Table 2 entry 1). As the amount of catalyst was increased, the contact surface for the reaction was also increased, which subsequently increased the conversion and yield of the product. The most satisfactory result was obtained when 20 mg of the catalyst was used, where a slight decrease in the isolated yield was observed with the use of a higher amount of OPA (Table 2 entries 2–5). This may be due to the fact that after reaching the optimal catalyst loading, the slurry becomes more viscous and it hampers the dispersal of the reactants, thus slowing down the reaction and reducing the overall yield at the same time.²⁴

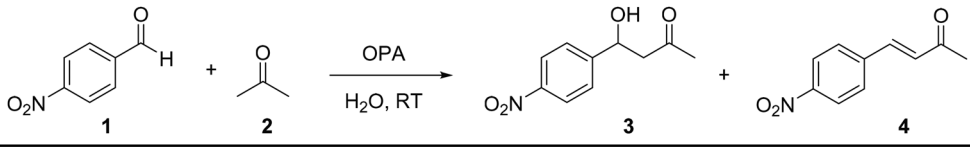
Next, several solvents with different polarities were examined to study their influence on the reaction. The reaction was also performed under neat conditions and these results are summarized in Table 2, entries 6–12. No apparent formation of the desired product was observed under solvent-free conditions. Similar outcomes were seen when DCM and chloroform were used as a solvent. Even after a prolonged reaction time,

Table 1 Aldol reaction using different biomass-waste derived catalysts^a

			
No.	Catalyst	Time	Yield of 3 (%) ^b
1	Orange peel ash (OPA)	5 min	96
2	Bamboo leaf ash (BLA)	2 h	67
3	Banana peel ash (BPA)	1.5 h	88
4	Bagasse ash (BA)	1.5 h	71
5	Corn husk ash (CHA)	45 min	79
6	Mango peel ash (MPA)	15 min	91
7	Cucumber peel ash (CPA)	10 min	93
8	None	24 h	—

^a Aldehyde (1 mmol), acetone (2 mmol), room temperature. ^b Isolated yield.

Table 2 Optimization of aldol reaction using OPA^a

						
No.	Catalyst (mg)	Solvent	Time (min)	Acetone (equiv.)	Product yield ^b (%)	
					3	4
1	5	H ₂ O	30	2	88	Nil
2	10	H ₂ O	10	2	92	Nil
3	20	H ₂ O	5	2	96	Nil
4	30	H ₂ O	5	2	93	Nil
5	40	H ₂ O	5	2	87	Trace
6	20	—	90	2	—	—
7	20	CH ₂ Cl ₂	90	2	—	—
8	20	CHCl ₃	90	2	—	—
9	20	EtOH	90	2	Trace	—
10	20	CH ₃ CN	90	2	Trace	—
11	20	DMF	20	2	83	—
12	20	DMSO	20	2	89	—
13 ^c	20	H ₂ O	5	2	67	21
14 ^d	20	H ₂ O	5	2	95	—
15	20	H ₂ O	5	1	36	—
16	20	H ₂ O	5	1.5	57	—
17	20	H ₂ O	5	3	92	—
18	20	H ₂ O	10	2	69	12

^a Aldehyde (1 mmol). ^b Isolated yield. ^c 2 mL of H₂O was used. ^d 8 mL of H₂O was used.

only a trace amount of the final product was obtained using ethanol and acetonitrile. The use of polar aprotic solvents such as DMF and DMSO exponentially increased the rate and yield of the reaction. However, the ideal result was obtained when water was used as a solvent. This result demonstrated that the presence of water as a solvent is essential to achieving the best result with our catalyst.

It was also noticed that the amount of solvent loading plays a significant role in the outcome of the reaction. With 2 mL of water, the dehydration product formed instantly even after only

5 min of reaction time (Table 2, entry 13). However, increasing the solvent amount beyond 5 mL does not show any noticeable improvement in the yield (Table 2, entry 14).

We further investigated the impact of acetone equivalents on the yield of the reaction. With 1 equivalent of acetone, the reaction gave only 36% isolated yield, which was increased to 57% with 1.5 equivalents (Table 2, entries 15 and 16). No substantial enhancement was observed by increasing the amount of acetone beyond 2 equivalents (Table 2, entry 17). While keeping other the parameters constant, we then

increased the reaction time to investigate its effect on the reaction. After 10 min of reaction time, formation of the condensation product was found with a substantial decrease in the aldol reaction product (Table 2 entry 18).

With the optimized conditions in hand, we then explored the scope and limitation of this reaction with a variety of aromatic aldehydes and ketones (Table 3, entries 1–18). All the reactions were completed within 5–120 min giving good to excellent yields, but there is a distinct dissimilarity based upon the electron-withdrawing/electron-donating nature of the aldehydes on the rate of the reaction. Electron-withdrawing aldehydes generally favor faster reactions while electron-rich aldehydes usually need a longer reaction time. However, interestingly, when the nitro ($-\text{NO}_2$) group is at the *ortho* position, the reaction rate decreases substantially giving a lower yield of the product (Table 3, entry 3). This may be due to the intramolecular hydrogen bond formed between the aldehydic hydrogen and the oxygen atom from the nitro group, which diminished the reactivity of the aldehyde.^{79,80} And, an elevated temperature of 55 °C was required for aldol acceptors having *p*- CH_3 - and *p*- OCH_3 -substituents when cyclohexanone was used as a substrate (Table 3, entries 9 and 10). With acetone, all the reactions proceeded effortlessly at room temperature but the use of acetophenone as an aldol donor slightly lengthened the reaction time, even with electron-deficient aldehydes (Table 3, entries 17 and 18).

The high activity of the catalyst towards the aldol reaction was attributed to the high basic strength of the catalyst, which was found to contain K_2O , CaO , K_2CO_3 , CaCO_3 , etc., in its analyses. The basic strength of the catalyst was also investigated using the Hammett indicator method as reported in the

literature,^{76,81} and a basicity value of $9.8 < H_- < 15.0$ is shown. Based on this, we postulated a mechanistic pathway through the general base-catalyzed aldol reaction involving an enolate mechanism (see Scheme S1, ESI†). The mesoporous nature of the catalyst and its large surface area may also have played an important role in the catalytic activation.

3.3 Reusability of the catalyst

Reusability is one of the significant properties of a heterogeneous catalyst for scaling up its practical and industrial applications. Accordingly, the reusability potential of the present OPA catalyst was investigated under the optimum reaction conditions. After completion of the reaction, the catalyst was recovered from the reaction mixture under filtration, and it was washed repeatedly with ethyl acetate and dried at 80 °C for 5 h before being used in a subsequent cycle. It was found that there was a loss of about 5–10% by weight of the catalyst in each case, which was compensated with fresh catalyst. The reaction of 4-nitrobenzaldehyde with cyclohexanone catalyzed by the recovered catalyst was then carried out under the optimized conditions to study its reusability (Table 4). It was surprising to find that, even after four catalytic cycles, the recovered catalyst still gave an excellent yield but a gradual increase in reaction time was observed. This slight increase in reaction time after repeated cycles may be due to the loss of active sites during the course of the reaction, and the reused catalyst after completion of the 4th cycle was examined using EDX, SEM and TEM analysis.

Analysis of the recycled catalyst *via* the EDX technique revealed significant degradation of potassium concentration in comparison with the fresh catalyst from 21% to 0.48% (see Fig. S3, ESI†). The tendency of potassium to be leached more readily than any other elements during the reaction process clearly affects the aldol reaction when using the recovered catalyst after repeated cycles.⁸² Also, SEM and TEM analyses of the reused catalyst disclose an irregular surface showing a hexagonal, cylindrical or spherical shape of the catalyst with mesoporous characteristics almost similar to that in the fresh catalyst (see Fig. S4 and S5, ESI†).

3.4 Methanolysis of PET waste using OPA

To elaborate the catalytic utility further, the depolymerization of PET waste *via* methanolysis was performed using OPA as the catalyst. After completion of the reaction, the crude product

Table 3 Aldol reaction catalyzed by OPA^{ab}

No.	Substrate (R)	Ketone	Product	Time	Yield ^c (%)
1	<i>p</i> - NO_2	Cyclohexanone	7a	10 min	96
2	<i>m</i> - NO_2	Cyclohexanone	7b	15 min	90
3	<i>o</i> - NO_2	Cyclohexanone	7c	1 h	72
4	<i>p</i> -Cl	Cyclohexanone	7d	15 min	95
5	<i>m</i> -Cl	Cyclohexanone	7e	15 min	93
6	<i>o</i> -Cl	Cyclohexanone	7f	20 min	81
7	<i>p</i> -Br	Cyclohexanone	7g	30 min	90
8	H	Cyclohexanone	7h	20 min	70
9 ^d	<i>p</i> - CH_3	Cyclohexanone	7i	30 min	88
10 ^d	<i>p</i> - OCH_3	Cyclohexanone	7j	1 h	88
11	<i>p</i> - NO_2	Acetone	7k	5 min	91
12	<i>m</i> - NO_2	Acetone	7l	30 min	87
13	<i>p</i> -Cl	Acetone	7m	10 min	80
14	H	Acetone	7n	45 min	76
15	<i>p</i> - CH_3	Acetone	7o	1 h	90
16	<i>p</i> - OCH_3	Acetone	7p	2 h	91
17	<i>p</i> - NO_2	Acetophenone	7q	45 min	87
18	<i>m</i> - NO_2	Acetophenone	7r	2 h	80

^a Aldehyde (1 mmol), ketone (2 mmol). ^b At room temperature unless otherwise stated. ^c Isolated yield. ^d Reaction was carried out at 55 °C.

Table 4 Catalyst reusability test^a

Catalytic cycle	Reaction time (min)	Yield ^b (%)
1st cycle	10	96
2nd cycle	14	94
3rd cycle	20	92
4th cycle	30	92

^a Aldehyde (1 mmol), ketone (2 mmol), room temperature. ^b Isolated yield.

was analyzed using HPLC, which revealed the formation of ethylene glycol (EG) and DMT as the main products, with small amount of 2-hydroxyethyl methyl terephthalate (HEMT) and bis-(2-hydroxyethyl) terephthalate (BHET) also formed as a side product (see Fig. S6, ESI†). This was confirmed by the HPLC analysis of commercially available EG, DMT, BHET and HEMT and by comparing them with the crude spectra (see Fig. S7–S10, ESI†). After recrystallization, the analysis of DMT by ^1H NMR revealed the presence of two singlets at $\delta = 8.012$ (Ar-H) and 3.860 (–OCH₃) ppm while its ^{13}C NMR data showed peaks at $\delta = 166.29, 133.89, 129.54$ and 52.44 ppm, confirming the formation of the desired products (see Fig. S11 and 12, ESI†). To optimize the reaction conditions, several factors such as the catalyst and reagent loading, the reaction time and the reaction temperature were studied (Table 5).

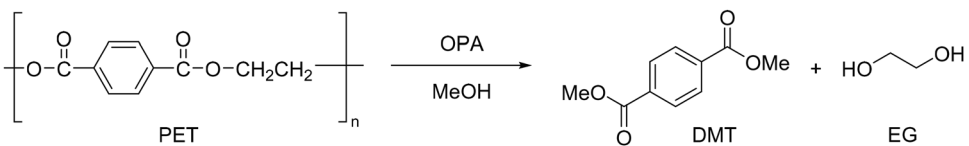
The catalyst loading was found to greatly influence both the rate of methanolysis and product formation when the process temperature, the reagent loading and the reaction time were fixed at $200\text{ }^\circ\text{C}$, 5 mL and 1 h, respectively (Table 5, entries 1–6). Even at just 2% w/w OPA loading, the reaction gave 56% yield of recrystallized DMT with the production of 53% EG. The highest yield of DMT monomer and EG was obtained when the catalyst amount was increased to 6% w/w. Above this, a gradual decrease in the overall yield of the depolymerized products was seen. This may be due to the depolymerization process involved during methanolysis in which the PET chain first cleaved into oligomers followed by degeneration into the monomer. The monomer then repolymerized into oligomers as the reaction proceeds further, creating a chemical equilibrium. However, after passing the optimal catalytic loading, PET granules degrade much faster to form the monomer, but cause the repolymerization process to be stimulated during the degradation process itself, thereby

simultaneously shortening the chemical equilibration time and reducing the yield of the desired product.⁸³

The ratio of methanol to PET flakes also influences the product composition as well as the yield of the monomer (Table 5, entries 7–9). Decreasing the methanol loading to 3 mL decreases the recrystallized DMT yield, but the formation of side products such as BHET and HEMT was shown to increase through HPLC analysis (see Fig. S14, ESI†). However, with a further increase in reagent loading, formation of the monomer dwindles, which is possibly due to a reduced OPA concentration in the reaction medium.

We then examined the effect of reaction time on the degradation process and the results are listed in Table 5, entries 10–12. The depolymerization process was found to be completed surprisingly after a reaction time of only 30 min, yielding 69% and 67% DMT and EG, respectively. Nevertheless, a 60 min reaction time gave the best results; but then again, when the degradation time was increased to 90 min or above, we observed the steady augmented generation of BHET and HEMT monomer with a reduced yield of DMT and EG. Likewise, the process temperature also substantially affected the degradation outcome, as seen in Table 5, entries 13–15. At $190\text{ }^\circ\text{C}$, the reaction was completed after 3 h with a DMT monomer yield of 65%, which indicates that methanolysis can be carried out at a reduced temperature, but at the expense of an extended processing time. After the preliminary increase, we again observed a decrease in the yield of DMT monomer as we raised the reaction temperature above $200\text{ }^\circ\text{C}$. This phenomenon of an initial increase and then decrease in the DMT yield, accompanied by the increased formation of other depolymerized products, is due to the depolymerization of PET and then the repolymerization process during the reaction.⁶⁶

Table 5 Optimization of methanolysis of PET using OPA^a

						
No.	Catalyst loading (mg)	MeOH loading (mL)	Reaction time (h)	Reaction temp. ($^\circ\text{C}$)	DMT yield ^b (%)	EG yield ^c (%)
1	—	5	48	200	0.8	—
2	10	5	1	200	56	53
3	20	5	1	200	62	62
4	30	5	1	200	79	73
5	50	5	1	200	73	67
6	70	5	1	200	66	66
7	30	3	1	200	68	69
8	30	8	1	200	73	71
9	30	10	1	200	69	70
10	30	5	0.5	200	69	67
11	30	5	1.5	200	71	69
12	30	5	2	200	68	62
13	30	5	3	190	65	56
14	30	5	1	210	77	74
15	30	5	1	220	75	76

^a PET (500 mg). ^b Recrystallized product. ^c Isolated yield.

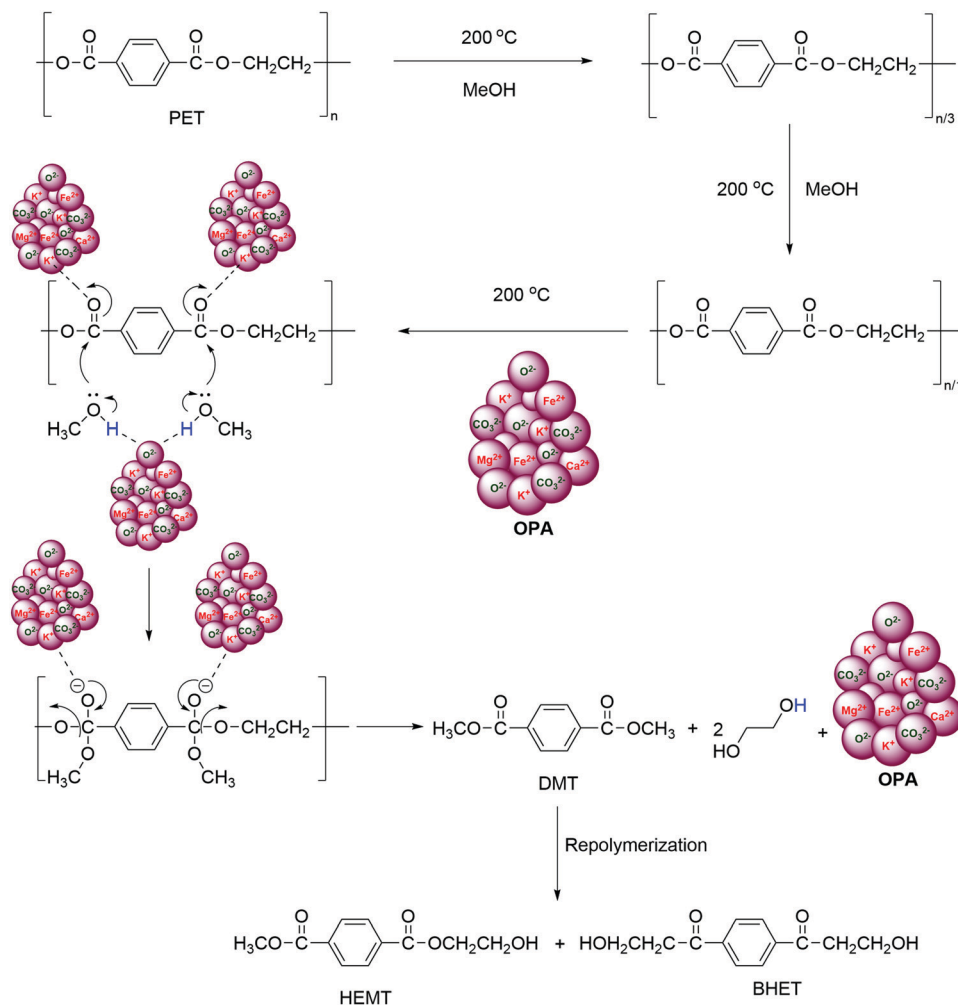


Fig. 4 Proposed mechanistic pathway for the methanolysis of PET waste using OPA.

From in-depth analysis of the OPA catalyst, it is believed that the oxides and carbonates of K, Ca, Mg, Mn, Fe, *etc.*, present in the catalyst are the active sites for PET depolymerization.^{31,32} And, the PET transesterification process is strongly assumed to be from a cation–anion collaborative effect, and the proposed reaction mechanism is shown in Fig. 4. It is also believed that the methanolysis of PET proceeds through three steps: (i) shortening of the PET chain to about 1/3, (ii) depolymerization into the oligomers, and (iii) formation of the monomers using the catalyst.⁶⁶ As OPA is composed of various metals in the form of their oxides and carbonates, these metal cations act as Lewis acids, which protonate the oxygen of the carbonyl in the ester groups, enhancing the polarity as well as electrophilicity at the carbonyl carbon. The subsequent abstraction of hydrogen from methanol by the carbonates or oxides of OPA facilitates nucleophilic attack from the oxygen of methanol. This results in cleavage of the ester linkage with the subsequent formation of a new C–O bond, yielding DMT and EG as the depolymerized products. However, as the reaction proceeds further, DMT and EG re-amalgamate to form 2-hydroxyethyl methyl terephthalate (HEMT) and bis(2-hydroxyethyl) terephthalate (BHET) in a reversible process.⁶⁷

3.4.1 Methanolysis of color bottles. We then demonstrated the depolymerization of red, light-yellow and green PET bottles under the optimized conditions to study the effect of added colors on the catalyst efficacy (see Table S2, ESI†). The product formation was lower with colored bottles. This may be attributed to the fact that colored pigments usually contain acidic components, which may be responsible for inhibiting the OPA catalyst.⁸⁴ The recrystallized DMT was similar to that obtained from clear bottles and any residual pigments can be removed by adding 20 mg of activated charcoal followed by filtration (see Fig. S16, ESI†).

3.4.2 Isolation of EG and reusability of the catalyst. The catalyst recovered by filtration was washed with ethyl acetate as mentioned previously and dried for reprocessing in another run of the reaction. A compensation of fresh catalyst for each weight loss was given and the catalyst was reused without any alteration of the conditions for four successive runs. For the second run, the reaction was completed after 1.5 h, giving a 73% yield of the DMT monomer (see Table S3, entry 2 ESI†). After every subsequent run using the recovered catalyst, there is a gradual increase in the reaction time accompanied by a lower

yield of the desired product. This, as explained earlier, may be due to leaching of the catalyst's active sites during the reaction and recovery process.

4. Conclusion

In summary, we have described the preparation and use of biomass waste-derived orange peel ash (OPA) as a heterogeneous catalyst for the aldol reaction with the selective formation of β -hydroxy carbonyl compounds. The reaction was carried out under mild and environmentally benign conditions with several aromatic aldehydes and ketones as the substrate. The catalytic effectiveness was extended further to the methanolysis of PET waste to the DMT monomer and ethylene glycol. The reagent loaded can be recovered and the catalyst was recycled for up to four catalytic cycles in both the reactions. The catalyst was easily prepared without the need for calcination at high temperature and further functionalization, and, as it is a waste material, it is therefore low-cost. The simplicity, high yield, short reaction time and eco-friendliness of the protocol coupled with the possibility of resolving a waste problem using another waste are some of the advantages of this procedure.

Author contributions

Z. T. Laldinpui: investigation, formal analysis, writing – review and editing; C. Lalmuanpuia: investigation, formal analysis, writing – original draft; Samson Lalmangaihzuale: data curation, software, writing – original draft; Vanlalngaihawma Khiangte: investigation, validation, writing – review and editing; Zodinpuia Pachau: supervision, writing – review and editing; K. Vanlaldinpui: conceptualization, methodology, funding acquisition, resources, supervision, writing – review and editing.

Conflicts of interest

There are no conflicts of interest to declare.

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Certificate

This is to Certify that

Prof./Dr./Mr./Ms. Er. T. Laldinpuii



delivered oral/poster presentation on the topic titled,
“Upcycling of Plastic Waste Using Biomass-derived Catalysts”
at the Earth Sciences discipline technical session in the 4th Mizoram Science Congress
held at Aijal Club, Aizawl during 24-25 November, 2022.

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Certificate of Appreciation



Z T Laldinpuii

has presented a paper on the topic
“ *Chemical recycling of PET waste using biomass derived catalysts* ”
in the International Conference on Current Trends in Green and Sustainable Chemistry
(ICCTGSC-2023) held on 11th -12th May, 2023 at Pachhunga University College, Aizawl, Mizoram.

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Works (8 of 8)

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DEGREE	: Doctor of Philosophy (Ph.D.)
DEPARTMENT	: Department of Chemistry
TITLE OF THE THESIS	: Waste biomass derived heterogeneous catalysts and their applications in organic transformations.
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APPROVAL OF RESEARCH PROPOSAL

1 DRC	: 24 th April 2020
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3. SCHOOL BOARD	: 12 th June 2020
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Department of Chemistry

ABSTRACT

**WASTE BIOMASS DERIVED HETEROGENEOUS CATALYSTS
AND THEIR APPLICATIONS IN ORGANIC
TRANSFORMATIONS**

**AN ABSTRACT SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
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**DEPARTMENT OF CHEMISTRY
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WASTE BIOMASS DERIVED HETEROGENEOUS CATALYSTS AND THEIR
APPLICATIONS IN ORGANIC TRANSFORMATIONS

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Submitted

In partial fulfillment of the requirement of the Degree of Doctor of Philosophy in
Chemistry of Mizoram University, Aizawl.

ABSTRACT

The escalating global concern over plastic waste, dwindling resources, and climate change has catalyzed a paradigm shift toward sustainable alternatives for industrial chemical processes. Polyethylene terephthalate (PET), one of the most widely used synthetic polymers, contributes significantly to environmental pollution due to its non-biodegradable nature and extensive usage in packaging and textiles. Simultaneously, the global generation of agro-waste remains largely underutilized despite its rich inorganic and carbonaceous content. Against this backdrop, biomass-derived heterogeneous catalysts have emerged as promising green alternatives for facilitating polymer recycling and carbon–carbon bond-forming reactions.

This thesis investigates the synthesis and application of three distinct biomass-based solid catalysts: Orange Peel Ash (OPA), Bamboo Leaf Ash (BLA), and nanostructured Orange Peel Ash-supported magnetite (OPA@Fe₃O₄), for use in sustainable chemical transformations. These catalysts were derived from waste biomass using environmentally benign techniques including thermal calcination for OPA and BLA and green co-precipitation for OPA@Fe₃O₄. The synthesized materials were thoroughly characterized using a comprehensive array of physicochemical and spectroscopic techniques.

X-ray diffraction (XRD) confirmed the presence of catalytically active oxides such as CaO, K₂O, Fe₃O₄, and SiO₂. Fourier Transform Infrared Spectroscopy (FTIR) revealed the existence of metal–oxygen bonds and surface hydroxyls. Surface morphology and particle size distribution were investigated through Scanning and Transmission Electron Microscopy (SEM/TEM), with results showing a transition from aggregated, ash-like textures in OPA and BLA to a rod-shaped, nanoscale morphology in OPA@Fe₃O₄. Surface chemistry and oxidation states were studied via X-ray Photoelectron Spectroscopy (XPS), while porosity and specific surface area were evaluated using the Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halenda (BJH) model; OPA (4.97 m²/g) < BLA (21.85 m²/g) < OPA@Fe₃O₄ (31.23 m²/g), with all three showing mesoporosity favorable for diffusion-controlled catalysis. Thermogravimetric Analysis (TGA) demonstrated thermal stability up to

900°C, with BLA showing the least mass loss due to its high silica content. Analytical techniques such as High-Performance Liquid Chromatography (HPLC), Nuclear Magnetic Resonance (NMR), and FTIR were used to verify the purity, structure, and yield of reaction products.

The performance of these catalysts was systematically assessed in the glycolysis and methanolysis of PET, targeting the recovery of high-value monomers such as bis(2-hydroxyethyl) terephthalate (BHET) and dimethyl terephthalate (DMT). Comparative studies revealed that each catalyst displayed unique strengths: OPA demonstrated high basicity and fast PET depolymerization but limited surface area; BLA exhibited excellent thermal stability and moderate reactivity due to its silica-rich matrix; and OPA@Fe₃O₄ showed the most balanced performance with high surface area, rapid depolymerization, and effective magnetic recovery. OPA@Fe₃O₄ achieved the highest BHET yield of 89% in glycolysis and 82% DMT yield in methanolysis under mild reaction conditions. Moreover, OPA@Fe₃O₄ maintained catalytic activity over six cycles, outperforming both OPA and BLA in terms of reusability and structural integrity.

In addition to polymer depolymerization, OPA and OPA@Fe₃O₄ were employed as base catalysts in Aldol condensation reactions involving aromatic aldehydes and ketones. The reactions were carried out under aqueous or solvent-free conditions to demonstrate environmental compatibility. Electronic substituents on the aldehydes significantly influenced reactivity; electron-withdrawing groups enhanced rate and yield, while electron-donating groups showed slower kinetics. OPA catalyzed Aldol reactions with yields as high as 96%, demonstrating strong basicity and broad substrate compatibility. Recyclability tests indicated a minor decrease in efficiency due to the gradual leaching of surface potassium, confirmed via elemental analysis. TEM images of spent catalysts showed partial pore collapse, although the overall mesoporous structure was largely retained.

Mechanistically, both PET depolymerization and Aldol condensation were facilitated by surface basic sites, including Ca²⁺, K⁺, and Fe³⁺ oxides. For PET recycling, nucleophilic attack by ethylene glycol or methanol on the ester carbonyl of

PET formed tetrahedral intermediates that subsequently yielded monomers such as BHET or DMT. In Aldol condensation, deprotonation of ketone substrates formed enolate ions which attacked electrophilic aldehydes, followed by dehydration to form α,β -unsaturated ketones. These reactions were significantly accelerated by the catalysts' high surface basicity and porosity. The nanostructured surface architecture and increased dispersion of OPA@Fe₃O₄, in particular, allowed for greater accessibility of active sites, thereby enhancing turnover frequency and selectivity. The high activity observed across multiple substrate types and recycling runs highlights the robustness and generalizability of these catalysts.

The novelty of this research lies in the development of catalysts from abundantly available, low-cost biomass wastes and the demonstration of their dual functionality in both polymer degradation and carbon–carbon bond formation. The systematic evaluation of physicochemical properties in relation to catalytic performance bridges a critical gap between materials science and green chemistry. Furthermore, this study contributes to the emerging discourse on circular economy by valorizing agricultural waste into functional materials capable of addressing environmental and industrial challenges.

This thesis thus offers a comprehensive comparative study of low-cost, biomass-derived solid catalysts, providing insight into the relationship between preparation method, physicochemical properties, and catalytic activity. OPA and BLA serve as scalable, renewable catalysts suitable for small-to-medium-scale applications, while OPA@Fe₃O₄, with its magnetic separability and superior efficiency, emerges as a viable candidate for industrial-scale PET recycling and green organic synthesis. By valorizing agricultural waste into functional, high-performance materials, this research contributes to circular economy principles and reinforces the transformative potential of biomass-based heterogeneous catalysts in addressing global sustainability challenges. The integration of waste remediation with catalysis highlights an innovative route toward resource-efficient, low-impact chemical manufacturing in alignment with the broader goals of green chemistry and environmental stewardship. In doing so, the present investigation not only advances

catalyst science but also provides a replicable model for sustainable development that merges scientific innovation with ecological responsibility.