Research in Next Generation Materials Engineering

GLINT OPEN ACCESS

Volume 1, Issue 1

Research Article

Date of Submission: 29 September 2025
Date of Acceptance: 21 October 2025
Date of Publication: 28 October 2025

Valorization of Agro-Industrial Residues for Bioethanol: A Comparative Review of Brewer's Spent Grain, Cassava, and Yam Peels

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Citation: Okorie, O. (2025). Valorization of Agro-Industrial Residues for Bioethanol: A Comparative Review of Brewer's Spent Grain, Cassava, and Yam Peels. *Res Next Gen Mater Eng*, 1(1), 01-37.

Abstract

Escalating global energy demand and the environmental consequences of fossil fuel dependence have intensified the urgent imperative for sustainable renewable energy sources. Bioethanol derived from lignocellulosic biomass represents a promising and strategic alternative. This critical, comparative review provides an original synthesis of the valorization pathways for three high-impact agro-industrial residues—yam peels, cassava peels, and brewer's spent grain (BSG)—for advanced bioethanol production, focusing on the interplay between feedstock composition, rigorous pretreatment, and bioprocess optimization. Crucially, the analysis establishes an original analytical framework demonstrating that the significant variability in reported ethanol yields is directly correlated with the inherent heterogeneity in the proximate and chemical composition of the feedstocks, compounded by disparities in pretreatment methodologies and saccharification protocols. Pretreatment plays an indispensable role in overcoming lignocellulosic recalcitrance, thereby enhancing the enzymatic hydrolyzability of structural polysaccharides. The comparative assessment identifies BSG as the superior fermentation substrate, exhibiting high carbohydrate and low inhibitory compound profiles, with documented ethanol yields approaching 94% in optimized processes. Current research trends mandate the adoption of advanced statistical optimization and kinetic modeling techniques for enhancing conversion kinetics, reducing operational costs, and improving the techno-economic feasibility. This waste-to-energy paradigm directly contributes to a circular bioeconomy by converting low-value waste streams into high-value biofuel, thereby addressing

challenges in waste management and climate change mitigation. The review concludes by delineating critical future research trajectories in strain engineering and AI-driven bioprocess modeling to realize the full, sustainable potential of 2G bioethanol production.

Keywords: Bioethanol, lignocellulosic biomass, circular bioeconomy, pretreatment methods, fermentation, bioprocess modeling.

Introduction

Energy resources are a cornerstone of global socioeconomic development and are under increasing scrutiny due to rising demand and environmental pressures. Notwithstanding this focus, the global energy matrix remains overwhelmingly reliant on fossil fuels. Contemporary analyses indicate that coal, natural gas, crude oil, and their derivatives collectively account for approximately 80% of worldwide energy production. Demand for these finite resources continues to escalate at an annual rate of 1.3%, with a substantial proportion consumed by household and industrial sectors, notably transportation and agriculture.

This dependency poses two critical global challenges. First, the rapid depletion of global fossil fuel reserves presents a formidable barrier to long-term energy security. Second, and more critically, approximately 89% of global greenhouse gas emissions that drive climate change originate from fossil fuel combustion. This reality has catalyzed intensified scientific and political efforts to develop economically viable alternative energy sources that mitigate environmental degradation. In this context, renewable energy sources are widely regarded as promising solutions, offering multifaceted environmental and socioeconomic benefits. Within the transportation sector—a domain requiring high-energy-density fuels—biofuels emerge as a particularly viable renewable alternative. Although other renewables such as solar, wind, and hydroelectric power generate electricity, they are presently outperformed by liquid fuels in terms of specific energy density and compatibility with incumbent transportation infrastructure. A key advantage of biofuels is their markedly reduced lifecycle environmental footprint; emissions are substantially lower than those from fossil fuels due to their biodegradable composition and efficient combustion.

The biofuel industry has demonstrated sustained expansion. According to the World Bioenergy Association, global biogas output has increased at an average annual rate of roughly 9% over the past two decades, while liquid biofuel production has grown at 12% per annum. By 2019, global production attained 62.3 billion cubic meters of biogas and 159 billion liters of liquid biofuels, possessing energy contents of approximately 23 MJ/m^3 and 21.1 MJ/l, respectively. Ethanol dominates the liquid biofuel market, constituting over 80% of global production and thereby establishing itself as the preeminent biofuel worldwide. Projections for 2024 estimate global bioethanol production will surpass 135 billion liters, with the United States (42%) and Brazil (31%) serving as the principal producers.

To sustain this trajectory without competing with food supplies, the research focus has shifted toward second-generation feedstocks. Agricultural residues such as cassava peel, yam peel,

brewer's spent grain, along with municipal solid waste (MSW), wood processing by-products, and dedicated energy crops, represent the most promising and abundant lignocellulosic biomass sources for advanced bioethanol production. Population growth has precipitated a substantial increase in the generation of such agricultural waste. These feedstocks are inexpensive, widely accessible, and non-edible, rendering them ideal substrates for sustainable bioethanol synthesis and integrated waste valorization strategies. This lignocellulosic biomass presents considerable potential as a sustainable alternative to first-generation biofuels. Within a circular biorefinery paradigm, it can be utilized not only for the cost-effective production of biofuels but also for the co-generation of a suite of value-added products, including biopolymers, biochar, organic acids, and enzymes, without imposing environmental burdens or compromising food security.

However, the efficient conversion of this biomass is constrained by its inherent structural complexity. Lignocellulosic feedstocks are primarily composed of structural polysaccharides—38–50% cellulose and 23–32% hemicellulose—intricately cross-linked by 10–25% lignin, a recalcitrant aromatic polymer, alongside minor fractions of minerals and organic extracts. The distribution and ratio of these constituents are species-dependent. This natural recalcitrance, wherein lignin forms a protective barrier that limits access to the fermentable sugar polymers, presents a formidable challenge for industrial-scale deployment. Consequently, a rigorous and efficient pretreatment process is an indispensable prerequisite to disrupt the lignin-carbohydrate complex, reduce cellulose crystallinity, and facilitate the subsequent enzymatic saccharification to release fermentable monosaccharides. This review critically examines recent advancements in pretreatment technologies and bioconversion processes designed to overcome these barriers, thereby unlocking the full potential of lignocellulosic waste for a sustainable and secure energy future.

Agro-Industrial Waste: A Dual Challenge of Abundance and Opportunity

Agricultural production, while fundamental to global food security, also generates immense volumes of residual biomass, collectively termed agricultural waste. This category encompasses the non-commodity solid and liquid fractions generated across the agri-food value chain, including crop residues and livestock effluents . These residues are conventionally classified into four primary streams: (1) field-based crop residues (e.g., straw, stalks, leaves), (2) post-harvest fruit and vegetable waste, (3) livestock manure and processing by-products, and (4) secondary outputs from agro-industrial operations.

The magnitude of this biomass generation is substantial, with global agricultural systems producing an estimated 998 million tons annually. This volume is projected to increase at a rate of 5–10% per year, a trend driven by the intensification of farming practices required to support a growing population and rising living standards. The uncontrolled accumulation of this waste poses significant environmental threats, contributing to ecosystem degradation and the deterioration of soil, air, and water quality, with consequent risks to public health. Paradoxically, this environmental challenge also presents a valuable resource opportunity. A significant proportion of agricultural waste is lignocellulosic, comprising variable proportions of

cellulose, hemicellulose, and lignin. This biochemical composition renders it a promising, low-cost feedstock for biofuel production and other valorization pathways within a circular bioeconomy framework. However, the inherent structural recalcitrance of lignocellulose, primarily imparted by the cross-linked lignin matrix, severely limits the enzymatic hydrolyzability of the constituent polysaccharides.

Consequently, a robust pretreatment step is indispensable for deconstructing the lignocellulosic matrix and improving the biomass's amenability to subsequent conversion processes. A diverse suite of pretreatment methodologies—categorized as physical, chemical, physicochemical, and biological—has been developed to this end, as extensively documented in the literature. Each technique presents a distinct profile of advantages and limitations pertaining to efficiency, economic viability, and environmental impact. Collectively, these pretreatment strategies provide a foundational technology for the sustainable upgrading of biomass, thereby transforming a critical waste management issue into a viable resource for renewable energy and biobased products.

Yam Peels: A Lignocellulosic Feedstock from a Major Crop

Nigeria's status as a global leader in root and tuber crop production is underscored by its dominance in yam (*Dioscorea* spp.) cultivation, with an annual output exceeding 50.1 million tons—constituting approximately 67% of the worldwide supply. The processing and consumption of this vast agricultural commodity generate substantial quantities of residual biomass, primarily in the form of yam peels. Rather than representing a simple waste stream, this residue constitutes a valuable lignocellulosic feedstock with significant potential for integrated biorefining. Research confirms that yam peels serve as an excellent substrate for biofuel production, including bioethanol and biogas, due to their favorable biochemical composition. Their distinct physicochemical properties also make them effective biosorbents for treating contaminated water, highlighting their potential in both energy and environmental applications.

The efficacy of yam peels in these valorization pathways is intrinsically linked to their material composition. The proximate and chemical characteristics summarized in Tables 1 and 2 offer fundamental insights into their structural and nutritional properties, which directly influence conversion efficiency and optimal application. The compositional data reveal a substrate rich in polysaccharide (cellulose and hemicellulose), conducive to fermentation, although values vary with cultivar and analytical method. This profile substantiates the promise of yam peels as a renewable and sustainable resource for bioconversion, aligning waste management with the production of energy and high-value products.

Table 1. Proximate composition of yam peel reported in the literature.

Authors	Moisture (%)	Crude Protein (%)	Crude Fibre (%)	Ether Extract (%)	Ash (%)	Nitrogen Free Extract (%)	Volatile Matter (%)
Kitson-Hytey et al. (2024)	69.7	NR	NR	NR	NR	NR	NR
Bashir et al. (2021)	11.11	NR	NR	NR	5.93	NR	69.7
Popoola et al. (2021)	4.66	4.89	12.24	3.34	9.78	69.75	NR
Isah et al. (2019)	2.18 ± 0.18	3.15 ± 0.05	11.96 ± 0.4	1.87 ± 0.36	12.98 ± 0.78	NR	NR
Ekpo et al. (2019)	NR	11.14	6.30	4.12	7.30	71.14	NR
Lawal et al. (2014)	11.75 ± 0.03	3.46 ± 0.90	41.00 ± 6.90	1.30 ± 0.20	10.00 ± 0.10	NR	NR

NR: Not Reported

Table 2. Chemical composition of yam peel.

References	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)	Ash (%)	Carbon (%)	Hydrogen (%)
Bashir et al. (2021)	29.02	28.91	27.43	NR	NR	NR	NR
Oladiran (2014)	9.67 ± 0.51	21.98 ± 0.51	3.19 ± 0.04	65.17 ± 1.56	8.49 ± 0.23	39.40 ± 0.67	6.12 ± 0.02

Cassava Peels: A Substantial and Widespread Lignocellulosic Residue

The industrial processing of cassava (*Manihot esculenta* Crantz) yields substantial residual biomass, with peels constituting a dominant fraction of post-harvest losses and the magnitude of this waste stream is considerable. In Nigeria—a preeminent global cassava producer—the annual processing of an estimated 10 million tons of roots for garri production results in the discard of approximately 2.96 million metric tons (MMT) of peels. More contemporary analyses suggest this figure may surpass 15 million tons annually. These peel residues, characterized by a typical thickness of ~1 mm, account for 10–13% of the root's dry matter composition.

This abundant, fibrous lignocellulosic residue presents a highly promising feedstock for advanced biorefinery applications, particularly bioethanol synthesis, owing to its favorable biochemical constitution. Its suitability is principally underpinned by a high starch content, reported in the range of 56–60%, complemented by significant hemicellulose (15–18%) and comparatively lower proportions of lignin (2–3%), protein (1.5–2%), pentosan (2%), and reducing sugars (0.4–5%). Standard proximate characterization further delineates cassava peels by a dry matter content of 86.5–94.5%, organic matter of 81.9–93.9%, crude protein of 4.1–6.5%, neutral detergent fiber of 34.4%, and lignin of 8.4%. It is critical to note that reported values for these compositional parameters exhibit notable inter-study variability. These discrepancies are likely attributable to a confluence of factors, including genotypic diversity among cassava cultivars, divergent agricultural practices, and heterogeneity in sample preparation and analytical protocols. The proximate and chemical compositions of cassava peels reported in the literature are summarized in Tables 3 and 4, respectively.

Table 3: Proximate composition of cassava peels

Components	Olutosin & (2019); Kayode (2021) and Tonukari et al. (2023)		Isah et al.	Idugboe et al. (2017) Cassava peels obtained from				Ebabhi et al. (2018)
	UCP	FCP		Benin city	Okada	Warri	Koko	
Moisture content (%)	86.29	31.60	2.18±0.18	8.500	7.200	7.967	8.000	14.16±0.056
Ash (%)	4.88	10.23	12.98±0.78	7.500	8.1	7.517	8.000	2.25±0.026
Protein (%)	6.24	11.22	3.15±0.05	4.600	5.000	3.900	4.100	5.23±0.015
Lipid (%)	1.39 (fat)	2.91 (fat)	1.89±0.36					7.20±0.032
Crude fiber (%)	10.88	8.87	11.96±0.4	12.00	11.50	12.50	12.7	5.10±0.031
Cyanide (ppm)	118.86	20.46	NR	NR	NR	NR	NR	NR
Starch (%)	56.72	20.09	67.39±0.15	NR	NR	NR	NR	NR

Keys: UCP- Unfermented cassava peels

FCP- Fermented cassava peels

Table 4: Chemical composition of cassava peels

Parameter	Composition			
	Tonukari et al. (2023)	Widiarto et al. (2019)	Daud et al. (2014)	Pooja and Padmaja (2015)
Cellulose	NR	40.5%	37.9%	14.17%
Hemicellulose	NR	21.4%	37.0%	23.40%
Lignin	NR	11.7%	7.5%	10.88%
Organic carbon content (%)	48.7	NR	NR	NR
Total nitrogen content (%)	1.0	NR	NR	NR
C/N Ratio	48.7	NR	NR	NR
K (%)	1.1	NR	NR	NR

P (%)	1.6	NR	NR	NR
NO3 (%)	0.16	NR	NR	NR
Zn (mg/kg)	125	NR	NR	NR
Cu (mg/kg)	15	NR	NR	NR
Mn (mg/kg)	180	NR	NR	NR
Ph	6.4	NR	NR	NR
Na (%)	0.15	NR	NR	NR
Ca (%)	0.9	NR	NR	NR
Pb (mg/kg)	16.7	NR	NR	NR
Ash (%)	52.6	NR	4.5	3.7

Brewer's Spent Grain as a Lignocellulosic Biomass

Brewer's spent grain (BSG)— the principal solid by-product of the brewing industry— is produced during the mashing stage, when malted and adjunct cereals are solubilized in hot water to extract fermentable sugars, amino acids, and other soluble compounds into the wort. This process transfers approximately 60–70% of the initial dry mass into the wort, leaving the insoluble fraction as BSG. Although barley (*Hordeum vulgare*) is the main cereal used, other grains— such as wheat and unmalted barley (substitution levels up to 45%)—introduce significant variability into the final composition of BSG.

Following mashing, the residual solids are recovered via filtration (e.g., in a lauter tun) and subjected to sparging with hot water (~78°C) to maximize sugar recovery. The resultant BSG possesses an elevated moisture content, typically ranging from 75% to 85%, and is subsequently handled as a wet material. Macroscopically, BSG presents as a light to dark brown, coarse particulate material with a characteristic malty aroma. Its physical structure comprises the undissolved grain fractions, including the husk, pericarp-seed coat (tegument), endosperm particles, non-saccharified starch, and protein-polyphenol complexes formed during mashing. As the most voluminous brewing by-product, BSG accounts for roughly 85% of the industry's total residues. Production metrics indicate an output of approximately 20 kg of wet BSG per 100 liters of beer produced, equating to ~270 kg per m^3 of beer, derived from about 30% of the initial malt input.

The high valorization potential of BSG stems from its rich and complex chemical composition, although this composition shows substantial heterogeneity. Key determinants of this variability include the barley cultivar and processing (e.g., roasting, kilning), specific malting parameters, and mashing regimen conditions. Despite this variability, a consistent core nutritional profile has been documented, as summarized in Table 5.

BSG is distinguished by its high dietary fiber content, predominantly constituted by hemicellulose (19–42% dry matter, d.m.), with arabinoxylans as the principal component, cellulose (15–29% d.m.), and lignin (3–28% d.m.) (Lynch et al., 2016; Tisma et al., 2018). It

also serves as a significant source of protein (14–31% d.m.), along with appreciable quantities of lipids (3–13%), ash (1–5%), and residual starch (1–12%) (Jackowski et al., 2020; Rojas-Chamorro et al., 2020).

Table 5. Compositional characterization of brewer's spent grain (BSG) from various studies.

Parameter	Mata et al. (2015)	Wilkinson et al. (2017)	Bieniek et al. (2022)	Pabbathi et al. (2022)	Consolidated Ranges (e.g., Jackowski et al., 2020; Lynch et al., 2016)
Particle size (mm)	0.149-1.190	NR	NR	NR	NR
Moisture (%)	72.0	NR	NR	NR	75–85 (wet basis)
Ash (% d.m.)	4.4	2.7 ± 0.21	NR	1–4	1–5
Higher Heating Value (MJ/kg)	19.8	NR	NR	NR	NR
Lipid (% d.m.)	5.4	6.3 ± 1.4	NR	2.5–6	3–13
Cellulose (% d.m.)	6.09	22.1 ± 0.8	17.18	26–60	15–29
Hemicellulose (% d.m.)	39.7	19.3 ± 1.8	34.16	19–60	19–42
Lignin (% d.m.)	34.8	10.7 ± 2.2	3.12	13–56	3–28

Parameter	Mata et al. (2015)	Wilkinson et al. (2017)	Bieniek et al. (2022)	Pabbathi et al. (2022)	Consolidated Ranges (e.g., Jackowski et al., 2020; Lynch et al., 2016)
Total Organic Carbon (% d.m.)	97.9	NR	NR	NR	NR
Starch (% d.m.)	NR	1.2 ± 0.11	NR	NR	1–12
Protein (% d.m.)	NR	27.9 ± 0.18	NR	NR	14–31
Extractives (% d.m.)	NR	8.6	45.54	NR	NR

NR: Not Reported; d.m.: dry matter

This nutrient-dense and lignocellulose-rich profile establishes BSG as a highly attractive, low-cost substrate for bioprocessing. It is extensively employed in both solid-state (SSF) and submerged fermentation (SmF) as a nutrient source for microbial cultivation, enabling the synthesis of a diverse portfolio of value-added products. These include enzymes, organic acids, biofuels, and prebiotic compounds. The integration of BSG into such biorefinery concepts epitomizes the implementation of circular economy principles, effectively upgrading an industrial waste stream into a renewable resource for biochemical production.

Enzymatic Conversion of Agro-Waste Starch to Glucose

The efficient conversion of starch derived from agricultural waste into fermentable sugars is a critical step in the bioethanol production pipeline. This process is predominantly achieved through enzymatic hydrolysis, a method favored for its high specificity and yield. The hydrolysis occurs in two main stages: liquefaction, which reduces the viscosity of gelatinized starch, and saccharification, where the resulting dextrins are broken down into glucose. The saccharification process employs a synergistic cocktail of hydrolytic enzymes to target the specific glycosidic bonds within the starch polymer. α-*amylase* (endo-*amylase*; EC 3.2.1.1) acts internally on α-1,4 linkages to rapidly reduce polymer length. β-*amylase* (exo-*amylase*; EC

3.2.1.2) then cleaves maltose units from the non-reducing ends of the chains. Finally, gluco*amylase* (amyloglucosidase; EC 3.2.1.3) acts on both α-1,4 and, at a slower rate, α-1,6 linkages to release β-D-glucose monomers.

A key strategy to enhance the efficiency of this process is the supplementation with a debranching enzyme, such as pullulanase (EC 3.2.1.41). Pullulanase specifically hydrolyzes the α-1,6 glycosidic bonds at the branch points in amylopectin. Its co-application with gluco*amylase* is particularly effective due to their shared optimal pH and temperature ranges, leading to a more complete and rapid conversion of starch to glucose. While chemical hydrolysis using agents like sulfuric acid is a possible alternative, the enzymatic method is strongly preferred at an industrial scale. The primary advantages include superior glucose yields, the avoidance of equipment corrosion, and, most significantly, the prevention of undesirable and inhibitory by-product formation (e.g., furans and organic acids) that can impede subsequent fermentation. The resulting high-purity glucose stream is an ideal substrate for microbial fermentation, primarily by *Saccharomyces cerevisiae*, for bioethanol production. Furthermore, this glucose syrup can be diverted to other high-value bioconversion processes, such as the enzymatic production of high-fructose syrup, underscoring the versatility of enzymatically hydrolyzed agro-waste within an integrated biorefinery model.

Microbial Fermentation for Bioethanol Production

Fermentation constitutes the central phase of the bioethanol production process, where fermentable sugars obtained from hydrolysis are biologically converted into ethanol and carbon dioxide by suitable microorganisms. This biochemical transformation is catalyzed by a suite of microbial enzymes, facilitating the catabolism of C5 and C6 sugars into the target biofuel.

Microbial Biocatalysts and Industrial Selection

A diverse consortium of microorganisms is employed as biocatalysts for this purpose, spanning fungal species such as *Saccharomyces cerevisiae* and *Aspergillus niger*, to facultative bacteria including *Zymomonas mobilis* . These strains demonstrate efficacy in fermenting sugars derived from a wide spectrum of agricultural residues, including cassava, yam, and potato peels, as well as brewer's spent grain. For industrial-scale applications, the yeast *Saccharomyces cerevisiae* and the fungus *Aspergillus niger* are particularly favored. This preference is predicated on their robust tolerance to inhibitory compounds, high ethanol volumetric productivity, and broad substrate specificity, which enables the concurrent fermentation of both pentose and hexose sugars. A comparative overview of key microbial strains is provided in Table 6.

Table 6: Characteristics of Prominent Ethanologenic Microorganisms

Microorganism	Type	Key Advantages	Primary Substrates	Industrial Relevance
Saccharomyces cerevisiae	Yeast	High ethanol yield, robust inhibitor tolerance, well-established genetics	Glucose, Sucrose	High; Industry standard
Aspergillus niger	Fungus	Broad substrate specificity, high hydrolytic enzyme production	Pentoses, Hexoses	Moderate-High; Often used in co-cultures or SSF
Zymomonas mobilis	Bacterium	High specific uptake rate, low biomass yield, high ethanol tolerance	Glucose, Sucrose, Fructose	Moderate; Subject of metabolic engineering

Critical Process Parameters and Kinetic Optimization

The ultimate ethanol yield and volumetric productivity are critically dependent on a tightly controlled suite of physicochemical parameters. Key variables include medium pH, fermentation temperature, substrate concentration, process duration, and inoculum size. Among these, temperature exerts a particularly profound influence on fermentation kinetics, as it governs fundamental physiological processes including microbial growth rate, cellular membrane fluidity, and enzymatic activity. While reaction rates typically increase with temperature up to a species-specific optimum, supra-optimal temperatures—those exceeding 35°C for *S. cerevisiae*—elicit severe detrimental effects. Such thermal stress can compromise membrane integrity, induce protein denaturation, and trigger a metabolically costly heat-shock response. Furthermore, the inherent toxicity of accumulated ethanol is synergistically amplified at elevated temperatures, leading to exacerbated inhibition of microbial growth and metabolic activity.

Concurrently, nitrogen availability serves as a critical regulator of yeast proliferation and directs metabolic flux towards biosynthesis. The strategic supplementation with complex nitrogen sources, such as yeast extract, is a well-established methodology to enhance microbial vitality and maximize final ethanol titers.

Advanced Fermentation Strategies and Future Outlook

The systematic optimization of these parameters is therefore indispensable for maximizing the economic feasibility of bioethanol production, irrespective of whether monoculture or co-culture systems are employed. A principal challenge in industrial fermentation involves transcending the physiological limitations of conventional microbial strains. A promising avenue for enhancing process robustness and overall yield lies in the deployment of engineered or adaptively evolved strains exhibiting superior tolerance to both high ethanol titers and elevated temperatures (thermotolerance). The implementation of such specialized ethanologenic variants presents a strategic solution to mitigate end-product and thermal inhibition, thereby enabling more efficient, resilient, and productive industrial-scale fermentations.

Bioprocess Modelling and Kinetic Analysis for System Optimization

The development of economically viable bioprocesses is fundamentally contingent upon the systematic optimization of operational parameters, which exert a deterministic influence on overall system efficiency, productivity, and techno-economic feasibility. This optimization paradigm is critical for enhancing the cost-to-profit ratio and de-risking the scale-up of production to an industrial level. The performance and final product yield are governed by a complex interplay of factors, including fermentation conditions (pH, temperature), microbial strain physiology, substrate characteristics, and bioreactor configuration.

Advanced Frameworks for Bioprocess Optimization

The limitations of traditional one-variable-at-a-time (OVAT) approaches, which fail to account for variable interactions, have necessitated the adoption of sophisticated statistical and computational frameworks. Techniques such as Response Surface Methodology (RSM), Artificial Neural Networks (ANN), and Genetic Algorithms (GA) provide superior robustness for navigating high-dimensional, multi-factorial design spaces, enabling the identification of global optima. The efficacy of these tools is predicated on statistically designed experiments. Foundational designs, including Plackett-Burman for efficient variable screening, and Box-Behnken or Central Composite Design (CCD) for detailed response surface analysis, are instrumental. These methodologies allow for the precise elucidation of significant variables, determination of their optimal setpoints, and modeling of their synergistic effects, thereby culminating in maximized product yields.

Mechanistic Kinetic Modelling of Bioconversion Stages:

Complementing empirical optimization, kinetic modelling provides a powerful mechanistic framework for simulating and predicting the dynamics of critical bioprocess stages, including pretreatment, enzymatic hydrolysis, and fermentation.

A diverse suite of kinetic models is employed to describe microbial growth and product formation. Prominent examples include:

- The Monod model for substrate-dependent growth kinetics.
- The Logistic model for population dynamics under limiting conditions.
- The Modified Gompertz model, extensively applied to estimate critical fermentation parameters such as lag phase duration (λ), maximum product formation rate (R_m), and potential product concentration (P_{max}). Additional models, including Contois (for substrate inhibition), Luedeking–Piret (for growth- and non-growth-associated product formation), and Teisser, are frequently applied to capture specific microbial behaviors.

For the enzymatic hydrolysis of lignocellulosic biomass, kinetics are often described by Michaelis–Menten formalism, Langmuir adsorption isotherms, and pseudo-first-order rate equations. To address the inherent complexities of heterogeneous solid-liquid reactions, more intricate models such as the Kopelman model for fractal systems and deactivation–reactivation mechanisms are employed to account for enzyme inactivation and complex substrate interactions.

Synthesis and Modelling Imperative

A fundamental challenge in bioprocess kinetics is the absence of a universal model capable of fully capturing the heterogeneity of lignocellulosic biomass. The coexistence of multiple substrates, inhibitory compounds, and complex enzyme-substrate interactions creates a system with potentially concurrent rate-limiting steps. Therefore, the critical endeavor involves a judicious, multi-stage approach: identifying dominant influential factors through statistical screening, pinpointing the rate-determining step, and carefully selecting or formulating the most appropriate mechanistic model. Tailoring the kinetic modelling approach to specific bioprocess conditions is indispensable for achieving predictive accuracy, enabling robust process control, and ultimately realizing cost-effective optimization for industrial-scale production (Table 7).

Table 7: Summary of Prominent Kinetic Models in Lignocellulosic Bioprocessing

Model Category	Representative Models	Primary Application	Key Parameters
Microbial Growth	Monod, Logistic, Contois	Fermentation kinetics	μ_{max}, K_s, X_{max}

Model Category	Representative Models	Primary Application	Key Parameters
Product Formation	Modified Gompertz, Luedeking-Piret	Bioethanol production	P_{max}, R_m, λ, α, β
Enzymatic Hydrolysis	Michaelis-Menten, Langmuir Adsorption	Cellulose/Saccharification	V_{max}, K_m, K_{ads}
Complex Systems	Kopelman, Deactivation-Reactivation	Heterogeneous biomass hydrolysis	Fractal dimension, k_deact

Bioethanol: A Strategic Renewable Fuel and the Modelling Imperative

Bioethanol (EtOH), a clear, colorless, and biodegradable straight-chain alcohol, is synthesized via the microbial fermentation of sugars derived from lignocellulosic and starch-based biomass. As a renewable liquid fuel, it confers significant advantages within the transportation sector, including a superior octane rating, high latent heat of vaporization, and reduced automotive emissions. These attributes collectively enhance thermodynamic efficiency and operational performance in spark-ignition engines, positioning bioethanol as a pivotal gasoline additive or blending component for the displacement of fossil fuels.

Notwithstanding the well-established technical feasibility of its production from diverse feedstocks, including abundant agricultural residues, the economic viability and net yield of bioethanol are contingent upon a complex matrix of interdependent process parameters. This intricacy renders the accurate modeling and optimization of these bioconversion processes a critical scientific and engineering challenge, central to the realization of commercial-scale production. While empirical data are fundamental, they possess an inherent limitation in extrapolative predictive capacity across the entire operational domain. Consequently, the development and implementation of sophisticated predictive modeling frameworks are imperative.

Artificial intelligence (AI) paradigms encompassing artificial neural networks (ANNs), fuzzy logic systems, and machine learning (ML) algorithms offer a powerful methodological arsenal for elucidating the complex, non-linear dynamics inherent to bioprocess systems. However, the deployment of these data-driven modeling techniques within the bioenergy sector remains nascent and insufficiently exploited. This disparity underscores a critical research imperative: the formulation and integration of advanced mathematical, statistical, and computational models is indispensable for the robust estimation, sensitivity analysis, and optimization of critical process variables. The strategic application of such models is fundamental to the conceptualization and design of next-generation bioethanol production platforms characterized

by enhanced robustness, operational efficiency, and economic competitiveness. The performance of bioethanol production is highly sensitive to feedstock composition and the selected processing pathway. The variability in final ethanol yield attributable to these factors is exemplified in Table 8, which provides a comparative synopsis of documented yields from three distinct lignocellulosic residues—cassava peel, brewer's spent grain (BSG), and yam peel—under a range of pretreatment and fermentation conditions. The data depicts the significant influence of hydrolysis method (e.g., acid vs. enzymatic), process severity, and microbial biocatalyst on the efficiency of sugar conversion to ethanol

Table 8: Comparative analysis of bioethanol yields from prominent agricultural residues

Biomass	Pretreatment Method	Key Process conditions	Fermentation process	Bioethanol Yield	Reference
Cassava peel	Acid hydrolysis	200g of cassava peels powder to 1000 ml of 0.5 M sulfuric acid, 22 h, 98^{o}C	*S. cerevisiae* (period:18 hrs, temperature: 40^{o}C, pH: 4.5)	200 L/ton of cassava peels	Odongo et al. (2024)
Cassava peels	Acid hydrolysis	13.1M H_2SO_4 at 100^{o}C for 110 min	*S. cerevisiae* (72 h)	17.3%	Sokan-Adeaga et al. (2024)
BSG	Acid hydrolysis	sulfuric: 0.065-0.37M; Nitric: 0.01-0.5M; acid concentration, liquid-solid ratio (8-12w/w%)	Commercial strain of *Saccharomyces cerevisiae (De Danske Gaerfabrikker A/S, Malteserkors)(*30°C, 150 rpm, pH: 5.5)	82%	Lisci et al. (2024)
Cassava peel	Dilute acid hydrolysis	Laboratory experiment condition (50 mL of 0.1M; Different temperature range-25 to 70^{o}C); 45% reducing sugar	*Saccharomyces cerevisiae* (baker's yeast) (70^{o}C, period of 2days)	12%	Mweta et al. (2024)
		Field experiment conditions (30 L of 0.1M battery acid in a solar still)	*Saccharomyces cerevisiae* (baker's yeast) 45% reducing sugar (70^{o}C, period of 2days)	7.5%	
BSG	Enzymatic hydrolysis	48.6 °C, 6.7 % w/w biomass loading, and 0.22 mL gDM−1 as enzyme concentration, Glucose yield: 44%	NR	NR	Sibono et al. (2023)
Yam peels	Enzymatic hydrolysis	150rpm, temperature: 50^{o}C, pH: 5.0, time: 4 days	Instant dry yeast (*S. cerevisiae*); Yeast concentration up to 5.50% (w/v)	45.79%	Saulawa et al. (2023)

Cassava Peel	Acid hydrolysis	20% H_2SO_4, 65°C, pH was adjusted to 4.5 with 0.1M NaOH	Baker's yeast: 5%; 3-5 days	33.74g/cm^3	Madukasi (2023)
BSG	Dilute acid hydrolysis	15 w/w solid load, 0.3 L mini reactors fitted with a peg-mixer	SESF process	251 L EtOH/ton BSG	Wagner et al. (2022)
Yam peel	Acid hydrolysis	Temperature: 110°C, time:180 minutes, acid concentration: 1M of HCl, 30g peel sample	*S. cerevisiae* (5 days, 20g of yeast)	180 Ml	Bashir et al. (2022)
Cassava peels	Enzymatic hydrolysis		*S. cerevisiae*	28.8 g/100 g reducing sugar	Acheampong et al. (2022)
Cassava peels	Acid hydrolysis		Combination of *Aspergillus oryzae* and *Neurospora crassa*	38.33±2.03 ml	Bassey et al. (2022)
Pineapple peels			Combination of *Aspergillus oryzae* and *Saccharomyces cerevisiae*	48.67±5.7 ml	
Cassava peel	Pretreatment by pasteurization in a hot water bath	Temperature: 72°C, time: 30 minutes	*S. cerevisiae*	45ml	Adegbehingbe & Adeleke (2021)
			Z. mobilis	23ml	
Cassava peel	Alkaline-assisted hydrothermal pretreatment	72h, 150rpm	*Kluyveromyces marxianus* MTCC 4139, fermentation media (110°C, 15min, 10%v/v)	0.44g/g	Papathoti et al. (2021)
Cassava peel	Acid hydrolysis using empty sulfonated palm oil fruit bunches		*S. cerevisiae*	27.72%	Mardina et al. (2021)
BSG	Acid and enzymatic hydrolysis steps	Acid hydrolysis (90°C,1.85w/w% sulphuric acid, 19.5min) Enzymatic hydrolysis (15w/w% solid loading, 0.04g/g enzyme dosage)	*Saccharomyces cerevisiae* (at 30°C, 150rpm shaking for 72h)	72%	Bedo et al. (2021)
Cassava peel	Enzymatic hydrolysis	2.5hrs, 1mg/L enzyme loading, incubation time: 3 days	Simultaneous saccharification & fementation (SSF) by *S. cerevisiae*	1.911%	Osemwengie et al. (2020)
BSG	Dilute phosphoric and sulphuric	15w/v% solid loading, 72h, 150rpm, pH: 4.8	*S. cerevisiae*	222L EtOH/ton of the BSG	Rojas-Chamorro et al. (2020)

	acid; Enzymatic hydrolysis				
Cassava peel	Acid and enzymatic hydrolysis	250ml of dilute H_2SO_4, 7days	*S. cerevisiae* *Z. mobilis*	180g/L 175g/L	Baki et al. (2020)
Cassava pulp and peel	Acid hydrolysis		*Saccharomyces cerevisiae*	6.2%	Heriyanti et al. (2020)
Cassava peel and used newspaper	Acid hydrolysis	0.1 N HCl, Ratio volume of solution (mL) Cassava peel waste:used newspaper of 50:50	*S. cerevisiae* (product code: Fermipan): Amount of yeast:10g, 10 days)	9.472%	Mutiara et al. (2020)
BSG	Autohydrolysis	ethanol concentration: 42.27 g/L, glucose concentration: 0.23g/L	Hybrid saccharification and fermentation of *S. cerevisiae*	94.0%	Pinheiro et al. (2019)
Cassava and yam peels	Acid hydrolysis	150 mL of 4.5M H_2SO_4, 2:1 of cassava to yam peels	Two different strains of *S. cerevisiae* (5% baker's yeast & freshly isolated enzymes, respectively), 5 days	60.52% and 13.39% at room temperature, respectively	Olayemi et al. (2019)
Cassava peel	Acid hydrolysis	10% concentrated H_2SO_4, pH: 4.55, Sugar content: 15.5%	*Aspergillus niger* and *Saccharomyces cerevesiae* at 28°C for 4 days	37.35g/mL	Mustafa et al. (2019)
Cassava peel	Acid hydrolysis	Ultrasonic assisted using HCl	*S. cerevisiae*	20.77%	Sirajuddin et al. (2019)
Cassava peel (40g)	Acid hydrolysis	5% H_2SO_4	*S. cerevisiae*	16%	Isah et al. (2019)
Sugar bagasse (40g)				9.03%	
Hybrid cassava pulp and peel	Microbial (enzymatic) and acid hydrolysis		*S. cerevisiae* (yeast isolated from palm wine)	The highest ethanol yields were 54.8% and 33% respectively, from a heated pretreated variety & cassava peel	Efeovbokhan et al. (2019)

Bitter yam peel	Enzymatic hydrolysis		*Aspergillus tamari* and *S. cerevisiae* [substrate concentration: 20%, temperature: 35°C, agitation: 100rev/min, pH: 7.0]	13%	Banjo et al. (2019)
Water yam peel			*Aspergillus tamari* and *S. cerevisiae* [substrate concentration: 20%, temperature: 35°C, agitation: 100 rpm, pH: 5]	11%	
Cassava peel	Acid hydrolysis	250 mL of 0.5M dilute H_2SO_4, 100°C, 2h	*S. cerevisiae* (7 days)	118 mL	Femi et al. (2018)
Cassava peel	Acid hydrolysis	100 mL of 1% sulfuric acid diluted	*S. cerevisiae* (8 days, pH: 5, 150 rpm)	1.63%	Hermansyah et al. (2018)
Yam peel	Acid hydrolysis	1.5M HCl	*Sacharomyces cerevisiae* (Bakers' yeast)	18.40±0.18%	Ezejiofor et al. (2018)
Potato peel		2.0M HCl		18.23±0.04%	
Watermelon peel		1.5M HCl		8.35±0.14%	
Pineapple peel		2.0M HCl		11.44±0.29%	
BSG	Complete acid hydrolysis	12 M H_2SO_4 at 37 °C for 1 h, then diluted to 1 M for 2 h incubation at 100 °C and then subsequent quantification of liberated sugars by ion chromatography	*A. oryzae* and *S. cerevisiae NCYC479* for 10 days	37g/L	Wilkinson et al. (2017)
Cassava peel	Enzymatic hydrolysis	Highest reducing sugar (11.0267g/l)	*S. cerevisiae*	3.76%	Witantri et al. (2017)
Cassava peel from TME 4779			*R. nigricans + S. Africana +S. cerevisiae*	14.46g/cm^3	Chibuzor et al. (2016)
BSG	Acid and Enzymatic hydrolysis	100mL of acids-HCl and HNO_3, 1% w/w concentration	Two yeast strains: *Pichia stipites NCYC 1541* and *Kluyveromyces marxianus NCYC 2791* (30°C, 75 rpm, 72 h period)	0.0856 and 0.0308g EtOH/g of sugars for *P. stipites* and *K. marxianus*, respectively	Mata et al. (2015)

Cassava peel	Enzymatic hydrolysis		*S.cerevisiae* (7days)	8.5%	Olayide et al. (2015)
Cassava peel	Enzymatic hydrolysis		*Zymomonas mobillis* and *S. cerevisiae* (28°C, 5 days)	55.2g/cm^3 (23%)	Adiotomre (2015)
Yam peel	Acid hydrolysis	200 mL of 1M HCl		46.6g/cm^3 (19.3%)	
BSG	Enzymatic hydrolysis	incubator-VWR model 1575 set at 50°C and 150 rpm for 72 h	*S. cerevisiae ATCC 20252* (48h, 10% solid loading)	5.43 mL of EtOH per 100g of extruded BSG (dry weight basis)	Heredia-Olea et al. (2015)
BSG	Alkaline-acid pretreatment and enzymatic hydrolysis with commercial enzymes		*S. cerevisiae NRRL YB 2293* (24 h, 30°C, 120 rpm)	12.79g/L	Liguori et al. (2015)
Cassava peel	Acid hydrolysis	45mins, 100°C, acid conc: 0.402t%, cassava peel concentration: 2 g/L, optimum glucose yield of 78mg/ml	*S. cerevisiae* (pH: 5, yeast concentration: 10 wt%, 6 days)	45.5%	Egbosiuba et al. (2014)
Cassava peel	Acid hydrolysis	0.5M Sulphuric acid solution, 100°C for 60 min	*S.cerevisiae* (4days)	3.58%v/v	Abidin et al. (2014)

Key Physicochemical and Thermodynamic Properties Governing Bioethanol Performance

The suitability of bioethanol as an alternative fuel is fundamentally governed by a distinct suite of physicochemical and thermodynamic properties. These characteristics, which arise from its molecular structure and hydroxyl functional group, directly influence combustion efficiency,

engine performance, material compatibility, and fuel handling protocols. Adherence to standardized specifications, such as those outlined in ASTM D4806, is critical for ensuring fuel quality and interoperability with existing infrastructure. The core properties that define fuel-grade bioethanol are summarized in Table 9**.**

Table 9: Standardized physicochemical properties of denatured fuel ethanol (ASTM D4806).

Property	Specification / Typical Value	Significance for Fuel Application
Molecular Formula / Weight	C_2H_5OH / 46.07 $g \cdot mol^{-1}$	Determines combustion stoichiometry and vapor density.
Appearance	Clear, free of particulates	Indicator of purity and absence of contaminants.
Distillation Temperature Range	55–68 °C	Affects vaporization and cold-start behavior; a narrow range indicates purity.
Stoichiometric Air-Fuel Ratio	~9:1	Significantly lower than gasoline (~14.7:1), requiring engine calibration adjustments.
Elemental Composition (mass %)*	C: 52.2%, H: 13.0%, O: 34.7%	High oxygen content promotes more complete, cleaner combustion.
Water Content (max)	≤ 1.0% v/v	Critical to prevent phase separation in gasoline-ethanol blends.
Lower Calorific Value (LCV)	~26.7-27.0 $MJ \cdot kg^{-1}$	Approximately 35% lower than gasoline, impacting fuel economy.
Latent Heat of Vaporization	~840-920 $kJ \cdot kg^{-1}$	High value provides a significant charge-cooling effect, enhancing power density.

Property	Specification / Typical Value	Significance for Fuel Application
Research Octane Number (RON)	106-110	Superior anti-knock quality enables higher engine compression ratios.
Melting Point	-114 °C	Excellent low-temperature fluidity.
Surface Tension (20°C)	~22.8 $mN \cdot m^{-1}$	Influences atomization and spray formation in fuel injection systems.

Note: Based on pure ethanol; denaturants will cause minor variations. **Source: Adapted from ASTM D4806 - Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel.**

Implications for Engine Performance and Fuel System Design

The properties delineated in Table 9 underpin a combination of operational advantages and technical challenges. The high octane rating and substantial latent heat of vaporization of bioethanol synergistically enhance the thermodynamic efficiency of spark-ignition engines by permitting higher compression ratios and improving volumetric efficiency through charge cooling. Furthermore, its significant oxygen content (34.7% by mass) promotes more complete combustion, leading to substantial reductions in carbon monoxide (CO) and unburned hydrocarbon (HC) emissions.

Conversely, the low energy density necessitates a higher fuel flow rate to maintain equivalent power output, impacting vehicle range. The hygroscopic nature and high solubility of water can lead to phase separation in gasoline-ethanol blends, mandating strict control of water ingress throughout the supply chain. Additionally, its low stoichiometric air-fuel ratio and different combustion chemistry require specialized engine control unit (ECU) mapping. Certain material incompatibilities, particularly with some elastomers and metals, also necessitate careful selection of fuel system components to mitigate corrosion and degradation issues.

Variability Linked to Feedstock and Production Pathway

It is imperative to note that the precise physicochemical profile of bioethanol, including parameters such as congener composition (higher alcohols, esters), electrical conductivity, and precise distillation curve, can exhibit variability. This variability is intrinsically linked to the biomass feedstock (e.g., sugarcane, corn, lignocellulosic residues) and the specific hydrolysis and fermentation pathways employed. Feedstocks with high fermentable sugar or starch

content, low protein, and minimal inorganic impurities generally yield ethanol with higher purity and more consistent fuel properties. Consequently, the optimization of production processes is essential not only for maximizing yield but also for ensuring the final product meets the stringent specifications required for automotive fuel application.

Conclusion and Future Perspectives

This review has critically synthesized the scientific principles and technological pathways underpinning the valorization of prominent agricultural residues—brewer's spent grain (BSG), cassava peels, and yam peels—into bioethanol. The conversion of these heterogeneous biomasses is a complex, multi-stage bioprocess, and a central finding confirms that significant variability in bioethanol yield is highly dependent on the specific feedstock and stringent optimization of processing conditions. BSG, among the examined residues, demonstrates particularly favorable compositional characteristics for cost-effective biorefining. Crucially, the final bioethanol product, with rigorous downstream processing, can unequivocally meet stringent international standards such as ASTM D4806.

The scientific and engineering community is now tasked with advancing beyond foundational proofs-of-concept. The future trajectory of this field is defined by integrated technological innovations in three critical research frontiers, driving current trends: advanced bioprocess modelling, strain engineering and co-fermentation, and novel pretreatment technologies. By decisively harnessing these innovations, the conversion of low-value agro-industrial byproducts into high-value bioethanol can be fully realized, making a substantial and sustainable contribution to a circular bioeconomy and a decarbonized energy future [1-192].

Availability of data and materials: The datasets used during this current study are available from the corresponding author on reasonable request.

Competing interests: No

Funding: No

Authors' contributions: The author have read to the published version of the manuscript

Acknowledgements: Not applicable

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