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Introduction to Biomass Valorization and Green Chemistry

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1.1 Introduction

The global search for sustainable alternatives is expanding in response to growing concerns over environmental degradation, climate change, and the finite availability of fossil fuel resources. One of the most abundant and renewable resources on Earth is biomass, which is produced from organic wastes, forestry by-products, agricultural residues, and other associated biomass producers [1]. Biomass has the potential to lower greenhouse gas emissions and support a circular bioeconomy because it is a component of the short-term carbon cycle, unlike fossil fuels [2]. The global bioenergy sector, a key sector for biomass valorization, continues to grow, with global bioenergy production estimated to be 115.7 GW in 2020 [3]. Bioenergy currently contributes to 55% of global renewable energy and 6% of overall energy supply, with significant growth expected, particularly in emerging economies [4]. The broader biorefinery products market, which includes applications such as industrial, manufacturing, transportation, and health and hygiene, was valued at $586.8 billion in 2020 and is expected to grow to $867.7 billion by 2025, representing an 8.1% compound annual growth rate [5, 6]. The global biorefinery market is predicted to reach USD 1.1 trillion by 2027, with a compound annual growth rate of 9.8% from 2020 to 2027 [6]. These figures demonstrate the significant economic potential of biomass-based companies to contribute to global sustainability.

As a key component of sustainable development, the idea of biomass valorization for the conversion into valuable chemicals, fuels, and materials has drawn a lot of interest in the last 10 years. In addition to addressing waste management issues, biomass valorization creates new prospects for the production of bio-based products that can either replace or complement counterparts made from petroleum [7].

Subsequently, green chemistry has arisen as a framework that facilitates the environmentally responsible conversion of biomass into usable products. Green chemistry offers the basis for creating processes that reduce environmental impacts while retaining economic viability by focusing on concepts like waste prevention, energy efficiency, renewable feedstock utilization, and safer chemical design [8].

This chapter lies at the convergence of two fields, namely biomass valorization and green chemistry, to serve as a pathway to sustainable innovation. By integrating technological advances with ecological and economic considerations, biomass valorization within a green chemistry framework offers solutions to pressing global challenges, from energy security to the circular economy.

1.2 Biomass as a Renewable Feedstock

Biomass, which includes a wide variety of organic materials derived from plants, animals, and algae, is becoming an increasingly important renewable resource for energy generation and carbon-based feedstocks, owing to its abundance, renewability, and broad range of applications. As the only renewable carbon-based resource that can be harvested, stored, transported, and utilized by the current energy infrastructure, this organic matter, which is mostly derived from forestry wood, agricultural residues, and specialized energy crops, offers a sustainable substitute for fossil fuels [9]. By creating a carbon-neutral cycle in which CO_2 released during biomass conversion is reabsorbed by developing plants, its use provides a means of reducing climate change [10].

Growing concerns over rising global greenhouse gas emissions and the increasing demand for sustainable energy have further highlighted the importance of biomass as an alternative resource. Consequently, the shift toward biomass-based economies is accelerating, driven by challenges related to climate change, environmental pollution, and waste management. This transition not only reduces reliance on finite fossil fuel resources but also addresses the increasing accumulation of lignocellulosic wastes from agricultural and forestry activities. Beyond energy production, biomass also serves as a valuable renewable carbon source for the manufacture of biochemicals, biomaterials, and biofuels, thereby supporting the development of a circular and sustainable economy.

Driven not only by the global energy transition but also by advances in conversion technologies and integrated biorefinery systems, biomass utilization is becoming more efficient and economically viable. These developments enable more complete use of lignocellulosic components into various high-value and important products, while at the same time minimizing solid waste generation. However, large-scale implementation remains challenging due to biomass heterogeneity, logistics, pretreatment energy demand, and the need for more effective catalysts and microorganisms capable of processing inert biomass structures [11].

1.3 Relevance to Circular Economy Models

Agricultural residues, forestry by-products, and organic wastes, which were previously viewed as disposal difficulties, can be converted into valuable intermediates via biochemical, catalytic, or thermochemical routes, thereby promoting waste-to-resource and cascading-use approaches. Such valorization improves resource efficiency by recovering embedded energy and nutrients, decreasing landfill dependency, and lowering greenhouse gas emissions, all of which promote sustainable production and consumption patterns [12]. Recent developments in bio-based value chains show that circularity can be used throughout its entire life cycle, from raw material collection and pretreatment to manufacture, packaging, consumption, waste management, and reuse. The more substantial importance of biomass valorization to circular economy models is shown in its economic and technological ability to restructure industrial systems toward low-carbon output. Integrated biorefineries, which convert several biomass feedstocks into fuels, chemicals, and materials in a single facility, provide a solution for disengaging industrial performance from fossil fuels while increasing value-chain resilience. These technologies allow for the cascade use of biomass, prioritizing high-value biochemical extraction above energy recovery, thereby increasing resource efficiency and the overall circularity of the production cycle. However, maximizing the full potential of biomass-based circular value chains involves dealing with a number of challenges, including variable feedstock quality, high pretreatment costs, limited technological maturity for lignin valorization, and the need for sustainability standards [13].

In general, biomass fits into the circular economy through four simple steps, i.e., waste valorization by turning agricultural residues, forestry by-products, and organic municipal waste, often seen as problematic, into high-value resources; energy production which generates heat, electricity, and advanced biofuels (like sustainable aviation fuel) through processes like gasification, pyrolysis, and hydrothermal liquefaction (HTL), thereby reducing carbon footprints compared to fossil fuels; followed by material substitution that creates bio-based products such as bioplastics, resins, and fiber boards, thus reducing dependence on petrochemicals; and finally, nutrient recycling, which produces biochar (soil amendment) and animal feed from digestates, to promote the return of nutrients to the soil and complete the cycle.

1.4 Composition and Variability of Biomass Feedstocks

The suitability of the chemical composition from agricultural residues is crucial for different conversion pathways. These materials are primarily lignocellulosic, containing cellulose, hemicellulose, and lignin, with trace levels of extractives and inorganic chemicals [14]. Although a wide range of components can be obtained,

Table 1.1 Representative chemical composition ranges of common biomass feedstocks, including agricultural residues, forestry by-products, and organic waste streams.

Type of Feedstock	Examples	Typical Composition	Key Issues	Source
Agricultural residues	Rice straw, wheat straw, corn stover, fruit peels	Cellulose (40–50%), hemicellulose (25–35%), lignin (16–33%), ash (5–10%)	Seasonal availability, high silica (in straw), collection logistics	[11]
Forestry by-products	Sawdust, bark, lignin-rich residues	Holocellulose (58.53–69.56%), lignin (27.33–30.97%)	Heterogeneity in lignin, pretreatment challenges	[16]
Organic waste streams	Municipal solid waste, food waste, industrial effluents	Carbohydrates (41–62%), proteins (15–25%), lipids (13–30%)	Variability in composition, contamination, odor	[17]
Biomass composition variability	Cross-cutting across feedstocks	Cellulose (35–50%), hemicellulose (20–35%), lignin (15–20%)	Heterogeneity affects processing yields and efficiency	[15]

their exact proportions vary significantly depending on the type of biomass (such as softwood, hardwood, or agricultural residues), plant species, growth conditions (including age and geographical location), and even the harvesting time.

A significant challenge facing the biorefinery sector is biomass heterogeneity. This variability affects the physical and chemical characteristics of biomass and is caused by significant variations in plant tissue types and field conditions [15]. Table 1.1 illustrates the respective chemical composition of agricultural residues, forestry by-products and organic waste streams that highlight the compositional heterogeneity across various biomass categories.

1.5 Principles of Green Chemistry in Biomass Utilization

Green chemistry provides a guiding philosophy for designing the chemical and biotechnological processes that minimize environmental impact while maximizing resource efficiency. In the context of biomass valorization, this philosophy is not optional but essential. Unlike fossil-based feedstocks, biomass is structurally complex, chemically heterogeneous, and inherently rich in carbon [18]. Its utilization often involves multiple processing steps, including pretreatment processes, and biological or catalytic transformations, eventually amplifying inefficiencies if not guided by green chemistry principles. Consequently, aligning biomass utilization with green chemistry is vital to ensure that renewable feedstocks genuinely convert

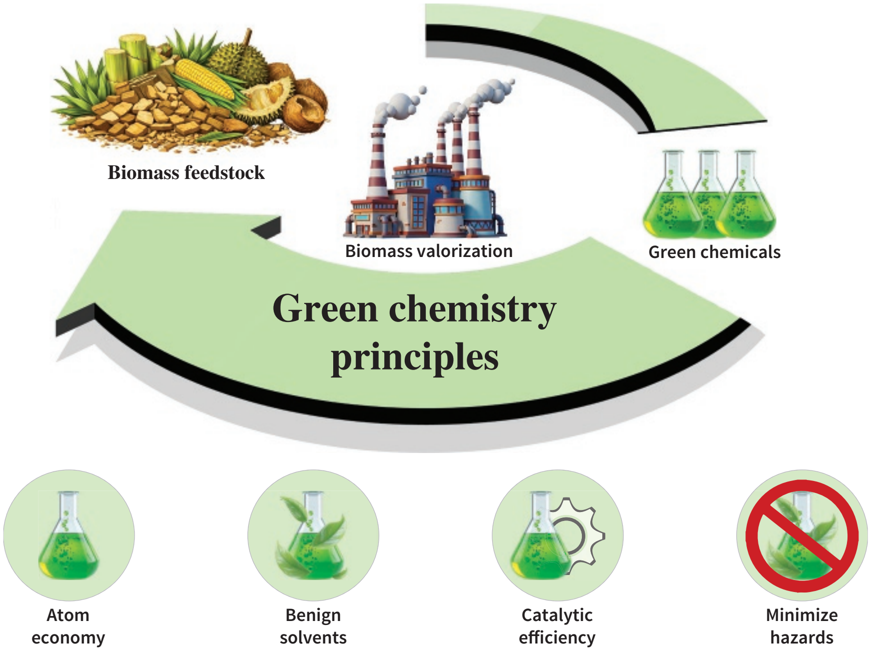

Figure 1.1 Principles of green chemistry in biomass utilization. *Source*: Drawn by authors zahirulislam1996/Adobe Stock Photos, Key/Adobe Stock Photos.

into sustainable products and processes rather than shifting environmental burdens elsewhere.

Within bioprocess-based valorization routes, four green chemistry principles emerge as especially decisive: atom economy (AE), use of benign solvents, catalytic efficiency, and minimalization of hazardous by-products as shown in Figure 1.1. Together, these principles govern three critical questions: how efficiently is biomass carbon retained in value-added products? How are environmental and safety impacts controlled through solvent selection? And how effectively do enzymes or microorganisms drive conversions under mild conditions?

Focusing on these interconnected principles provides a practical framework for evaluating and designing sustainable biomass utilization pathways that are both environmentally responsible and industrially scalable.

1.5.1 Atom Economy

AE is a core principle of green chemistry that evaluates how efficiently reactant atoms are incorporated into the desired product. The concept of AE was first developed by Trost [19]. The principle of AE emphasizes maximizing the incorporation of all atoms from the starting materials into the desired product, thereby reducing waste and improving overall process efficiency [20]. Unlike yield, which focuses on the amount of product obtained, AE provides insight into the intrinsic material efficiency of a conversion route. In the context of biomass utilization, particularly lignocellulosic biomass, AE must be interpreted beyond single chemical reactions and extended to process-level carbon and material flows. In its classical definition, AE is expressed as the ratio of the molecular weight of the desired product to the total molecular weight of all reactants involved. While this metric is straightforward for simple chemical syntheses, its application in biomass conversion is complex due to the heterogeneous and polymeric nature of lignocellulosic feedstocks.

Lignocellulosic biomass consists primarily of cellulose, hemicellulose, and lignin, each contributing differently to downstream products. Consequently, AE in biomass utilization should be viewed as the fraction of biomass carbon and functional groups that are retained in value-added products, rather than lost as waste, emissions, or low-value residues. From a bioprocess perspective, this shifts the focus from reaction stoichiometry to system-wide material efficiency, encompassing pretreatment, hydrolysis, fermentation, and product recovery. Achieving high AE in lignocellulosic biomass utilization is challenging. Significant atom losses occur during pretreatment, where harsh chemical or thermal conditions may degrade carbohydrates into non-fermentable by-products. These degradation pathways represent a direct loss of fermentable carbon and therefore reduce overall atom efficiency. During biological conversion, additional atom losses arise from microbial metabolism itself. A portion of substrate carbon is inevitably diverted toward cell biomass formation, maintenance energy requirements, and gaseous by-products such as carbon dioxide and hydrogen. While these losses are unavoidable in living systems, their magnitude varies depending on microbial strain, metabolic pathway, and operating conditions [21].

Several bioprocess-oriented strategies can be employed to improve AE in lignocellulosic biomass utilization. One key approach is the integrated biorefinery concept, where all major biomass fractions are valorized rather than discarding residual streams. Another important strategy is process integration, such as simultaneous saccharification and fermentation (SSF) or consolidated bioprocessing (CBP). By reducing intermediate handling steps, sugar degradation and carbon losses are minimized, thereby effectively improving atom retention [22]. From a green chemistry standpoint, fewer unit operations also imply reduced auxiliary material use and waste generation. Co-production strategies will further improve EA by allocating biomass-derived carbon among multiple value-added products. In these systems, primary fermentation products are accompanied by secondary outputs, such as biogas, microbial biomass, or platform chemicals recovered from side streams. This approach is consistent with the green chemistry principle of waste prevention, as materials previously considered waste are instead recognized as valuable resources.

1.5.2 Use of Benign Solvents

Solvent selection is a critical determinant of the environmental footprint, safety, and technical feasibility of biomass utilization processes. Within the framework of green chemistry, benign solvents are defined not only by low toxicity and environmental impact, but also by their compatibility with sustainable processing, recyclability, and ability to support efficient conversion pathways [23]. In lignocellulosic biomass utilization, solvent choice is particularly consequential due to the recalcitrant nature of the biomass and the need to integrate pretreatment, conversion, and downstream processing. Solvents play versatile roles throughout biomass valorization routes, including biomass fractionation, polymer solubilization, enhancement of enzymatic processes, and the extraction or purification of target products. Unlike petrochemical feedstocks, lignocellulosic biomass is insoluble, heterogeneous, and structurally complex. As a result, solvent systems are often required to disrupt hydrogen bonding networks in cellulose, solubilize hemicellulose, or partially depolymerize lignin [24]. From a green chemistry perspective, the challenge lies in balancing solvent effectiveness with environmental acceptability and process integration, particularly when biological catalysts such as enzymes or microorganisms are employed.

Water is widely regarded as the greenest solvent and remains the dominant medium in bioprocess-based biomass utilization. Its non-toxicity, abundance, low cost, and intrinsic compatibility with enzymes and microbial systems make it the solvent of choice for hydrolysis and fermentation steps. In enzymatic saccharification of lignocellulosic biomass, aqueous environments preserve enzyme activity and enable selective depolymerization of polysaccharides without extensive chemical modification. However, reliance on water-based systems also introduces inherent limitations. Lignin exhibits poor solubility in water, leading to incomplete fractionation and reduced accessibility of cellulose [25]. Additionally, aqueous processes often operate at low substrate concentrations, resulting in high volumetric solvent usage and increased downstream separation costs [26]. From a quantitative standpoint, excessive water consumption can offset the environmental benefits of using a benign solvent, particularly at an industrial scale. Despite these challenges, aqueous bioprocessing aligns strongly with green chemistry principles when process integration and water recycling strategies are implemented. The benign nature of water allows for one-pot or sequential biological conversions, reducing the need for solvent exchange and minimizing waste generation.

1.5.3 Catalytic Efficiency

Catalytic efficiency is a central principle of green chemistry, as catalysts enable chemical transformations to proceed with lower energy input, higher selectivity, and reduced waste generation. In biomass utilization, particularly for lignocellulosic feedstocks, catalytic efficiency extends beyond traditional chemical catalysis to encompass enzymatic and whole-cell biocatalytic systems. From a bioprocess and biotechnology perspective, catalytic efficiency directly influences AE, solvent requirements, and overall process sustainability. For example, zeolite-based catalysts have enabled selective conversion of cellulose into 5-hydroxymethylfurfural (HMF) with yields exceeding 60% under moderate conditions [27]. In green chemistry, an efficient catalyst is characterized by high activity, selectivity, and stability, often expressed through quantitative parameters such as turnover number (TON) and turnover frequency (TOF). While these metrics are well established in chemical catalysis, their application to biomass utilization requires adaptation due to the complexity of polymeric substrates and biological reaction environments. Unlike homogeneous or heterogeneous chemical catalysts, biological catalysts operate under mild conditions and exhibit high substrate specificity. These features are particularly advantageous for lignocellulosic biomass, where selective depolymerization of polysaccharides is essential to avoid excessive degradation and carbon loss. Consequently, enzymatic and microbial catalysis can be regarded as inherently green catalytic platforms, provided their efficiency is sufficiently high to offset longer reaction times and higher catalyst costs.

Enzymatic catalysis plays a pivotal role in the conversion of lignocellulosic biomass, particularly during the hydrolysis of cellulose and hemicellulose. Cellulases, hemicelluloses, and accessory enzymes function cooperatively to depolymerize complex carbohydrates into fermentable sugars. The catalytic efficiency of these enzymes is influenced by substrate accessibility, enzyme synergy, and reaction conditions. Biocatalytic processes, such as enzymatic hydrolysis, further enhance efficiency by operating under ambient conditions, lowering energy inputs compared to thermal treatments [28]. Recent developments in immobilized enzyme systems have reported catalytic turnovers three to five times higher than conventional free-enzyme systems, improving both stability and recyclability. A major limitation in enzymatic biomass conversion is the restricted access of enzymes to cellulose fibers, often caused by lignin shielding and crystallinity. This constraint reduces effective turnover and necessitates higher enzyme loadings, which can compromise economic and environmental performance. Strategies to improve enzymatic catalytic efficiency include enzyme cocktail optimization, enzyme immobilization, and pretreatment methods that enhance substrate accessibility without excessive carbohydrate loss. From a green chemistry standpoint, improved enzymatic efficiency contributes directly to higher AE by reducing sugar degradation and minimizing by-product formation. Additionally, enzymes function optimally in aqueous environments, reinforcing the alignment between catalytic efficiency and the use of benign solvents in bioprocess-based biomass utilization.

To address the limitations of single catalytic systems, hybrid approaches that integrate chemical and biological catalysis are increasingly used in biomass valorization. In these systems, chemical catalysts are typically applied for initial depolymerization or upgrading, followed by enzymatic or microbial conversion under mild conditions. Such hybrid systems enhance process efficiency by reducing reaction steps and minimizing solvent use. When designed carefully, these systems can enhance overall catalytic efficiency while maintaining compatibility with green chemistry principles. However, mismatches in operating conditions and solvent requirements remain a significant challenge, reinforcing the need for integrated design strategies that prioritize bioprocess compatibility. At industrial scale, catalytic efficiency determines not only reaction performance but also process economics and environmental impact. High-efficiency catalysts reduce catalyst loading, energy demand, and waste generation, contributing to lower operating costs and improved sustainability metrics. In bioprocess-based lignocellulosic biomass utilization, the longevity and reusability of enzymes, the robustness of microbial catalysts, and the feasibility of catalyst recovery are critical considerations [29]. Enhancing catalytic efficiency, therefore, supports scalable biomass valorization pathways that are consistent with green chemistry principles and industrial feasibility.

Catalytic efficiency in biomass utilization cannot be considered in isolation. It is intrinsically linked to AE and solvent selection, as efficient catalysts minimize unnecessary transformations, operate in benign media, and promote selective conversion of biomass into desired products. From a bioprocess and biotechnology perspective, catalytic efficiency represents the operational core of green chemistry in biomass valorization, enabling sustainable conversion of complex renewable feedstocks into valuable chemicals and materials.

1.6 Minimization of Hazardous By-products

The minimization of hazardous by-products is a core objective of green chemistry and a critical criterion for assessing the sustainability of biomass utilization processes. In biomass valorization, hazardous by-products may arise unintentionally during pretreatment, conversion, or downstream processing, undermining the environmental benefits of using renewable feedstocks. From a bioprocess and biotechnology perspective, controlling by-product formation is essential not only for environmental protection but also for maintaining catalyst performance, product quality, and process robustness. In lignocellulosic biomass processing, hazardous by-products are most commonly generated during pretreatment and high-severity conversion steps. Degradation of carbohydrates can lead to the formation of inhibitory compounds such as furans, organic acids, and phenolic derivatives from lignin. These compounds may exhibit toxicity toward enzymes and microorganisms, reducing catalytic efficiency and necessitating additional detoxification steps. Such interventions increase process complexity, solvent usage, and waste generation, thereby contradicting multiple green chemistry principles simultaneously.

Hazardous by-products in lignocellulosic biomass utilization typically originate from nonselective reactions driven by excessive temperature, acidity, or oxidative conditions. Although these reactions may enhance biomass deconstruction, they reduce EA and compromise downstream biological steps. In bioprocess-based systems, by-product formation is also influenced by microbial metabolism. Under suboptimal conditions, microorganisms may redirect carbon flux toward unwanted side products, such as organic acids or alcohols, which can inhibit growth or interfere with product recovery. Therefore, hazardous by-products should be considered not only as chemical degradation products but also as process-induced metabolic outcomes that reflect insufficient control over reaction environments.

Minimization of hazardous by-products in biomass utilization is best achieved through preventive design strategies rather than post-formation remediation. One effective approach is the use of milder pretreatment conditions that balance biomass deconstruction with preservation of carbohydrate integrity [30]. When combined with efficient enzymatic or microbial catalysis, such strategies reduce the need for aggressive chemical inputs and limit the formation of inhibitory compounds.

Catalytic selectivity plays a central role in by-product control. Highly selective enzymes and engineered microbial pathways promote targeted conversions while suppressing side reactions. Improvements in catalytic efficiency directly contribute to by-product minimization by enabling lower reaction severity and shorter residence times. This interdependence highlights how green chemistry principles operate synergistically rather than independently.

Process integration further supports by-product minimization by reducing intermediate handling and exposure to harsh conditions. Integrated systems such as SSF limit sugar accumulation, thereby decreasing the likelihood of degradation into toxic by-products [31]. In addition, aqueous bioprocessing environments inherently restrict the formation of highly hazardous compounds due to their mild operating conditions and compatibility with biological catalysts. The minimization of hazardous by-products strengthens the overall sustainability of lignocellulosic biomass utilization by enhancing process safety, reducing environmental impact, and improving compatibility with biological systems. Rather than treating hazardous by-products as unavoidable consequences of biomass conversion, green chemistry encourages their prevention through informed catalyst selection, solvent choice, and process integration. When embedded within bioprocess-based designs, this principle ensures that biomass valorization pathways remain aligned with the fundamental goal of green chemistry: transforming renewable resources into valuable products with minimal harm to human health and the environment.

1.7 General Conversion Routes for Biomass Valorization

Biomass valorization generally involves converting renewable biological resources into fuels, chemicals, and materials through several well-established pathways. These conversion routes are commonly classified into biochemical, thermochemical, catalytic, and/or physicochemical processes that enable flexible and efficient utilization of biomass as a sustainable alternative to fossil-based resources. Figure 1.2 summarizes these routes with the desired end product, aiming for sustainability and reduced environmental impact.

1.7.1 Biochemical Processes

Biochemical conversion (Table 1.2) employs microbial and enzymatic routes to transform biomass into fuels and bioproducts. Enzymatic hydrolysis of pretreated lignocellulose produces fermentable sugars with yields often exceeding 80% under optimized conditions [32]. Microbial fermentation, particularly using engineered *Saccharomyces cerevisiae* and *Clostridium* strains, has enabled high titers of ethanol (>100 g/L), butanol, and organic acids. Metabolic engineering has further expanded product portfolios to biopolymers, succinic acid, and bio-based aromatics [33]. The advantages of biochemical processing lie in its high product specificity. Recent techno-economic studies indicate enzyme costs contribute up to 30–40% of total

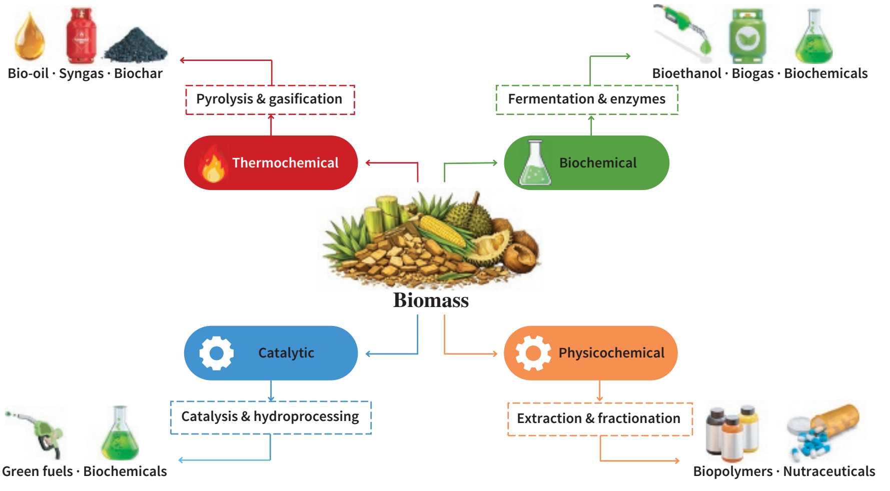

Figure 1.2 Biomass valorization routes. *Source*: Drawn by authors.

Table 1.2 Typical products through biochemical routes.

Biochemical Route	Typical Products	Source
Enzymatic hydrolysis	Glucose, xylose	[32]
Microbial fermentation	Ethanol, butanol, organic acids	[33]
Metabolic engineering	Biopolymers, aromatics	[33]

operating expenses. Integration with CBP, where enzyme production and fermentation occur simultaneously, offers promising cost reductions.

1.7.2 Thermochemical Routes

Thermochemical conversion (Table 1.3) encompasses pyrolysis, gasification, HTL, and direct combustion. Fast pyrolysis can yield up to 70 wt.% bio-oil, though upgrading is essential due to instability and high oxygen content [34]. Gasification generates syngas ($CO + H_2$), enabling downstream synthesis of Fischer–Tropsch fuels and methanol, with efficiencies approaching 60–70%. HTL, operating in subcritical water, achieves biocrude yields of 35–55% from algae and lignocellulosic feedstocks under mild conditions [35]. Combustion remains the most established route, supplying bioheat and electricity at Technology Readiness Levels (TRLs) > 9.

While thermochemical routes exhibit broad feedstock flexibility and high throughput, challenges include feedstock drying, tar formation in gasification, and catalyst requirements for upgrading. Capital intensity is substantial, particularly for pressurized gasifiers and HTL reactors. Nevertheless, hybrid approaches such as integrating pyrolysis with fermentation or coupling HTL with catalytic hydrotreating are gaining traction for maximizing carbon recovery.

Table 1.3 Typical products through thermochemical routes.

Thermochemical Route	Typical Products	Source
Pyrolysis	Bio-oil, biochar, syngas	[34]
Gasification	Syngas, methanol, FT fuels	[34]
Hydrothermal liquefaction	Biocrude, gases, nutrients	[35]
Combustion	Heat, electricity	[35]

Table 1.4 Typical products through catalytic routes.

Catalytic Route	Typical Products	Source
Heterogeneous (zeolites, oxides, metals)	HMF, aromatics, alkanes	[36]
Homogeneous (acid/base)	Levulinic acid, esters	[36]
Photocatalysis	Aromatics, H_2, organics	[37]

1.7.3 Catalytic Pathways

Catalytic conversion (Table 1.4) represents a cornerstone in biomass valorization, enabling selective transformation of lignocellulosic substrates into fuels and value-added chemicals. Heterogeneous catalysts, particularly zeolites, metal oxides, and supported noble metals, dominate due to their stability, ease of separation, and recyclability. Homogeneous systems, though offering higher activity and selectivity in certain hydrolysis and esterification reactions, face limitations in catalyst recovery and corrosivity [36]. Photocatalysis is a light-driven process in which a photocatalyst (typically a semiconductor material) absorbs photons with energy equal to or greater than its bandgap, generating electron–hole pairs. These energized charge carriers migrate to the catalyst surface and initiate redox reactions with surrounding molecules, forming reactive species that can drive chemical transformations such as breaking down pollutants or converting biomass-derived intermediates without being consumed in the reaction itself. Semiconductors like TiO_2 and g-C_3N_4 are commonly used because they can harness visible or UV light to activate these reactions under mild conditions, offering a potentially energy-efficient route for sustainable chemical processes [37].

Performance improvements are notable: metal-doped zeolites have achieved > 80% selectivity to HMF from fructose, while photocatalytic lignin depolymerization reports quantum yields up to 10% under solar irradiation. However, deactivation via coking, high catalyst synthesis cost, and solvent dependence remain key challenges. Current TRLs are 5–7, with demonstration-scale projects mostly focused on upgrading bio-oils and bioethanol derivatives.

Table 1.5 Typical products through physicochemical routes.

Physicochemical Route	Typical Products	Source
Solvent extraction	Oils, polyphenols, bioactive compounds	[38, 39]
Fractionation/separation	Cellulose, hemicellulose, lignin	[38, 39]
Dissolution–precipitation	Biopolymers, functional materials	[38, 39]
Mechanical/thermal-assisted extraction	Nutraceuticals, antioxidants	[38, 39]
pH/chemical precipitation	Purified hemicellulose, protein isolates	[38, 39]

1.7.4 Physicochemicals

Physicochemical conversion routes (Table 1.5) involve the use of physical and chemical techniques to fractionate, extract, and modify biomass components without extensive molecular decomposition. Typical processes include solvent-based fractionation, extraction, dissolution–precipitation, and other pretreatment methods aimed at separating cellulose, hemicellulose, and lignin, as well as recovering high-value bioactive compounds. These routes are particularly important in biorefinery systems as they operate under relatively mild conditions, preserve the structural integrity of biomass constituents, and enhance the efficiency of subsequent biochemical or catalytic conversions. Recent advances in physicochemical pretreatment technologies and the use of deep eutectic solvents have further improved the sustainability and selectivity of biomass valorization processes [38, 39].

1.8 Biomass-derived Products

Biomass-derived products encompass a diverse array of chemicals, fuels, materials, and functional compounds generated from renewable organic feedstocks. By valorizing lignocellulosic and other biomass types, these products offer sustainable alternatives to fossil-based commodities while supporting circular bioeconomic principles. Table 1.6 summarizes several biomass-derived products and key challenges of their processes.

1.8.1 Fine Chemicals

Fine chemicals derived from biomass represent an important class of renewable products with applications across chemicals manufacturing, materials, and intermediates for further transformations. Among these, biomass-derived organic acids, alcohols, and furan-based platform compounds have attracted significant research attention due to their versatility and potential to replace fossil-based feedstocks. Recent analyses demonstrate the potential to replace petrochemical feedstocks with biomass-derived alternatives, reducing life-cycle greenhouse gas emissions by more

Table 1.6 Biomass-derived products with typical applications and key challenges.

Product Type	Example Feedstocks	Typical Applications	Key Challenges	Source
Fine chemicals	Lignocellulose, food/agro-waste, glycerol	Organic acids (succinic, lactic), alcohols, HMF, levulinic acid	Selectivity in catalytic pathways, high separation/purification costs, feedstock heterogeneity	[40]
Biofuels	Starch crops, oilseeds, lignocellulosics, algae	Bioethanol, biodiesel, biogas, biohydrogen	Land-use conflicts (1G),[a] pretreatment cost (2G),[b] scalability of algae (3G),[c] economic competitiveness	[41]
Functional materials	Agricultural residues, forestry waste, food waste	Bioplastics, cellulose acetate, carbon composites, adsorbents	Cost-effective processing, mechanical/thermal performance, end-of-life management (microplastics risk)	[42]
Emerging applications	Microalgae, food waste, crop residues	Nutraceuticals, pharmaceuticals, PHAs, green solvents	Regulatory uncertainty, scalability of novel processes, ensuring biocompatibility and safety	[43]

a. 1G: first-generation biofuels,
b. 2G: second-generation biofuels, and
c. 3G: third-generation biofuels

than 40% in optimized pathways. Despite their promise, challenges remain in process selectivity, purification costs, and feedstock heterogeneity, which have limited commercialization. Nonetheless, integrated catalytic and biochemical strategies continue to drive the field toward scalable and cost-effective fine chemical production from waste biomass streams [40].

HMF and levulinic acid (LA) are two of the most studied platform chemicals obtained via catalytic dehydration and rehydration of sugars released from lignocellulosic biomass. HMF, formed by acid-catalyzed dehydration of hexose sugars such as glucose and fructose, serves as a precursor to a broad range of value-added derivatives including 2,5-diformylfuran, 2,5-furandicarboxylic acid (FDCA), and 2,5-bis(hydroxymethyl)furan, which are used in polymer precursors, solvents, and specialty chemicals. Recent advances with heterogeneous catalysts have enabled direct synthesis of HMF from raw biomass under relatively mild conditions, with heterogeneous systems facilitating easier catalyst separation and reuse compared to homogeneous catalysts. Quantitatively, yields of HMF from carbohydrate feedstocks vary widely with feedstock and catalyst system. For instance, catalytic conversion studies report HMF yields in an H_2O–NaCl/THF biphasic system; 92.1% glucose conversion and 84.1% HMF yield were achieved under optimized conditions [44], demonstrating the effects of feedstock complexity on product distribution. LA, another key platform chemical, is typically produced via rehydration of HMF or direct acid hydrolysis of hexoses and is recognized as a strategic biomass-derived building block for fuels, solvents, and chemical intermediates. Recent catalytic systems, including dual-functional acid catalysts in biphasic systems, have achieved LA selectivities of ~95.6% from HMF conversion under mild conditions with nearly complete HMF conversion (100%) [45].

Beyond HMF and LA, other biomass-derived fine chemicals include organic acids such as formic acid, acetic acid, and furan derivatives like furfural, which originate from pentose and hexose dehydration pathways. 2,5-Diformylfuran and related oxidation products of HMF have been selectively produced using tailored catalysts and represent important intermediates for polymers and specialty chemicals. These biomass-derived fine chemicals illustrate the productive intersection of catalysis, renewable biomass feedstocks, and green chemistry principles, and form a foundation for sustainable chemical manufacturing.

1.8.2 Biofuels

Biofuels are a class of renewable energy carriers derived from biomass that can directly replace or blend with fossil fuels in transportation and power applications. They are commonly categorized by generational feedstock types, which influence sustainability, production pathways, and performance metrics. The evolution of biofuel production demonstrates a clear progression from first-generation systems reliant on food crops to advanced biological and thermochemical processes that valorize nonfood biomass. Second-generation lignocellulosic biofuels are moving rapidly toward commercial viability as pretreatment and fermentation technologies improve. Third-generation algal biofuels offer attractive performance metrics, though scaling remains a key barrier. Across all biofuel generations, integrating green chemistry principles such as minimized hazardous by-products, solvent benignity, and catalytic efficiency into bioprocess design is crucial for reducing environmental impact and enhancing economic feasibility. Table 1.7 illustrates biofuels production from various feedstocks.

Table 1.7 Biofuels production from various feedstocks.

Feedstock	Biofuel	Process	Production Yield	Source
Lignocellulosic biomass	Bioethanol	Pretreatment + fermentation	223–358 L ethanol/tons biomass	[46]
Waste oil	Biodiesel	Heterogeneous transesterification	> 90% biodiesel yield	[47]
Biomass hydrolysate	Biohydrogen	Anaerobic fermentation	~2.0 mol H_2/mol sugar	[48]
Microalgae	Biofuel	Cultivation + extraction	2–50% lipid content	[47]

The evolution of biofuel production demonstrates a clear progression from first-generation systems reliant on food crops to advanced biological and thermochemical processes that valorize nonfood biomass. Second-generation lignocellulosic biofuels are moving rapidly toward commercial viability as pretreatment and fermentation technologies improve. Third-generation algal biofuels offer attractive performance metrics, though scaling remains a key barrier. Across all biofuel generations, integrating green chemistry principles, such as minimized hazardous by-products, solvent benignity, and catalytic efficiency, into bioprocess design is crucial for reducing environmental impact and enhancing economic feasibility.

1.8.3 Functional Materials

Biomass-derived materials have emerged as sustainable alternatives for polymers and functional materials, driven by advances in bioconversion and material engineering. In bioplastics development, lignocellulosic hydrolysates are increasingly utilized for the microbial production of polyhydroxyalkanoates (PHAs), which exhibit mechanical properties comparable to conventional plastics alongside excellent biodegradability. Nonfood biomass sources, such as sugarcane bagasse, have demonstrated high PHA accumulation under optimized fermentation conditions. In parallel, cellulose nanofibrils extracted from biomass are incorporated into bioplastic matrices to enhance tensile strength and barrier properties, supporting their application in biodegradable packaging.

Beyond polymers, biomass is widely valorized into carbon materials, composites, and adsorbents for energy, structural, and environmental applications. Activated carbons and biochars derived from agricultural residues show high surface areas and strong adsorption capacities for heavy metals and greenhouse gases, while porous carbon materials exhibit promising performance in energy storage devices such as supercapacitors. Biomass-based composites reinforced with cellulose or lignocellulosic fibers provide lightweight materials with competitive mechanical properties, and emerging mycelium-based composites further expand sustainable construction options. Additionally, biomass-derived adsorbents demonstrate high removal efficiencies for pollutants in water and air, highlighting the versatility of biomass as a platform for circular and environmentally responsive material systems. Figure 1.3 summarizes the functional materials derived from biomass and their applications.

1.8.4 Emerging Applications

Biomass-derived products are increasingly transitioning from traditional chemical and material uses toward novel high-value applications in nutraceuticals, pharmaceuticals, and green solvent technologies. These emerging sectors leverage bioactive compounds, sustainable processing methods, and renewable feedstocks to address

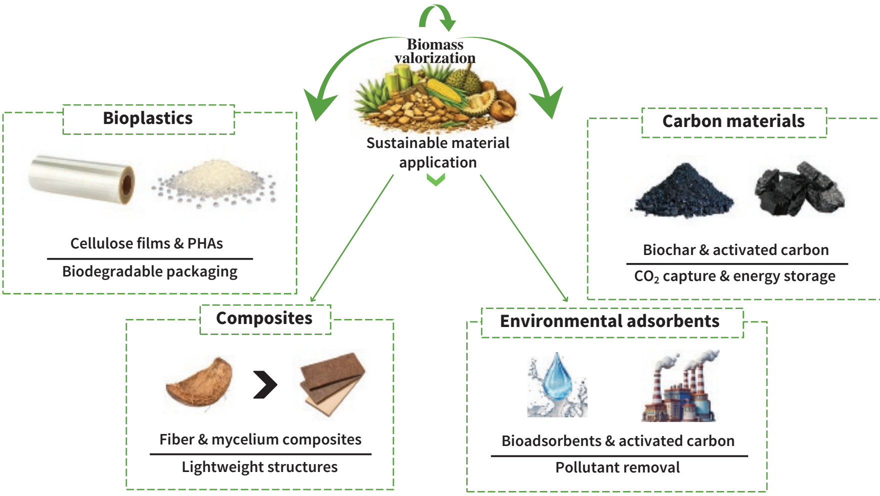

Figure 1.3 Summary of the functional materials derived from biomass and their applications. *Source*: Drawn by authors.

market and regulatory pressures for environmental sustainability while maintaining performance and safety.

In nutraceutical applications, bioactive compounds derived from food or plant biomass with health-promoting properties represent one of the fastest-growing fields in biomass valorization. Plant residues and agricultural by-products such as grape seeds, pomegranate peel, and citrus peels are rich in polyphenols, flavonoids, carotenoids, and other phytochemicals that exhibit antioxidant, anti-inflammatory, and cardioprotective effects. Standardized grape seed extracts enriched in low-polymer procyanidins have been developed commercially and are supported by clinical evidence for cardiovascular benefits, illustrating successful translation of winery by-products into high-value nutraceutical products [48]. This trend is part of a broader shift toward valorizing agrifood residues for health-oriented ingredients in supplements, functional foods, and fortified products. Green extraction technologies such as enzyme-assisted extraction, supercritical fluid extraction (SFE), and microwave-assisted techniques have significantly improved yields and bioactivity retention of these compounds. For example, enzyme-assisted SFE of pomegranate peel increased extraction yields and concentrations of phenolic antioxidants compared with conventional methods, while also reducing environmental impact by minimizing solvent use and energy consumption. These innovations underline how principles of green chemistry can enhance both the efficiency and quality of nutraceutical production from biomass.

Biomass-derived chemicals and materials are finding increasing relevance in pharmaceutical and biomedical applications. Lignocellulosic biomass fractions, especially lignin, are being investigated as platforms for drug carriers, anti-inflammatory agents, and controlled release matrices. Reviews show growing interest in lignin derivatives and lignin-based materials for pharmaceutical applications, linking source biomass, processing routes, and potential clinical indications such as antioxidant and antimicrobial functionalities [49]. In addition to chemical derivatives, fiber-based materials obtained from biomass, such as cellulose nanofibrils and chitin scaffolds, have been investigated for biomedical applications, including wound dressings, tissue engineering, and drug delivery systems. These fibrous biomaterials offer a combination of biodegradability, biocompatibility, and adjustable mechanical properties, making them suitable for applications such as injectable hydrogels for wound care and composite scaffolds that support bone mineralization in tissue engineering. The emergence of these novel applications underscores a broader shift in biomass valorization from commodity chemicals and fuels toward high-value, sustainability-aligned sectors. Nutraceuticals enable added economic value from low-cost biomass residues; pharmaceutical and biomedical applications exploit unique biomaterial properties; and green solvents address critical environmental and regulatory challenges in chemical processing. Together, these trends exemplify how biomass-derived products are integrating into the circular bioeconomy, supporting both environmental goals and market innovation across diverse industries.

1.9 Conclusions

Biomass valorization is a viable and promising approach for sustainable energy generation, with significant potential for contributing to renewable energy goals, scientific innovation, policy evolution, and industrial transformation. While challenges such as feedstock heterogeneity, process scalability, and regulatory uncertainty remain, the convergence of advanced catalysis, biotechnology, digitalization, and circular chemistry offers unprecedented opportunities to overcome these barriers. As the chemical industry faces increasing pressure to decarbonize, biomass emerges not merely as an alternative feedstock but as a strategic enabler of sustainable growth. Recent advancements in biomass valorization techniques have led to the development of more efficient and sustainable processes. By bridging technical, economic, and societal dimensions, biomass valorization has the potential to redefine resource utilization and anchor the chemical sector in a net-zero future. To advance the field of biomass waste valorization, further research is needed to address the technical, economic, and environmental challenges, which include developing more efficient and cost-effective methods for producing value-added products, improving process scalability, and evaluating the environmental impacts of different valorization pathways. Through a balanced and nuanced understanding of biomass waste valorization techniques, this chapter contributes to the development of sustainable and effective waste management strategies that can support a circular economy and reduce our reliance on fossil fuels.

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