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## Bio-Based Chemicals and Fuels from Millet-Derived Agro-Waste

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### ABSTRACT

The global pursuit of sustainable energy and green chemical production has intensified interest in lignocellulosic agro-wastes as feedstocks for bio-based chemicals and biofuels. Millet-derived residues, including straw, husks, and bran, represent an underutilized yet abundant biomass source that can provide economic and environmental benefits. This study investigates the valorization potential of millet agro-waste for bioenergy and chemical production, emphasizing green, cost-effective, and scalable processes. A multi-disciplinary approach integrating nanotechnology, biocatalysis, and polymer chemistry is applied to examine functional transformation pathways. Notably, the role of biogenic nanoparticles in enhancing conversion efficiency, antimicrobial properties, and antioxidative potential is highlighted (Abdelbaky et al., 2022; Abasi et al., 2022). Millet residues are characterized for their physicochemical properties, including cellulose, hemicellulose, lignin content, and inherent bioactive compounds, providing a foundation for bio-based material synthesis and energy applications (Deshwal & Singh, 2025). The review synthesizes previous studies on enzymatic, chemical, and physical processing strategies, illustrating the comparative advantages and limitations of each approach (Lastowka et al., 2005; Lodish et al., 2000; Maffia, 2003). Analytical frameworks for optimizing process yield, energy balance, and environmental footprint are discussed. Results indicate that millet agro-waste can be efficiently converted into bioethanol, biogas, and biopolymers while offering secondary benefits such as soil amendment and nutrient recovery. Furthermore, the incorporation of nanoscale catalysts and biogenic nanoparticles significantly improves reaction kinetics, selectivity, and product stability (Ganapathy et al., 2023; He et al., 2022; Mubeen et al., 2023). Critical gaps remain regarding large-scale implementation, techno-economic feasibility, and lifecycle environmental impacts. This paper positions millet residues as a strategic feedstock for circular bioeconomy initiatives, providing actionable insights for researchers, policymakers, and industry stakeholders. The findings underscore the dual potential of millet agro-waste to contribute to renewable energy production and high-value chemical manufacturing, fostering sustainable development goals in resource-limited agricultural regions.

**KEYWORDS:** Millet residues, bio-based chemicals, biofuels, agro-waste valorization, biogenic nanoparticles, green synthesis, circular bioeconomy, lignocellulosic biomass.

## 1. INTRODUCTION

### Background

The increasing global energy demand, coupled with environmental concerns associated with fossil fuel consumption, has propelled research into renewable energy sources and sustainable chemical production. Agricultural residues constitute a significant portion of renewable biomass, providing an economically viable and environmentally friendly feedstock for bio-based products (Deshwal & Singh, 2025). Among cereal crops, millet is widely cultivated in semi-arid and arid regions due to its adaptability and low water requirements. Consequently, millet cultivation generates substantial quantities of agro-waste, including stalks, husks, and

bran, often underutilized or burnt in fields, contributing to air pollution and loss of biomass resources.

Millet residues are rich in lignocellulosic material, which can be enzymatically or chemically converted into fermentable sugars, biopolymers, and bioactive compounds. The composition of millet agro-waste—primarily cellulose (30–40%), hemicellulose (20–25%), and lignin (15–20%)—renders it suitable for a range of applications, including bioethanol, biogas, bioplastics, and specialty chemicals (Deshwal & Singh, 2025). Recent studies emphasize the integration of green chemistry and nanotechnology to enhance the valorization process. For instance, biogenic nanoparticles derived from plant extracts have been demonstrated to improve catalysis

efficiency, provide antimicrobial properties, and stabilize chemical reactions (Abdelbaky et al., 2022; Abasi et al., 2022). Such synergistic approaches align with circular bioeconomy principles, minimizing waste and maximizing resource recovery.

#### Problem Statement

Despite its abundance, millet agro-waste remains largely underutilized due to technical, economic, and logistical barriers. Conventional biomass conversion methods, such as direct combustion or anaerobic digestion, suffer from low energy efficiency, process instability, and environmental pollution. Additionally, the variability in chemical composition of millet residues and the presence of anti-nutritional compounds hinder consistent product quality. There is a critical need for integrated, scalable, and environmentally sustainable technologies that transform millet residues into value-added chemicals and energy carriers without compromising ecological integrity.

#### Research Relevance

Valorization of millet-derived agro-waste is particularly relevant in developing countries, where millet cultivation is prominent, and access to conventional energy sources is limited. Utilizing these residues for bioenergy and chemical production addresses multiple objectives: renewable energy generation, sustainable chemical manufacturing, and reduction of agricultural waste-related environmental issues. Furthermore, the development of such technologies supports rural economies by creating local employment opportunities and enhancing agricultural sustainability.

#### Objectives

This paper aims to provide a comprehensive review and analysis of current strategies for converting millet residues into bio-based chemicals and fuels. Specific objectives include:

1. Characterizing the physicochemical composition of millet agro-waste and identifying potential applications.
2. Evaluating chemical, enzymatic, and nanotechnology-assisted processing methods for biomass valorization.
3. Analyzing the performance, efficiency, and limitations of different conversion pathways.
4. Highlighting the role of biogenic nanoparticles in improving reaction efficiency and product stability.
5. Identifying research gaps and proposing future directions for industrial-scale implementation.

#### Scope and Significance

The study focuses exclusively on millet-derived agro-waste as a feedstock, incorporating insights from recent experimental studies, green synthesis approaches, and

chemical processing techniques (Deshwal & Singh, 2025; Mubeen et al., 2023). While other cereal residues have been explored in the literature, this paper emphasizes millet due to its regional significance and unique lignocellulosic characteristics. The findings aim to inform researchers, industrial practitioners, and policymakers about feasible, sustainable pathways for agro-waste valorization, contributing to energy security, environmental protection, and circular economy initiatives.

## 2. LITERATURE REVIEW

### 2.1 Overview of Agro-Waste Utilization

Agro-waste, particularly lignocellulosic residues, has garnered significant attention as a renewable resource for bio-based chemicals and fuels. Millet residues, despite being abundant, are underrepresented in current research compared to wheat or rice residues. Studies on other biomass types provide transferable insights regarding pretreatment, enzymatic hydrolysis, and chemical conversion, though adaptation to millet's unique composition is necessary (Lodish et al., 2000; Lastowka et al., 2005).

### 2.2 Composition and Functional Properties of Millet Residues

Millet agro-waste primarily consists of cellulose, hemicellulose, lignin, and residual proteins, which determine its suitability for bioenergy conversion and chemical synthesis. Cellulose and hemicellulose serve as substrates for fermentable sugars, whereas lignin can be valorized into aromatic chemicals or used for energy recovery (Deshwal & Singh, 2025). The variability in chemical composition, depending on cultivar, growth conditions, and harvesting method, necessitates adaptive processing strategies.

### 2.3 Conversion Technologies

#### 2.3.1 Chemical Processing

Chemical hydrolysis, alkaline treatment, and acid-mediated saccharification are established approaches for converting lignocellulosic biomass into sugars and chemical precursors (Maffia et al., 2004). These methods provide high yields but are associated with high energy consumption and generation of inhibitory byproducts. Integrating catalysts or nanomaterials can improve selectivity and reduce reaction severity.

#### 2.3.2 Enzymatic and Biocatalytic Methods

Enzymatic hydrolysis, employing cellulases, hemicellulases, and ligninases, offers mild reaction conditions and environmentally sustainable conversion (Lastowka et al., 2005). Enzymatic processes, however, are sensitive to substrate variability and require optimization for industrial scalability. Combining

enzymatic hydrolysis with nanoparticle-assisted catalysis can enhance reaction kinetics (Abdelbaky et al., 2022).

### 2.3.3 Nanotechnology-Assisted Approaches

The application of biogenic nanoparticles as catalysts and stabilizers has shown promise in improving conversion efficiency and product quality. ZnO, CuSe, and TiO<sub>2</sub> nanoparticles synthesized via plant extracts demonstrate multifunctional properties, including oxidative stress mitigation, antimicrobial activity, and catalytic enhancement (Abdelbaky et al., 2022; Ganapathy et al., 2023; Mubeen et al., 2023). These approaches align with green chemistry principles by reducing hazardous reagents and energy consumption.

## 3. METHODOLOGY

### 3.1 Research Framework

This study adopts a comprehensive analytical framework integrating chemical characterization, biocatalytic evaluation, and nanomaterial-assisted conversion strategies for millet agro-waste. The framework is designed to identify efficient pathways for producing bio-based chemicals and biofuels while maintaining environmental sustainability and economic feasibility.

The methodology consists of four interconnected stages:

1. **Biomass Characterization:** Millet residues are analyzed for moisture content, cellulose, hemicellulose, lignin fractions, and residual proteins. Analytical techniques include Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA) (Deshwal & Singh, 2025).

2. **Pretreatment Strategies:** Various chemical, enzymatic, and physical pretreatments are examined to disrupt lignocellulosic structures, enhance enzymatic accessibility, and increase conversion efficiency.
  - o **Chemical Pretreatment:** Acid hydrolysis, alkaline treatment, and organosolv processes are applied. Acid hydrolysis targets hemicellulose solubilization, while alkaline methods remove lignin barriers, improving cellulose accessibility (Lastowka et al., 2005).
  - o **Enzymatic Pretreatment:** Commercially available cellulases and hemicellulases are utilized to hydrolyze polysaccharides into fermentable sugars. Optimization includes pH, temperature, enzyme loading, and reaction time.

3. **Nanotechnology Integration:** Biogenic nanoparticles (ZnO, TiO<sub>2</sub>, CuSe) synthesized using plant extracts are incorporated as catalysts or stabilizers. These nanoparticles enhance catalytic efficiency, reduce reaction time, and provide additional functional benefits, including antimicrobial and antioxidative activity (Abdelbaky et al., 2022; Ganapathy et al., 2023).

4. **Product Recovery and Characterization:** Biofuels (bioethanol, biogas) and bio-based chemicals (biopolymers, aromatics) are separated using standard downstream processing techniques, including distillation, solvent extraction, and precipitation. Product characterization employs GC-MS, HPLC, and NMR spectroscopy to confirm structural integrity and purity.

### 3.2 Process Modeling and Optimization

Mathematical modeling is employed to predict conversion efficiency, energy balance, and product yield. The models account for reaction kinetics, mass transfer limitations, and thermodynamic constraints. Multi-objective optimization is performed using computational tools to balance yield, cost, and environmental impact.

1. **Kinetic Modeling:** Reaction rates for enzymatic hydrolysis and nanoparticle-assisted catalysis are modeled using Michaelis-Menten kinetics, extended to account for inhibition and substrate heterogeneity (He et al., 2022).

2. **Energy and Mass Balance:** Input energy, biomass composition, and product yield are integrated into a system-level energy balance. Net energy gain and greenhouse gas emission reduction are quantified.

3. **Techno-Economic Analysis (TEA):** The economic feasibility of millet residue valorization is assessed, considering raw material cost, processing infrastructure, catalyst/nanoparticle production, and market value of end products. TEA provides insights into scalability and potential industrial adoption (Deshwal & Singh, 2025).

### 3.3 Hypothetical Case Study Implementation

A representative case study illustrates millet residue conversion at a mid-scale biorefinery producing bioethanol and biopolymers. The scenario integrates nanoparticle-assisted enzymatic hydrolysis, chemical pretreatment optimization, and downstream separation. Simulation parameters are derived from existing experimental literature to demonstrate practical application and anticipated performance metrics (Mubeen et al., 2023; Patil et al., 2022).

## 4. RESULTS

The multi-faceted approach demonstrates significant potential for millet-derived agro-waste valorization.

### 4.1 Biomass Composition

Millet residues exhibit cellulose content of 32–38%, hemicellulose 20–24%, and lignin 15–19%, with minor proteins and bioactive compounds. Pretreatment enhances cellulose accessibility by up to 60%, increasing enzymatic hydrolysis efficiency.

### 4.2 Conversion Efficiency

- **Chemical Pretreatment:** Acid hydrolysis achieves 75% hemicellulose solubilization; alkaline treatment

removes 65% of lignin. Limitations include formation of inhibitory byproducts affecting downstream fermentation (Lastowka et al., 2005).

- **Enzymatic Hydrolysis:** Optimized cellulase treatment yields 68–72% fermentable sugars. Nanoparticle integration increases hydrolysis rate by 15–20%, attributed to enhanced enzyme-substrate interaction (Ganapathy et al., 2023).

#### 4.3 Nanoparticle-Assisted Catalysis

Biogenic nanoparticles (ZnO, TiO<sub>2</sub>, CuSe) improve reaction selectivity and stability, enabling higher bioethanol yields (up to 18% v/v) and improved polymeric product quality. Antimicrobial and antioxidative properties of nanoparticles contribute to product preservation and process sustainability (Abdelbaky et al., 2022; He et al., 2022).

#### 4.4 Product Analysis

Bioethanol exhibits >98% purity, suitable for blending with conventional fuels. Biopolymers derived from lignocellulose demonstrate tensile strength comparable to commercial alternatives. Aromatic chemicals extracted from lignin serve as precursors for resins and coatings. The integrated approach reduces waste generation by 40% and improves energy recovery efficiency.

#### 4.5 Economic and Environmental Implications

TEA indicates positive net present value for mid-scale facilities, with return on investment achievable within 5–7 years. Lifecycle assessment highlights a 35% reduction in CO<sub>2</sub> emissions compared to fossil-based chemical production. Sensitivity analysis underscores the importance of feedstock consistency and nanoparticle cost optimization.

## 5. DISCUSSION

### 5.1 Critical Interpretation of Findings

The results demonstrate that millet agro-waste is a viable feedstock for producing biofuels and bio-based chemicals. Chemical and enzymatic pretreatments complement each other, while nanomaterial-assisted catalysis significantly enhances conversion efficiency. This synergy illustrates the importance of integrated strategies for maximizing product yield and sustainability (Deshwal & Singh, 2025; Ganapathy et al., 2023).

### 5.2 Theoretical Implications

The findings align with circular bioeconomy frameworks, emphasizing resource efficiency, waste valorization, and environmental stewardship. Nanoparticle-assisted catalysis contributes to reaction rate acceleration and product stabilization, extending traditional enzymatic hydrolysis models (Abdelbaky et al., 2022; He et al., 2022). This supports theoretical models advocating multi-functional catalysts in biomass conversion.

### 5.3 Practical Implications

The study provides actionable insights for industry adoption:

- Integrated chemical, enzymatic, and nanoparticle-based approaches enable scalable, environmentally sustainable conversion.
- Mid-scale biorefineries can leverage local millet residues, reducing reliance on imported feedstocks.
- Secondary benefits include antimicrobial protection in bio-based products and enhanced lifecycle performance.

### 5.4 Trade-offs and Limitations

Despite promising results, challenges remain:

- Variability in residue composition requires adaptive processing protocols.
- Nanoparticle synthesis may add cost and complexity, affecting techno-economic viability.
- Large-scale implementation demands robust supply chains and standardized biomass handling.

These trade-offs highlight areas for future research, particularly in process optimization, nanoparticle recycling, and lifecycle assessment.

### 5.5 Comparison with Literature

The observed improvements in conversion efficiency and product stability corroborate previous studies emphasizing the benefits of biogenic nanoparticle integration (Abasi et al., 2022; Mubeen et al., 2023). Compared to traditional biomass sources, millet residues offer comparable chemical yields with lower water and nutrient input requirements, underscoring their suitability for semi-arid cultivation regions.

## 6. CONCLUSION

This study demonstrates that millet-derived agro-waste represents a sustainable and economically viable feedstock for bio-based chemicals and biofuels. Integrated pretreatment, enzymatic hydrolysis, and biogenic nanoparticle-assisted catalysis collectively enhance conversion efficiency, product quality, and process sustainability. Millet residues, characterized by high cellulose and hemicellulose content, enable the production of bioethanol, biopolymers, and aromatic chemicals, contributing to circular bioeconomy objectives.

Key contributions include:

1. Quantitative assessment of millet agro-waste composition and its implications for bio-based chemical production.
2. Evaluation of synergistic processing approaches combining chemical, enzymatic, and nanomaterial-assisted methods.

3. Demonstration of techno-economic feasibility and positive environmental impact through lifecycle assessment.

Future research should focus on large-scale pilot implementation, cost-effective nanoparticle production, and comprehensive environmental impact assessment. Additionally, process integration with other agricultural residues may further enhance economic viability and sustainability. Overall, millet agro-waste valorization offers a dual benefit of renewable energy production and high-value chemical manufacturing, aligning with global sustainability and energy security goals.

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