

Review

Catalytic Transformation of Biomass: From Waste to Fuels, Chemicals, and High-Value Products

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Abstract

The necessity of biomass valorization arises from global energy and environmental and economic challenges. Catalytic transformation of biomass into fuels, chemicals, and other valuable products has emerged as a promising approach toward a sustainable and circular economy. The primary objective of this review is to provide a timely and comprehensive overview of the entire value chain for the high-value utilization of biomass, covering the entire process from biomass feedstock and its preliminary conversion to catalytic upgrading, and finally to the production of fuels, chemicals, and other high-value-added products. Recent advances in catalytic technologies reveal that there is a strong potential to convert diverse biomass wastes into a wide range of valuable fuels, chemicals, and other products, ranging from heterogeneous solid catalysts with advantages in recovery and reusability to single-atom catalysts with enhanced selectivity and activity, as well as electrocatalytic and photo-electrocatalytic systems that enable energy efficiency under mild conditions using renewable power. Although significant progress has been made in converting complex biomass into versatile platform molecules and end-products, the inherent complexity and variability of real-world biomass, together with the economic challenges of competing with established fossil systems, still currently limit large-scale applications.

Keywords: biomass conversion; catalytic upgrading; catalysts

1. Introduction

1.1. Global Energy and the Chemical Landscape: Shifting from Fossil Resources

The current global energy and chemical landscape faces two key realities: the decline of non-renewable fossil fuel reserves and the environmental impacts, particularly greenhouse gas emissions, associated with their combustion. In 2019, fossil fuels still accounted for approximately 81% of the global primary energy supply [1], while the Intergovernmental Panel on Climate Change (IPCC) emphasized the urgent need to limit global warming to 1.5–2 °C above pre-industrial levels [2]. This dual challenge of limited resources and the need to protect the environment underscores the urgent need for a shift towards sustainable, renewable carbon sources. Nowadays, biomass ranks as the fourth-largest energy source globally, trailing only oil, coal, and natural gas [3,4]. Biomass, as an abundant, renewable, and carbon-neutral resource, provides a promising alternative for producing fuels and chemicals, reducing reliance on fossil fuels, and offering the potential to achieve



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zero net CO₂ emissions through recycling. This shift is not only driven by economic considerations but also represents a change toward a more environmentally friendly energy and chemical industry.

Biomass is broadly defined as organic materials derived from plants, animals, and microorganisms, serving as a renewable carbon source in the global bioeconomy. According to the International Energy Agency (IEA), biomass includes agricultural residues, forestry byproducts, dedicated energy crops, and organic municipal wastes, which are primarily composed of lignocellulosic components of cellulose, hemicellulose, and lignin [5]. As summarized in Table 1, biomass classification has evolved from source- and moisture-based systems to broader frameworks incorporating resource availability, land use, ecological origin, and intended application [6–10]. The most widely adopted system divides it into five major groups, including woody biomass, herbaceous biomass, aquatic biomass, human waste biomass, and biomass mixtures.

Table 1. Classifications of biomass in studies.

Ref.	Classification Baseline	Categories	Notes
McKendry (2002) [7]	Source of origin, moisture content	Woody, herbaceous, aquatic, manures	Low moisture: thermochemical; moisture: biochemical/aqueous
Balat (2005) [8], Chiang et al. (2012) [9]	Source of origin	Forestry, agriculture, municipality, industry	Further classified by heating value and chemical composition [9]
Hoogwijk et al. (2003) [10]	Resource availability and land use	Energy crops, agricultural/forest residues, animal manure, organic wastes, biomaterials	Land-based and waste-based resources
Tursi (2019) [6]	Source of origin, ecological type and feedstock application	Woody, herbaceous, aquatic, human/animal waste, mixtures	Dual classification of origin and intended use

1.2. Fuels, Chemicals, and High-Value Products from Biomass

“Biorefinery” has been widely advocated for treating lignocellulosic biomass (LCB) as a whole resource and for obtaining valuable chemicals through graded treatment and catalytic conversion [11,12]. Biomass is widely recognized as a renewable feedstock for sustainable fuel production, offering alternatives to fossil-derived gasoline, diesel, and natural gas [13]. Conventional optional biofuels include first-generation bioethanol, biogas, and biodiesel. Bioethanol and biogas production relies on biochemical conversion. Bioethanol is produced by enzymatic hydrolysis of starch and lignocellulosic biomass to sugars, followed by fermentation, while anaerobic digestion of organic wastes represents a biochemical route for biogas production [11,14]. Biodiesel is typically obtained from the transesterification of triglycerides in plant oils or animal fats. These fuels not only contribute to decarbonization but also reduce reliance on petroleum-based energy sources. In contrast, second-generation bioethanol requires pretreatment and enzymatic hydrolysis of lignocellulosic biomass before fermentation.

Advanced biomass-derived transportation fuels are liquid hydrocarbon fuels with low oxygen content and high energy density, compatible with existing fuel systems. These fuels typically require catalytic upgrading from syngas, bio-oil, or oxygenated intermediates [15,16]. Thermochemical methods are a main route for producing hydrocarbon fuels from lignocellulosic biomass, including gasification to syngas followed by Fischer–Tropsch (FT) synthesis to jet fuel production, and pyrolysis or liquefaction to bio-oils that require catalytic upgrading, typically followed by oxygen removal to enhance fuel stability [17,18]. Gasification is a flexible route for producing syngas and downstream

hydrocarbon fuels, which requires syngas purification and precise control of the H_2/CO ratio [19]. Pyrolysis and liquefaction can yield liquid intermediates with high efficiency but typically contain water, acidic substances, and reactive oxygenated compounds, rendering them corrosive and unstable with a low heating value [20]. Non-sugar monomers such as lignin-derived phenolics and furfural also represent valuable precursors for fuels, which can be converted into liquid hydrocarbon fuels such as gasoline-, diesel-, or jet-range hydrocarbons mainly by hydrodeoxygenation [21] and hydrogenation [22], respectively. Recent IEA, National Renewable Energy Laboratory (NREL; now National Laboratory of the Rockies, NLR), and Pacific Northwest National Laboratory (PNNL) assessments agree that near-term growth of biofuels will be dominated by lipid-based sustainable aviation fuels (SAFs) and biomethane. In the aviation industry, HEFA-SAF (hydro-processed esters and fatty acids—sustainable aviation fuel) is the primary fuel supply, with additional ASTM International (formerly known as the American Society for Testing and Materials) approvals expanding alcohol-to-jet and other routes [23]. Lignocellulosic liquids, which are synthesized by pyrolysis, hydrothermal liquefaction (HTL), or FT, are the key mid-term focus for scale and carbon abatement once feedstock logistics, catalysts, and refinery integrations are optimized [23–26].

Beyond its use as fuel, biomass provides a foundation for the synthesis of platform chemicals that serve as intermediates for diverse industries. One major focus is the exploration of bio-advanced chemicals derived from carbohydrate fractions of biomass. Furfural and 5-hydroxymethylfurfural (HMF) are two important platform chemicals that can be produced from C_5 and C_6 sugars [27]. The furan-based intermediates can be further selectively upgraded to valuable chemicals, including 2,5-furandicarboxylic acid (FDCA), levulinic acid, and various polyols, via oxidation, rehydration, hydrogenation, or hydrogenolysis [28,29]. A rising strategy is electrocatalytic refinements using water as a hydrogen source, enabling HMF to be electro-reduced to 2,5-dihydroxymethylfuran (DHMF) and electro-oxidized to 2,5-diformylfuran (DFF), FDCA, maleic acid (MA), etc., without external hydrogen [30,31]. Key bio-based platform organic acids (e.g., lactic acid, succinic acid) are mainly produced from sugars via fermentation [32]. Lipid-based biomass is another important feedstock for bio-based chemical production. Typical biomasses include plant oil, animal fats, and microalgae, which have high contents of long-chain fatty acids and glycerol; with their carbon backbones, they could be converted into fatty acids or their derivatives through hydrolysis or transesterification from triglycerides [33].

Lignin depolymerization, followed by upgrading yields in phenolic and aromatic oxygenates by oxidation or reduction, such as phenol monomers, vanillin, and syringaldehyde, has applications in polymers, resins, and fine chemicals [34,35]. Lignocellulosic biomass (LCB) has a variety of chemical structural units (sugar, aromatic structures, etc.), which can be catalytically converted to platform monomers for producing high-performance polymers, such as polyesters, polyamides, polycarbonates, and polyurethanes, as well as resin and foam products, including phenol-formaldehyde resins, epoxy resins, and polyurethane foams [36,37]. Besides direct utilization, lignin-derived polymers utilize lignin's aromatic phenolic structures to produce engineering materials through chemical depolymerization followed by repolymerization, such as aromatic intermediates (e.g., phenols, guaiacols, and catechols) that can be incorporated into bio-polyesters, polyamides, and polycarbonates [37]. However, the C-C linkages and condensation tendency of lignin limit the selectivity and efficiency of selective lignin-derived aromatic production. However, the large-scale development of biomass-derived chemicals and processes is still limited by selectivity and feedstock variability. Current research is focusing on developing catalytic routes and stabilizing platform molecules, such as pretreatment strategies of reduction catalytic fractionation (RCF) and solvent systems based on deep eutectic solvents (DESs)

and ionic liquids (ILs) [38–41]. In addition, lignin, cellulose, and hemicellulose can be converted to nanocellulose (cellulose nanofibers (CNFs)/cellulose nanocrystals (CNCs)) or esters and ethers for high-performance films, hydrogels, superabsorbents, and poly-electrolytes [42–44]. Most of these polymers are renewable and biodegradable, supporting a move towards a sustainable economy.

1.3. Processes and Technologies for Biomass Valorization and the Role of Catalysis in Sustainable Biomass Transformation

Conventional biomass conversion methods mainly include two categories: thermochemical methods, including pyrolysis, gasification, combustion, torrefaction, and hydrothermal liquefaction (HTL) [45,46]; and biochemical methods, such as enzymatic hydrolysis followed by fermentation and direct anaerobic digestion [47]. These transformations can be achieved under milder reaction conditions with the use of catalysts, leading to reduced energy consumption and improved safety.

Catalytic conversion, widely recognized as one of the principal approaches, can facilitate the breakdown of complex biomass structures into simpler, more valuable compounds. During the initial decomposition of biomass, polysaccharide chains can be hydrolyzed into soluble sugars and other intermediates using homogeneous catalysts, such as mineral acids, metal salts, or heterogeneous catalysts, including sulfonated carbons, heteropoly acids, acidic ion-exchange resins, zeolites, and acidic metal oxides [48]. The resulting sugars and other biomass-derived intermediates can subsequently undergo chemo-catalytic upgrading through hydrogenation, hydrodeoxygenation (HDO), decarbonylation (DCO), decarboxylation (DCO₂), selective oxidation, and reforming [49–52].

Metal sites, including Ni, Ru, Pt, Pd, Cu, and Co, typically facilitate hydrogen activation, hydrogenation, and dehydrogenation, whereas acid–base or redox-active sites promote C–O and C–C bond transformations. Thus, bifunctional catalysts are widely employed in HDO and reforming. In addition to traditional catalysts, new catalysts were also explored. Single-atom catalysts (SACs) are promising because they can enable highly selective hydrogenation, oxidation, deoxygenation, and reforming through atomic active sites [53]. Metal carbides, phosphides, and nitrides, which have modified d-band electronic structures, could have higher selectivity in transforming C=O and C–O bonds [54]. Metal-free catalysts, such as frustrated Lewis pairs (FLPs) and doped carbon catalysts, have shown that hydrogen molecules could be activated without metal catalysts [55,56]. Moreover, other new routes, such as electrochemical and photocatalytic conversions, have also attracted attention in biomass valorization [57,58]. The strong focus on catalysis in biomass transformation underscores its essential role as one of the main routes that dictates the pace and success of transitioning from a fossil-based economy to a chemical industry driven by renewable resources.

Unlike reviews focusing on a single biomass component, conversion route, catalyst family, or product category, this review presents a comprehensive framework connecting biomass feedstocks, catalytic processes, catalyst features, intermediate products, and final applications. It combines established thermochemical and catalytic upgrading routes with emerging catalysts, and the scope also extends beyond fuels and chemicals to catalytic graphitization and other value-added products, as shown in Figure 1. Section 2 introduces the major biomass components and their derived intermediates and products. Section 3 reviews advanced catalytic processes for biomass conversion and the upgrading of biomass-derived intermediates. Section 4 discusses major classes of heterogeneous catalysts, including conventional and emerging catalyst systems. Section 5 summarizes the production of biofuels, value-added chemicals, and functional materials through major chemical transformations. Section 6 evaluates practical limitations related to biomass

feedstocks, catalytic processes, and catalyst performance and provides perspectives on future research.

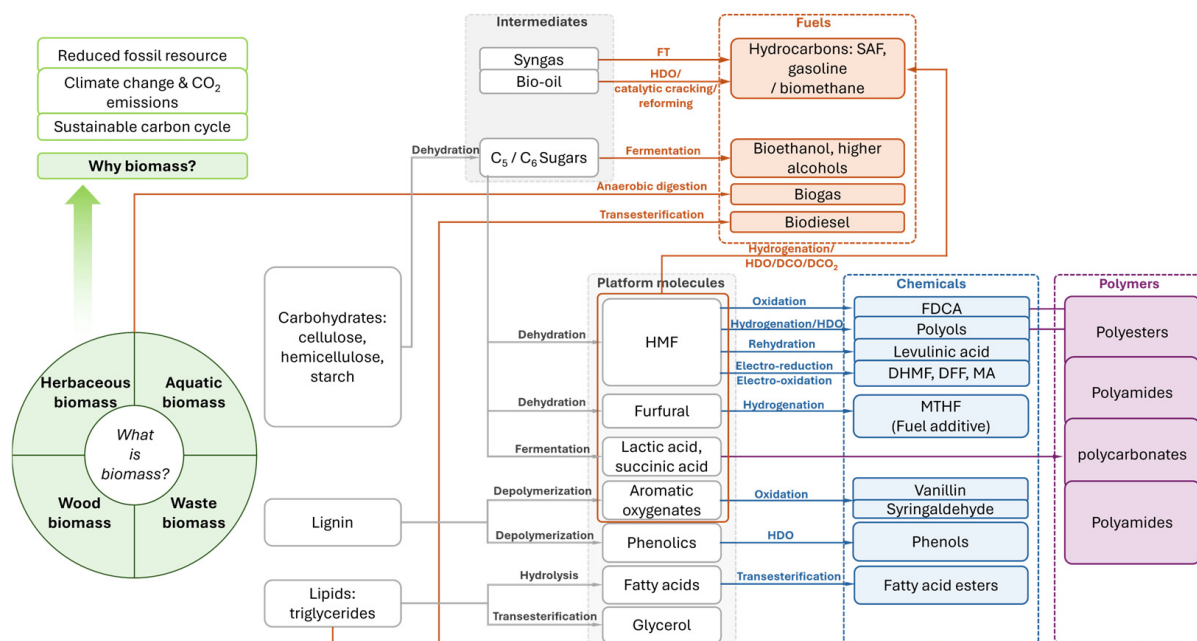


Figure 1. Schematic overview of biomass valorization and upgrading into fuels, platform chemicals, and polymers.

2. Biomass Feedstocks, Key Intermediate Products, and Platform Molecules

2.1. Lignocellulosic Biomass: Cellulose, Hemicellulose, and Lignin

Among all types of biomass, including lipid-rich biomass, protein-rich biomass, starch- and sugar-rich biomass, aquatic biomass, and organic waste, lignocellulosic biomass has attracted the greatest attention for valorization due to its abundance, renewability, and relatively low cost. It consists primarily of agricultural residues, forest waste, and dedicated energy crops and represents the most abundant and cost-effective renewable resource available globally. Lignocellulosic biomass is a complex composite material mainly composed of five major components: cellulose, hemicellulose, lignin, extractives (volatiles), and ash (inorganics) [59]. Its inherent complexity, arising from its diverse functional groups and heterogeneous composition, presents both challenges and unique opportunities for selective functionalization and conversion [60]. On the one hand, strong chemical linkages such as glycosidic, ether, or C-C bonds, together with the lignin network and tight association of cellulose and hemicellulose, hinder efficient depolymerization and separation [61,62]. On the other hand, this very complexity provides access to a wide spectrum of potential molecules, including sugars, furans, phenolics, and organic acids, which can serve as precursors for biofuels, bioplastics, and fine chemicals [63–65].

2.1.1. Cellulose and Hemicellulose

The initial step in valorizing cellulose and hemicellulose typically involves hydrolysis, which is a process that breaks down these complex polysaccharides into constituent monosaccharides [66,67]. Pretreatment conditions strongly influence the composition and yield of the resulting fractions. Dilute-acid and hydrothermal pretreatments preferentially solubilize hemicellulose into oligosaccharides and monosaccharides, whereas increasing pretreatment severity can promote their degradation into furfural, 5-hydroxymethylfurfural, and organic acid, thereby reducing recoverable sugar yield. Al-

kaline and organosolv pretreatments primarily promote delignification and facilitate the recovery of cellulose-rich solids [68].

Alternatively, cellulose can be retained as a polymeric material and processed into CNFs and CNC. Cellulose and hemicellulose-based derivatives serve as precursors for biodegradable films, hydrogels, and functional materials in applications of films, gels, functional membranes, and smart responsive materials [69]. Cellulose can be transformed into CNFs and CNC through ultrasonication, high-pressure homogenization, or acid hydrolysis [70], combined with mechanical, chemical, and enzymatic methods [71–74], and the nanoscale cellulose materials are increasingly used in composites, packaging, and biomedical applications due to their high strength, high specific surface area, and renewability.

However, dispersion, aggregation, and compatibility of cellulose nanomaterials still pose challenges due to hydrogen bonds and Van der Waals forces, and problems such as structural instability, changes in water absorption, and performance degradation in high-humidity environments need to be addressed. For example, carbon nanotubes (CNTs) can be combined with nanofibers to enhance dispersion and conductivity by preventing CNT aggregation [75]. Surface modifications, such as grafting [76,77], crosslinking [78], and the introduction of functional groups, are used in applications to improve interfacial compatibility [79], enhance dispersibility, or enhance conductivity.

Hemicellulose is a heterogeneous polysaccharide composed mainly of xylan, mannan, glucomannan, arabinan, and galactan, depending on the biomass source. Its hydrolysis can produce xylose, arabinose, mannose, galactose, glucose, and uronic acids, as well as partially hydrolyzed products such as xylo- and manno-oligosaccharides [80]. Because hemicellulose has amorphous structural properties, it is often branched, low in crystallinity, and exhibits poor thermal stability. Although hemicellulose's mechanical properties, durability, and swelling control are still relatively weak compared to cellulose, which is a crystalline material, it still has great potential. Xylan or its derivatives, combined with other polymers such as polylactic acid (PLA), polyvinyl alcohol (PVA), starch, etc., or nanofibers, can improve the performance of biodegradable packaging and barrier films [81–83]. In terms of hydrogels or responsive materials, hemicelluloses can be used as hydrophilic segments or network backbones for sensors and drug delivery [84]. Xylan fragments can also be converted into low-molecular-weight bio-based monomers such as xylose, xylitol, and furan derivatives as precursors for the synthesis of renewable polymers [85,86]. Purity is an important challenge because crosslinking and interactions with hemicellulose and lignin complicate its separation and extraction [87,88]. Its solubility, thermal stability, mechanical properties, and hydrophilicity can be adjusted through chemical modifications such as acetylation, graft copolymerization, and crosslinking [89,90].

2.1.2. Lignin

Lignin-related research has shifted from its previous use as a simple fuel or combustion material to high value-added applications. Lignin is one of the few renewable highly crosslinked aromatic biopolymers in nature [91]. Specifically, lignin can be used as a filler, reinforcement, or partial replacement component in composite materials, imparting properties such as UV shielding, antioxidant properties, flame retardancy, and electrical conductivity [92–95]. Lignin can also be combined with other conductive components, such as carbon nanotubes, graphene, and conductive polymers, to form composite electrodes or conductive films [96,97]. Also, the presence of polar functional groups facilitates interfacial interactions and chemical modification, enabling potential uses in adhesives, foams, and antioxidant additives [98]. In addition, using lignin as a carbon fiber precursor, carbonization material, or additive has been a hot topic in recent years, with research

focusing on processing optimization, precursor selection, and carbonization conditions to produce carbon fibers with higher rigidity, demonstrating the potential of lignin to replace petrochemical carbon fibers [99,100].

While cellulose and hemicellulose hydrolysis have achieved high yields under optimal catalyst and solvent systems, lignin catalytic hydrolysis remains challenging due to its strong C-C linkages, containing diverse ether linkages (especially β -O-4, which is important to achieve higher yields of aromatic monomers), and complex structures [101]. A number of modification routes, such as esterification [102], grafting [103,104], crosslinking [105], oxidation, and reduction [106], were used to modify lignin's structure (e.g., depolymerization), solubility, reactivity, and compatibility. Moreover, acid or acid-like catalysts such as Hydrogen-form Zeolite Socony Mobil-5 (HZSM-5), SO_3H -carbon, and NiMoS sulfide can help depolymerize β -O-4 linkages, producing guaiacol, syringol, and catechol for subsequent value-added uses. However, the yield reported in current studies remains relatively low, generally ranging from 10 to 30% [107,108]. Lignin-first biorefining integrates lignin valorization with biomass fractionation by stabilizing solubilized lignin and suppressing its condensation into recalcitrant structures [109].

The inherent variability of biomass properties, which can differ significantly by source, geographic location, and even harvest conditions, poses a significant challenge for designing efficient, valuable conversion processes. This variability, coupled with the distinct chemical nature of cellulose, hemicellulose, and lignin, underscores the necessity for specific pretreatment strategies and tailored catalytic approaches for each component. A “one-size-fits-all” catalytic system is unlikely to achieve optimal activity or selectivity across diverse biomass feedstocks.

2.2. Key Intermediate Products

2.2.1. Sugars

C_5 and C_6 sugars represent the primary carbon in lignocellulosic biomass, derived from cellulose and hemicellulose via hydrolysis. Hydrolysis yields hexose sugars (e.g., mannose, glucose, and galactose) and pentose sugars (e.g., xylose and arabinose), which serve as essential intermediates for bioethanol fermentation and platform chemical synthesis [80,110,111]. Early studies mainly focused on acid-catalyzed hydrolysis, but issues of equipment corrosion and sugar degradation limited industrial use [112–114]. Enzymatic hydrolysis became the dominant approach, with continuous efforts to improve enzyme activity and substrate accessibility through pretreatment methods such as ILs and DESs, which solubilize lignin via π - π interactions, hydrogen-bond disruption, reduced crystallinity, and partial solubilization, thereby improving enzymatic hydrolysis efficiency [115,116]. Sugars have multiple hydroxyl groups, high oxygen content, water solubility, and thermal instability. These properties enable diverse transformation pathways, including dehydration, isomerization, oxidation, hydrogenation, and retro-aldol reactions.

2.2.2. Bio-Oil

Bio-oil, typically produced through fast pyrolysis or hydrothermal liquefaction (HTL), is a complex liquid intermediate composed of oxygenated compounds such as phenols, aldehydes, and carboxylic acids from lignocellulosic biomass, algae, and organic wastes [117,118]. Zeolite-based catalysts, such as HZSM-5 and mesoporous silica, have been widely used in catalytic fast pyrolysis to enhance the yield of aromatic hydrocarbons [119]. However, excessive coke and deactivation remain critical challenges. Compared to fast pyrolysis, HTL uses wet feedstocks without drying and yields a more stable biocrude [120]. Bio-oil studies focus on improving stability, controlling the biocrude yield and quality by feedstock selection [121], optimization of reaction conditions [122], and catalyst de-

sign of homogeneous (alkaline catalysts and acidic catalysts) and heterogeneous catalysts (supported metal catalysts, metal oxide catalysts, and molecular sieve catalysts) [123,124].

2.2.3. Syngas

Syngas is a mixture of carbon monoxide and hydrogen, which is mainly produced via gasification or reforming processes that have evolved over the past decades. Its composition can be tailored by adjusting reaction temperature and oxidant ratio, enabling downstream conversion into fuels and chemicals through Fischer–Tropsch synthesis or methanol production [125–127]. While conventional air-blown gasifiers offer simplicity, steam and CO₂ co-gasification have been found to improve H₂/CO ratios (1.77–3.35) and reduce tar formation [128]. Catalytic gasification using Ni-, Fe-, or alkali-promoted catalysts further enhances conversion efficiency and minimizes carbon deposition [129–132]. More recent studies are exploring plasma- and microwave-assisted gasification to reduce the required activation energy and achieve near-complete carbon conversion [133]. It was reported that these processes can achieve bio-hydrogen yields of up to 95% and exhibit strong adaptability toward diverse biomass and waste materials [134]. The trade-off between syngas quality and the energy input required by the process continues to pose a major challenge for large-scale deployment.

2.3. Primary Biomass-Derived Platform Molecules

Platform molecules are bridges between complex biomass and monomers, polymer precursors, and diversified fuels and chemicals, and are molecularly well-defined with high oxygen content [135]. This could maximize the overall value derived from the biomass feedstock and provide flexibility in tailoring products to target demands. Sugars obtained from cellulose and hemicellulose can be converted into a series of oxygenated platform molecules, including furans and carboxylic acids, while lignin and carbohydrates could be converted to aromatic oxygenates and phenolics.

Furan platform molecules typically include HMF and furfural, which represent carbohydrate-derived platform molecules. HMF is produced through the dehydration of C₆ sugars. Fructose can be directly dehydrated to HMF, whereas glucose conversion generally requires its initial isomerization to fructose, followed by dehydration [136]. Furfural is commonly produced through the dehydration of C₅ sugars, particularly xylose and arabinose. During biomass pyrolysis, carbohydrate depolymerization can generate anhydrosugars such as levoglucosan, which undergo competing dehydration, fragmentation, and rearrangement reactions to form furfural and other furan derivatives [137,138]. HMF and furfural share a furan ring and an aldehyde functional group, which contribute to their high chemical activity after upgrading. Compared to furfural, HMF has additional hydroxymethyl groups that make its structure more complex. HMF can be upgraded to promising fuels and solvents such as 2,5-dimethylfuran (DMF), C₉–C₁₅ alkanes, and gasoline and diesel-range hydrocarbons, as well as polymer monomers such as 2,5-bis(hydroxymethyl) furan (BHMF) and 2,5-furandicarboxylic acid (FDCA), by selective conversion of an aldehyde and a hydroxyl functional group through selective oxidation or hydrogenation [139–141].

Furfural has a simpler molecular structure and can be upgraded to 2-methylfuran (2-MF), 2-methyltetrahydrofuran (2-MTHF), alkanes, and diesel-range hydrocarbons via hydrogenation, hydrogenolysis, and C–C coupling [142]. Besides furans, polyols- and alcohol-type platform molecules are structurally simpler and are derived from sugars by fermentation or catalytic hydrogenation. Representative molecules include ethanol, sorbitol, and xylitol. Multiple hydroxyl groups enable them to convert to acids (e.g., glyceric acid and lactic acid) and some smaller fuels and chemicals by upgrading routes [140,141].

Biomass-derived carboxylic acids, including levulinic acid, lactic acid, and succinic acid, are recognized as key platform molecules, which are essential for the large-scale production of a diverse range of chemicals. Levulinic acid is produced via dehydration and rehydration, while lactic acid and succinic acid are produced by fermentation routes. They have functional groups of carboxyl, ketone, or alcohol, which yield a wide range of downstream products, including alcohols, hydrocarbons, longer-chain chemicals, and polymers [143]. Overall, levulinic acid is generally more widely used due to its unique bifunctional structure. It could be converted not only to pentanol and pentanoic acid for chemical production [135], but also to ethyl levulinate (EL) and γ -valerolactone (GVL) for fuel applications [144].

Aromatic platform molecules derived from lignin and carbohydrates by reductive depolymerization are mainly aromatic oxygenates, primarily consisting of phenolic monomers including anisole, vanillin, cresols, guaiacol, syringol, and phenol [135,139]. Because of their aromatic backbone and oxygen-containing functional groups, they can serve as platform molecules for producing fuel-range hydrocarbons (e.g., aromatics and cycloalkanes) and phenolic chemicals through selective catalytic upgrading. Because of the complex structure of lignin, model compounds are studied to elucidate reaction pathways and catalytic mechanisms.

3. Advanced Catalytic Processes to Transform Biomass

3.1. Catalytic Thermochemical Conversion of Biomass

As illustrated in Figure 2, catalytic pyrolysis, carbonization, and gasification provide distinct biomass valorization pathways for producing bio-oil, biochar, and syngas, respectively. These processes differ in operating temperature, heating rate, and heating time, which determine product distribution and properties.

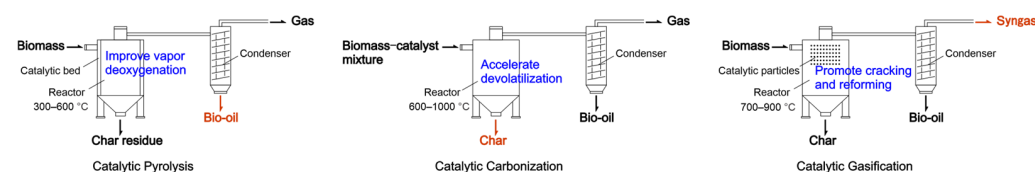


Figure 2. Pathways for biomass valorization by catalytic pyrolysis, carbonization, and gasification.

3.1.1. Catalytic Pyrolysis and Carbonization

Pyrolysis and carbonization are closely related thermochemical pathways, differing only in their target products. Pyrolysis aims to optimize bio-oil production. Catalytic pyrolysis of biomass is one of the most promising thermochemical conversion routes for producing higher quality liquid bio-oils and renewable hydrocarbons [145]. Traditional biomass thermal decomposition methods produce bio-oil with disadvantages, including a higher oxygen content (usually 35–40 wt.% [146]), higher acidity, greater corrosiveness, and chemical instability [20]. In situ catalytic pyrolysis, together with upgrading units, has been widely used to produce low-oxygen-content, highly stable fuels or chemicals. Catalytic pyrolysis involves introducing catalysts, such as zeolites, metal oxides, or carbon-based catalysts, to deoxygenate and reform the pyrolysis vapors generated during the thermal decomposition of biomass at 400–600 °C under anoxic conditions [147].

Coke formation is one of the main problems that hinders the industrial application of catalytic pyrolysis. Zeolites have been widely used to reduce diffusion resistance and lower coke formation due to their porous structure and window architecture [148,149]. Metal-modified zeolites such as Fe/ZSM-5, Ni/ZSM-5, and bimetallic Fe-Ni/ZSM-5 could combine the acidity of zeolites and deoxygenation functions of metal species to improve vapor-phase aromatization deoxygenation [150]. Li et al. reported that Fe-Ni/ZSM-5 produced the highest hydrocarbon content in bio-oil of 22.9% compared with 18.9% for

unmodified ZSM-5, and the activation energy decreased by 4.5–5.8% when compared with non-catalytic pyrolysis [151,152]. In Asadieraghi's study [153], incorporating gallium into the meso-HZSM-5 increased bio-oil yield from 32.6 wt.% to 35.8 wt.%.

Compared to pyrolysis, carbonization, a char-oriented form of slow pyrolysis, has slower heating rates and longer residence times to enhance solid carbon yields [154]. Lignin used as a carbonization material is not new, and traditional processes typically require temperatures of 600–900 °C, depending on the desired carbon structure [155]. Catalysts include alkaline and transition metals, which can tailor carbon formation by accelerating devolatilization, enhancing heteroatom removal, and promoting the development of more ordered or functional carbon frameworks at reduced temperatures (400–700 °C). The carbonization products serve as precursors for activated carbon, catalyst supports, biochar for soil application, and advanced functional carbons after activation or graphitization [156].

3.1.2. Catalytic Gasification

Gasification converts biomass into syngas at 700–900 °C with steam, air, oxygen, or carbon dioxide. Catalysts are used to promote cracking and reforming, which increase H₂ yields. However, gasification alone cannot produce clean and H₂-rich syngas; catalytic upgrading is necessary. Ni, with 10–20 wt.% loading, is one of the most commonly used catalysts for biomass gasification to produce optimal syngas and reform tar, but Ni is easily deactivated by H₂S poisoning and coking [157]. H₂ yield decreased significantly from 11.55 to 7.35 mol kg^{−1} after one cycle and almost deactivated to a non-catalytic level after two cycles [107].

Bimetallic or strong redox-active supports can burn deposited carbon via oxygen vacancies and migratable oxygen, thereby slowing down deactivation. For example, Wei et al. [158] evaluated Fe-Ni bimetallic oxygen carriers in an interconnected circulating fluidized bed for biomass chemical-looping gasification. XRD and SEM confirmed that an Fe-Ni alloy formed during reduction, and the oxygen carrier maintained better structural stability than Fe/Al₂O₃. Chemical-looping gasification (CLG) using Cu, Mn, or perovskite-based oxygen carriers has attracted attention due to their high oxygen mobility and strong resistance to sulfur and tar deposition, which can help achieve cleaner syngas generation with lower coke accumulation [159,160]. Recent studies also highlight that impregnated alkali/alkaline-earth metals (AAEMs) promoted char gasification and tar cracking via carbonate and char interactions, oxidized reaction intermediates, or deposited carbon, therefore reducing tar without additional catalysts [161,162].

3.1.3. Catalytic Hydrolysis, Hydrothermal Carbonization (HTC) and Hydrothermal Liquefaction (HTL)

Catalytic hydrolysis, one of the important pathways for aqueous-phase conversion, generally refers to the process of breaking bonds in carbohydrate fractions of lignocellulosic biomass to generate smaller oxygenated building blocks [163]. Hydrolysis cleaves glycosidic bonds to produce fermentable sugars such as glucose, fructose, xylose, and arabinose. Traditional methods using acid dilutions (e.g., H₂SO₄, HCl, and H₃PO₄), such as 0.1–2 wt.% H₂SO₄ with temperatures between 120 and 240 °C, achieved glucose yields as high as 80–90%; however, it was highly corrosive and needed an acid recovery system [164,165]. Unlike dilute mineral acids, which act as fully homogeneous sources, heteropoly acids, including H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀, have polyoxometalate structures with high proton activity and could be applied as strong Brønsted solid acids for more controlled cellulose depolymerization [166,167]. Lewis-acid zeolites such as Sn-Beta demonstrated the ability to enhance carbohydrate depolymerization by coupling glycosidic bond cleavage with glucose–fructose isomerization, thereby helping with more efficient utilization of hydrolyzed sugars [168,169]. In addition, carbon- or biochar-based solid acid, which was

added with $\text{-SO}_3\text{H}$, -COOH , and -OH , showed strong Brønsted acidity and high hydrothermal stability, making it more effective for cellulose and hemicellulose hydrolysis [170,171]. For example, SO_3H -activated carbon prepared by sulfonation in concentrated H_2SO_4 at 423 K (150 °C), followed by hydrothermal pretreatment, selectively hydrolyzed cellulose into glucose with a 40.5% yield [172]. In another study, the SO_3H -bearing carbon can also be prepared by carbonization followed by sulfonation in fuming sulfuric acid at 353 K (80 °C). Attributable to strong SO_3H Brønsted acid sites, the catalyst rapidly converted crystalline cellulose into water-soluble saccharides, achieving saccharification within 6 h [173].

HTC of high-moisture lignocellulosic biomass is always conducted in hot subcritical water, typically 215–295 °C, under autogenous pressure [174], where water serves as the solvent and reaction medium for biomass components. For high-moisture organic wastes, HTC conversion can be achieved at slightly lower temperatures, between 180 and 220 °C. HTC is not a very clean depolymerization process in terms of reaction selectivity and product distribution, and it is always accompanied by hydrothermal formation upgrading processes: biomass undergoes initial hydrolysis to break polysaccharides and other linkages, followed by dehydration, decarboxylation, and condensation reactions. These lignocellulosic structures are converted into lower-molecular-weight oxygenated compounds, such as organic acids, furans, and small oxygenates, along with CO_2 release and carbon-rich hydrochar production [175]. Carbon retention and energy densification are strongly influenced by the feedstock. Softwood biomass produced higher energy-density hydrochars due to lower hemicellulose and ash contents, whereas grass-type biomass exhibited lower mass and energy yields due to higher reactive hemicellulose and aqueous-soluble components [176]. Studies showed that across a wide range of organic wastes, approximately 50–80% of the carbon was retained in the solid phase, while 15–40% was transferred into the liquid phase as dissolved organic compounds, and ~2–11% was released as gas, mainly CO_2 [177,178].

HTL is a deep depolymerization process of biomass in water under pressure. Under subcritical and near-critical water conditions, HTL promotes the extensive depolymerization of biomass into energy-dense biocrude and low-molecular-weight oxygenated intermediates, without the need for feedstock drying [179]. These biocrude and oxygenated intermediates can be upgraded afterward. Compared to HTC, HTL requires higher pressures and temperatures and mainly produces liquid-phase products, functioning as a biomass-to-fuel conversion. High temperatures could enhance bio-oil yields, with an optimal range of ~300–330 °C for most lignocellulosic biomasses, while higher temperatures could promote secondary cracking and gas formation [118]. Lignocellulosic biomass produces more oxygenated and aromatic oils in HTL. A study showed that bio-oil yield increased nearly linearly with lignin content, while holocellulose content promoted the formation of soluble oxygenated compounds and solid char [180,181]. Also, lipid- and protein-rich feedstocks typically yielded higher biocrude fractions. Shafizadeh et al. [182] applied machine learning models to a large dataset of biomass feedstocks and operating conditions to predict HTL performance, and the results showed that the optimal biocrude yield was 48.7–53.5%.

3.2. Catalytic Upgrading of Biomass-Derived Intermediates

3.2.1. Catalytic Hydration and Dehydration

Dehydration involves the removal of water from alcohols, polyols, or sugars. As summarized in Table 2, catalytic dehydration processes can generally be categorized into conventional acid-catalyzed dehydration, pyrolytic dehydration, and tandem cascade reactions. Conventional acid-catalyzed dehydration is a widely studied route, typically catalyzing carbohydrates into furan-based platform molecules [183–185]. Under Brønsted

or Lewis acidic conditions, dehydration reactions reduce oxygen content and increase molecular desaturation or aromaticity. Catalytic activity and selectivity depend largely on the type, density, and strength of acid sites, as well as the catalyst's pore structure and the reaction medium. Brønsted acid sites typically promote dehydration reactions, whereas Lewis acid sites can facilitate sugar isomerization prior to dehydration. With an optimal Brønsted/Lewis acid ratio, Zr-P exhibits up to a 30-fold increase in furfural selectivity during the dehydration of xylose [183], whereas a sulfonated ionic liquid/ AlCl_3 system produced HMF yields of 59–65.1% from disaccharides and polysaccharides [184].

Table 2. Summary of catalytic dehydration studies of biomass-derived carbohydrates.

Catalytic Transformation	Feedstock	Catalysts	Conditions	Main Intermediates and Products	Yield and Performance	Ref.
Acid-catalyzed dehydration	Xylose	Zr-P, $\text{SiO}_2\text{-Al}_2\text{O}_3$, WO_x/ZrO_2 , $\gamma\text{-Al}_2\text{O}_3$, HY zeolite	160 °C, aqueous phase, 3–10 wt.% xylose, acid sites of 0.15–0.5 mmol, up to 270 min	Furfural, humins from side reactions	Up to 30 times higher furfural selectivity with high Brønsted/Lewis acid ratio (Zr-P).	[183]
Acid-catalyzed dehydration	Disaccharides; polysaccharides	Sulfonated ionic liquid $[\text{SO}_3\text{H-bmim}]\text{Cl}/\text{AlCl}_3$	170 °C, butanone-water (4:1); 0.05M IL, 1–3 min	monosaccharides (glucose/fructose), HMF	59–65.1% of HMF yield.	[184]
Acid-catalyzed dehydration	Sugars, cellulose, xylan, corncob with kraft lignin	H_3PO_4 acid catalyst in hot compressed water	Sugars: 200 °C; Cellulose, xylan: 230 °C; 0.1 M H_3PO_4 , 5 min, lignin loading of 0–50 wt.%, ~2.5 MPa N_2	glucose/xylose, isomerization to fructose, HMF and furfural	~26–30% glucose and furan yield from corncob.	[185]
Tandem cycloaddition and dehydration	Furans, ethylene	Solid acids (H-Y, H-Beta, H-ZSM-5)	~250–300 °C, vapor phase catalytic reactor	Toluene and BTX aromatics	70–90% selectivity to toluene.	[186]
Tandem dehydration-bioproduction	Corn-cob-derived xylose hydrolysate	$\text{SO}_4^{2-}/\text{SnO}_2$ -attapulgite solid acid, <i>E. coli</i> CCZU-A13 whole-cell biocatalyst	Dehydration: 170 °C, 20 min, 3.6 wt.% catalyst; Bio-reduction: 30 °C, pH = 6.5	Furfural, furfuryl alcohol (FOL)	44% FOL yield.	[187]
Dehydration during pyrolysis	Rice husk	$\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ (0–20wt% NiO)	Catalytic pyrolysis: 350 °C; Dehydration: 250–350 °C.	Anhydrosugars, furans, char precursors	Water yield increased from 6.45 (control) to 15.36% with catalysts indicate enhanced dehydration.	[188]
Hydrolysis, dehydration, aldol condensation, hydrogenation	Corn-cob, starch-derived carbohydrates	$\text{Pd}/\text{WO}_3\text{-ZrO}_2$; $\text{WO}_3\text{-ZrO}_2$ for hydrolysis-dehydration, 5wt% Pd sites for hydrogenation	Hydrolysis-dehydration: 573 K, 5 min; Aldol condensation: 353 K, 30 h; Hydrogenation: 393 K, 5 MPa H_2 , 6 h.	Sugars, HMF/Furfural, aldol condensation products, $\text{C}_5\text{-C}_{15}$ oxygenates	$\text{C}_5\text{-C}_{15}$ yield: 20.3% (flour) and 14.8% (corn-cob).	[189]

Dehydration can serve as a key intermediate step in cascading catalytic systems, enabling subsequent reactions [186,187] that sometimes occur during biomass thermochemical decomposition processes [188,189]. For example, the solid acid zeolite used in the tandem cycloaddition–dehydration reaction achieved a selectivity for toluene of 70–90%, indicating that the catalyst's acidity and pore structure can direct the conversion of furan intermediates into aromatic products [186].

Representative dehydration pathways include the conversion of sugars to furans, polyols (e.g., glycerol and diols) to aldehydes, ketones, and other unsaturated compounds, as well as alcohols to olefins, which can serve as platform chemicals [190,191]. Hydration is the reverse of dehydration, adding water to unsaturated intermediates to stabilize reactive intermediates and enabling chain growth, such as HMF, which could undergo rehydration to levulinic acid and formic acid [191]. Both conversions always occur simultaneously, and dehydration generates reactive intermediates, whereas hydration redirects the process and leads to secondary products. Catalyst type determines which direction dominates.

3.2.2. Catalytic Hydrogenation and Hydrogenolysis

Hydrogenation is widely used to reduce unsaturated bonds and carbonyl groups in biomass platform molecules, and it yields more saturated and stable intermediates for upgrading [192,193]. Traditional H_2 -involved hydrogenation used catalysts to activate hydrogen on metal surfaces, thereby adding hydrogen species onto $C=C$ or $C=O$ bonds [194]. Catalytic transfer hydrogenation (CTH) proceeds via hydrogen transfer from organic donors such as alcohols, formic acids, and polyols, enabling selective carbonyl reduction under milder conditions [195]. Unlike traditional catalytic hydrogenation that relies on activated external hydrogen on metal surfaces, CTH avoids high-pressure hydrogen; however, its practical application in certain systems may be limited by hydrogen donor consumption, the need for product separation, and relatively slow reaction rates. Hydrogenolysis and hydrogenation share the same hydrogen-activation step and the same metal active sites. Hydrogenation is a typical selective reduction process that adds hydrogen to unsaturated functional groups without bond cleavage, while hydrogenolysis promotes bond cleavage of $C-O$ and $C-C$ bonds, and hydrogen stabilizes the fragments. Therefore, the balance between hydrogenation and hydrogenolysis determines whether aldehydes, ketones, furans, and lignin-derived phenolic compounds are converted into saturated oxygenated compounds, deoxygenated products, or smaller fragments [195]. Figure 3 compares hydrogenation and hydrogenolysis reactions.

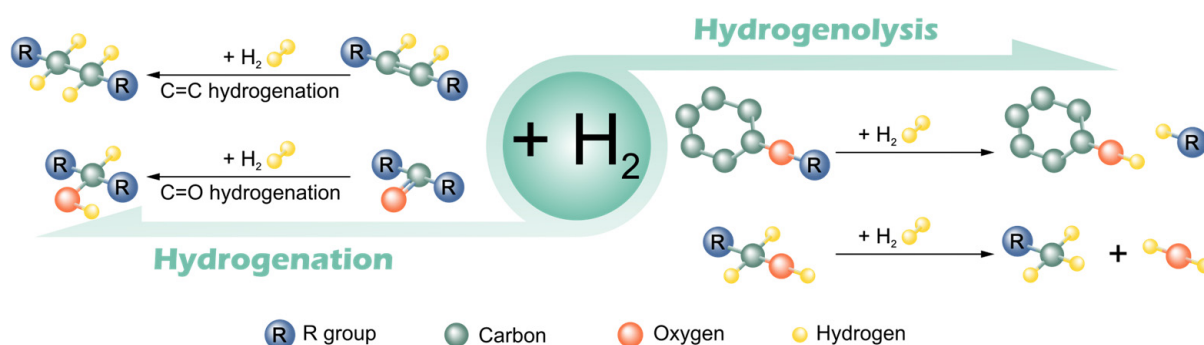


Figure 3. Comparison of hydrogenation and hydrogenolysis reactions.

The selectivity of these reactions is governed by the synergistic functions of metal sites, acid–base sites, and the metal–support interface. Ru-, Pd-, Pt-, Ni-, and Cu-based bifunctional metal–acid catalysts were commonly used for hydrogen activation. For example, bimetallic Pd–Ni catalysts can convert diphenyl ether and other linkages such as α -O-4, β -O-4, and 4-O-5 into alcohols and hydrocarbons with high selectivity. Pd mainly promotes hydrogenation, and Ni promotes C–O hydrogenolysis, while combining the two metals creates a synergistic interface that enhances both hydrogen activation and C–O cleavage [196]. In addition, using the support of carbon, Al_2O_3 , TiO_2 , ZrO_2 , and zeolites strongly affects the reaction activity [195]. Combining metallic active sites (e.g., Ru, Rh, Ir, and Ni) with metal oxides such as ReO_x , MoO_x , WO_x , and NbO_x enables highly selective cleavage of

C-O bonds while preventing excessive hydrogenation or C-C bond breaking, promoting hydride and proton species that help selective hydrogenolysis of alcohols, ethers, and lignin-derived phenolics. Reaction selectivity is shown to be governed by oxide acidity, oxygen affinity, and hydrogen coverage on metal sites [197,198].

3.2.3. Selective Oxidation

Selective oxidation is a controlled partial oxidation process that retains oxygen and enhances polarity and reactivity, enabling the conversion of biomass-derived carbohydrates, polyols, and lignin-derived aromatics into oxygenated products, including aldehydes, ketones, and organic acids [199]. The reaction typically proceeds via activation of molecular oxygen on metal surfaces, generating reactive oxygen that facilitates oxidation of hydroxymethyl groups while suppressing overoxidation to CO₂. The composition and surface properties of the catalyst are crucial, as the oxidation state of the active metal, the acidity or basicity of the support, oxygen vacancies, and metal-support interactions all influence oxygen activation and adsorption of oxygenated intermediates. However, excessive oxidative activity can trigger C-C bond cleavage, lead to CO₂ formation, or generate unwanted acidic byproducts.

With molecular oxygen as the oxidant, converting HMF to 2,5-diformylfuran (DFF) and FDCA [200,201], glycerol to glyceric acid [202,203], and lignin to vanillin, syringaldehyde, and aromatic acids [204] are commonly used oxidation pathways using metal catalysts. Noble metal catalysts generally achieved 70–100% HMF conversion and 70–100% FDCA selectivity, with most optimized systems exceeding 95% conversion and 98% selectivity. However, direct comparison remains difficult because the reported data were obtained under conditions involving significant differences in reaction time, oxygen pressure, alkali concentration, and metal loading; research on glycerol oxidation has expanded from thermal catalysis to electro-, photo-, and photoelectron-catalytic systems. Key performance for representative target products typically ranges from ~44% to over 90%; the catalytic oxidation of lignin typically yields approximately 5–43% (mass fraction, based on lignin mass) of aromatic aldehydes. Catalysts generally increase aldehyde yields by approximately 1.5–2 times, but most studies report aldehyde yields based on mass rather than lignin conversion, carbon-based selectivity, or a complete product mass balance.

Selective oxidation is also of great significance for the upgrading of biomass-derived liquids, as the reactive alcohols and aldehydes present can be converted into more stable or higher-value ketones, aldehydes, and carboxylic acids. However, the complex composition of actual biomass-derived liquids can trigger competitive adsorption and catalyst deactivation, resulting in lower selectivity compared to that achieved with single model compounds. Nowadays, renewable electricity-driven and light-driven oxidation strategies are being investigated to find alternatives to conventional thermal oxidation [205,206].

3.2.4. Hydrodeoxygenation (HDO)

HDO is a catalytic hydrogen-assisted upgrading process that removes oxygen from biomass-derived compounds via C-O bond cleavage in the presence of H₂ over metal catalysts, converting biomass-derived oxygenated compounds such as bio-oil, lignin-derived phenolics, oxygenated aromatics, furan derivatives, esters, and acids with high oxygen content into lower oxygen content hydrocarbons or upgraded oil with closer fuel properties [139,207–209].

Noble metal catalysts have also been widely used for HDO under milder conditions owing to their excellent hydrogenation properties [210,211]. Transition metal-based catalysts, including Ni, Co, and Cu, particularly Co-Mo or Ni-Mo sulfide catalysts supported on Al₂O₃, have shown high activity and relatively low cost for HDO reactions. Co-MoO_x

is a representative bifunctional metal–oxide interfacial catalyst, in which the interfacial $\text{Co}^{\delta+}$ sites act as adsorption-active centers that promote $\text{C}=\text{O}$ hydrogenation and $\text{C}-\text{O}$ bond cleavage. It has been reported to efficiently convert levulinic acid (LA) into γ -valerolactone (GVL) [212] or convert stearic acid to diesel-range hydrocarbons [213]. Most recently, metal–oxide catalysts such as $\text{Cu}/4\text{CoO}_x$ and Co@CoO have attracted increasing attention due to the synergistic interactions between metal sites and oxygen-vacancy-rich oxide interfaces, which facilitate $\text{C}-\text{O}$ bond cleavage [214,215]. In addition, non-sulfided metal catalysts, including Ni, Fe, and Cu, combined with acidic supports, were reported to enhance cracking and aromatization reactions, whereas acidic supports (such as $\text{SiO}_2\text{-Al}_2\text{O}_3$ and HZSM-5) strongly promote $\text{C}-\text{O}$ bond cleavage in saturated intermediates [216].

3.2.5. Decarbonylation (DCO) and Decarboxylation (DCO_2)

DCO and DCO_2 are two other deoxygenation pathways that remove oxygen from a wide range of biomass-derived oxygenates, generating CO and CO_2 , respectively. Noble metal catalysts, such as Pd, Pt, and Ru, supported on carbon, Al_2O_3 , SiO_2 , transition metals (e.g., Ni and Co), solid acids, or photocatalysts, have been reported to promote DCO and DCO_2 reactions without the need for external hydrogen, with an amount of carbon loss comparable to HDO, achieving high conversion and selectivity. DCO and DCO_2 are closely related but have different mechanisms of deoxygenation, with the selectivity routes being highly sensitive to metal catalysts, supports, and reaction environments [217]. According to density functional theory (DFT) investigations, DCO_2 typically proceeds via surface carboxylate intermediates, in which $\text{C}-\text{C}$ bond cleavage adjacent to the carboxyl group directly leads to CO_2 evolution, whereas DCO involves metal-acyl species formed after the initial $\text{C}-\text{O}$ bond activation, followed by selective $\text{C}-\text{C}$ bond scission and CO extrusion [218,219]. Unlike DCO_2 , DCO relies on precise control of metal–substrate interactions to enable CO removal while largely preserving the molecular backbone [220].

Beyond static catalytic effects, reactions can be dynamically tuned through metal–oxide interfacial chemistry. Chen et al. showed that by adjusting the metal–oxide interfacial chemistry during fatty acid upgrading, hydrogen reduction was reversibly switched in Pt-WO_x catalysts between HDO-dominant and DCO/ DCO_2 -dominant routes [221]. These catalytic deoxygenation routes yielded fuel-range hydrocarbons and upgraded oils. The substrate functionality played an important role in determining which route was dominant. As summarized in Table 3, for well-defined platform molecules (such as HMF and levulinic acid), target product yields of nearly 90–99% can typically be achieved under relatively mild conditions; in contrast, complex bio-oils and mixtures of oxygenated compounds usually require high temperatures of 300–400 °C and result in a broader product distribution. While DCO and DCO_2 reactions reduce the demand for external hydrogen, they entail carbon loss through the removal of CO or CO_2 , with hydrocarbon selectivity ranging from over 50% to over 95%.

Table 3. Summary of studies on catalytic deoxygenation.

Catalytic Deoxygenation	Conditions	Catalyst/Loading	Substrate Concentration	Final Products	Conversion/Yield/Selectivity	Ref.
HDO of bio-oil	Supercritical ethanol medium, 300–400 °C	Mo ₂ C/CNF (13 wt.% Mo), catalyst/bio-oil = 1:10 (<i>w/w</i>)	2.3 g bio-oil in 23 g ethanol (9.1 wt.%)	Upgraded bio-oil	Yield = 69%	[207]
HDO of fatty-acid-derived compounds	~340 °C, ~10 bar H ₂	SiO ₂ /Al ₂ O ₃ supported metal (5 wt.% Pd, Pt, Re, Rh, Ru, Ir, Au, or Ni)	40 g neat rapeseed oil	Hydrocarbons	Yield = 49.8–85.1%; Re gave highest at 85.1%	[210]
HDO of oxygenate mixtures	~300 °C, ~30 bar H ₂	1 wt.% Pt/C + HZSM-5 (Si/Al = 19)	2 wt.% isoeugenol in n-decane	Saturated cyclic hydrocarbons (Propyl cyclohexane, PC)	Yield = 35.5%	[211]
HDO of levulinic acid	190 °C, 2 MPa H ₂ , 2 h	Co-MoO _x ; catalyst/LA = 1:10 (<i>w/w</i>); Co/Mo molar ratio = 1:1	0.5 g levulinic acid in 15 mL 1,4-dioxane	γ-Valerolactone (GVL)	Conversion = 99%; selectivity = 98%, remain after 5 cycles	[212]
HDO of stearic acid	543 K, ~20 bar H ₂ , 2 h	2.4Co1.7Mo/γ-Al ₂ O ₃ , Co/Mo molar ratio = 3:2	5 g stearic acid in 0.1 L n-dodecane (10 wt.%)	C ₁₅ –C ₁₈ alkanes	Selectivity = 86.6%	[213]
HDO via CTH of HMF	150 °C, 1 MPa N ₂ , 12 h	Cu/4CoO _x , Cu/Co molar ratio = 1:4,	0.3 g HMF in 40 mL 2-propanol, catalyst/HMF = 1:3 (<i>w/w</i>)	DMF	Conversion = 100%; yield and selectivity = 99%	[214]
Hydrogenolysis /HDO of HMF	130 °C, 1 MPa H ₂ , 3 h	Co@CoO with oxygen vacancies, catalyst/HMF = 20 wt.%,	150 mg HMF in 5 mL THF	DMF	Conversion >99%; yield = 89.2%	[215]
DCO/DCO ₂ of stearic acid	350 °C, 2 MPa N ₂ , 1.5 h	Pt-WO _x /SiO ₂ (Pt/W = 1.5:9 (<i>w/w</i>))	100 mg stearic acid in 10 mL dodecane	Heptadecene and Heptadecane	Conversion = 99%; yield > 85%; selectivity = 57.1%	[221]
DCO of furfural	325 °C, 10 bar H ₂	0.5Pd/5K-modified γ-Al ₂ O ₃ , (Pt/K = 0.5:5 (<i>w/w</i>))	10 wt.% furfural in cyclopentyl methyl ether	Furan	Conversion = 97%; selectivity = ~100%; maintained >95% and >99% during repeated cycles for 168–200 h	[222]
DCO of stearic acid	350 °C, 2 MPa N ₂ , 4 h	Co _{1.66} @MNC-800 (N-doped carbon supported Co)	100 mg SA in 10 mL dodecane	Heptadecane	Conversion = 79% selectivity = 70%; at 7 h, conversion reached 89% with a 56% yield and 63% selectivity	[223]
Photocatalytic DCO ₂ of stearic acid	Concentrated light irradiation, ~254 °C (photothermal heating)	SnS photocatalyst	0.05 M SA in total reaction volume of 25 mL	N-heptadecane	Yield = 95.2%; selectivity = 97.7%	[224]
DCO ₂ of Valerolactone (GVL)	350 °C, 2 h	Al-impregnated mesoporous MCM-41 (10 wt.% relative to GVL)	1 g neat GVL	Butene isomers	Yield = ~90%; reusable of 66% after 8 cycles	[225]

3.2.6. Catalytic Reforming

Catalytic reforming includes aqueous-phase reforming (APR), steam reforming (SR), dry reforming (DR), and their synergistic reactions. Current studies on catalytic reforming are mainly focused on biomass tar reforming, driven by the need to eliminate tar and upgrade syngas in biomass gasification routes. Biomass tar is a highly complex mixture of oxygenated and aromatic hydrocarbons [226–229]. APR, SR, and DR are designed to convert tar into H₂-rich syngas, enabling downstream hydrogen production. Alternative reforming routes aim at CO-rich syngas, which is desirable for downstream Fischer–Tropsch (FT) synthesis of light hydrocarbons (e.g., C₂–C₄ olefins) [230].

APR over noble metal catalysts generally proceeds via dehydrogenation of oxygenated hydrocarbons followed by C–C bond cleavage to form CO, which is subsequently converted to CO₂ and H₂ by water–gas shift (WGS) reactions. Hydrogen production, especially from ethylene glycol and methanol by APR, can be achieved with high hydrogen selectivity of ~99% using Pt/Al₂O₃ catalysts, but in the same situation, glucose reforming yielded lower hydrogen selectivity of ~50% due to the competing homogeneous decomposition reactions in the aqueous phase, which directed carbon toward liquid byproducts and alkanes [231]. Ni-based catalysts are the most promising cost-effective alternatives to noble metals and exhibit strong activity for large-scale biomass gasification tar reforming by SR of aromatic and oxygenated tar compounds, compared to WGS reactions, which enhance H₂-rich syngas production [232]. DR is a route that forms carbon via CH₄ methane decomposition and Boudouard reactions, using catalysts [233].

Coke formation directly competes with reforming reactions through dehydrogenation and condensation of aromatics, C–C bond cracking followed by carbon polymerization, Boudouard reactions, and methane decomposition, which is the primary limitation to the long-term industrial application of catalytic reforming routes [232]. To address different catalyst deactivation mechanisms, several strategies have been used. Perovskites, spinels, and core–shell structures offer metal–support interactions, improve Ni dispersion and prevent Ni sintering. Noble metals, including Rh, Ru, Pt, and Pd, provide high reactivity and coke resistance. Oxygen-mobile supports of CeO₂, ZrO₂, and La₂O₃ enhance coke gasification by providing active oxygen species. In addition, Ni-based bimetallic systems of Ni–Fe, Ni–Cu, or Ni–Co could reduce coke formation through tuning carbon solubility [233–235]. High-temperature SR and DR accelerate metal migration and sintering, whereas the hydrothermal environment of APR can lead to metal leaching and support instability.

3.2.7. Catalytic Cracking

Catalytic cracking is a process that involves not only C–C bond cleavage but also a series of interconnected reactions that reduce molecular size reduction and carbon-number distribution control by cracking large molecules or high-molecular-weight intermediates into smaller molecules or light hydrocarbons. This reaction is commonly carried out using acidic or metal–acid bifunctional catalysts and is an important method for converting biomass-derived oils or heavy oxides into combustible fuels or light chemicals. Fluid catalytic cracking (FCC) is a core form of catalytic cracking used in petroleum industry refineries, which convert biomass-derived oxygenates into hydrocarbons, and is specifically used on glycerol and sorbitol [236]. Low-cost mineral catalysts can be used for real biomass gasification tars and bio-oils, achieving high tar cracking [237] and high bio-oil quality [238], respectively. For example, alcohols, ketones, acids, and polyols can be efficiently converted into BTX (benzene, toluene, and xylene) aromatics and C₂–C₄ olefins through dehydration, C–C scission, oligomerization, cyclization, and aromatization pathways with the use of ZSM-5 as a catalyst [239]. The balance among these pathways is strongly governed by the designed catalyst acidity, pore structure, and the reaction condi-

tions. Brønsted acid sites promote dehydration, cracking, oligomerization, and cyclization, while the shape-selective micropores of ZSM-5 favor the formation and diffusion of light olefins and monocyclic aromatics.

Carbon deposition is widely recognized as the main cause of catalyst deactivation [240,241], as it can result in pore blockage and reduce active metal catalyst sites. Carbon-supported Ni-based catalysts are attractive for biomass tar cracking because they combine the high cracking and reforming activity of Ni with the porous structure and thermal stability of carbon materials [241]. Ni-Fe bimetallic catalysts with a dense carbon nanofiber shell could achieve a tar conversion efficiency of 95%, where the hierarchical porous structure of carbon promotes diffusion of tar molecules, while Fe promotes cracking and prevents coke formation [242].

3.2.8. Catalytic Graphitization

Catalytic graphitization is a solid-state structural conversion process in which carbon-rich intermediates obtained from carbonization or pyrolysis are further transformed into graphitic or graphene-like materials at high temperatures. Traditional graphitization uses temperatures between 2500–3000 °C, while catalytic carbonization uses transition metals, which enable graphitization of biomass or biochar transfer to graphene and graphene-like materials at temperatures below 1500 °C [243].

These transition metals play a crucial role in the catalytic formation of graphene materials due to their unique electronic structures and high solubility for carbon. Metals such as Fe, Co, Cu, and Ni have been widely recognized as effective catalysts that can significantly reduce the graphitization temperature, enabling the formation of ordered graphene layers at 700–1000 °C [244–246]. The underlying mechanism is generally described as the dissolution–precipitation process, in which carbon atoms first dissolve into the metal lattice and subsequently precipitate onto the surface, nucleating and growing graphitic layers [247,248]. The surface of transition metal nanoparticles provides heterogeneous nucleation sites that lower the energy barrier for carbon–carbon bond rearrangement [249], while their nanoscale size further enhances catalytic efficiency by linking the atomic-scale bonding strength of the catalysts.

Lignocellulosic biomass waste is an ideal carbon precursor because it has a high carbon content [250]. Lignin, with its natural abundance, low cost, and environmentally friendly properties, has attracted significant attention as a precursor for graphene-based materials via catalytic carbonization [92], including multilayered graphene-like structures such as graphene quantum dots (GQDs) and porous graphene. Thermal decomposition occurs below 600 °C, releasing volatile compounds and leaving the remaining aromatic rings, which start to fuse and form small graphitic domains. As the temperature increases, these domains grow into well-ordered 3D-shaped graphene layers [251]. At higher temperatures, graphene nanodomains gradually enlarge, leading to the formation of graphene and graphite structures with improved functional properties such as electrical conductivity [252]. Researchers have reported that lignin carbonized at 1300 °C (C-1300) formed well-developed graphene layers with expanded interlayer spacing (0.403 nm) and a high microporous surface area (207.5 m² g^{−1}) [253]. One green and sustainable approach is laser-induced carbonization, in which a lignin film is directly converted into laser-induced graphene (LIG), which rearranges aromatic rings to form a porous graphene structure with potential applications in disposable electrochemical biosensors [254], supercapacitors [255], and ultrasensitive strain sensors [256]. However, because there is a strong relationship between lignin structural features and the resulting LIG [257], it remains amorphous carbon and exhibits poor electrical conductivity [258].

4. Advanced Heterogeneous Catalysts for Biomass Transformation

Heterogeneous solid catalysts have been extensively investigated and developed for their efficacy in converting diverse biomass feedstocks into high-value-added chemicals and fuels, including micro- and mesoporous materials, metal oxides, metal-supported catalysts, and sulfonated polymers [259]. They play a pivotal role in numerous biomass conversion processes because, unlike homogeneous catalysts, they are generally easier to separate from reaction mixtures, thereby offering the potential for catalyst recovery and reuse; however, the loss of activity due to coking, sintering, leaching, or structural changes remains a significant challenge requiring urgent attention. Catalyst activity and selectivity depend strongly on acidity and basicity, structural features, and electronic properties. As illustrated in Figure 4, heterogeneous catalysts enable diverse catalytic pathways for converting biomass-derived compounds into value-added products.

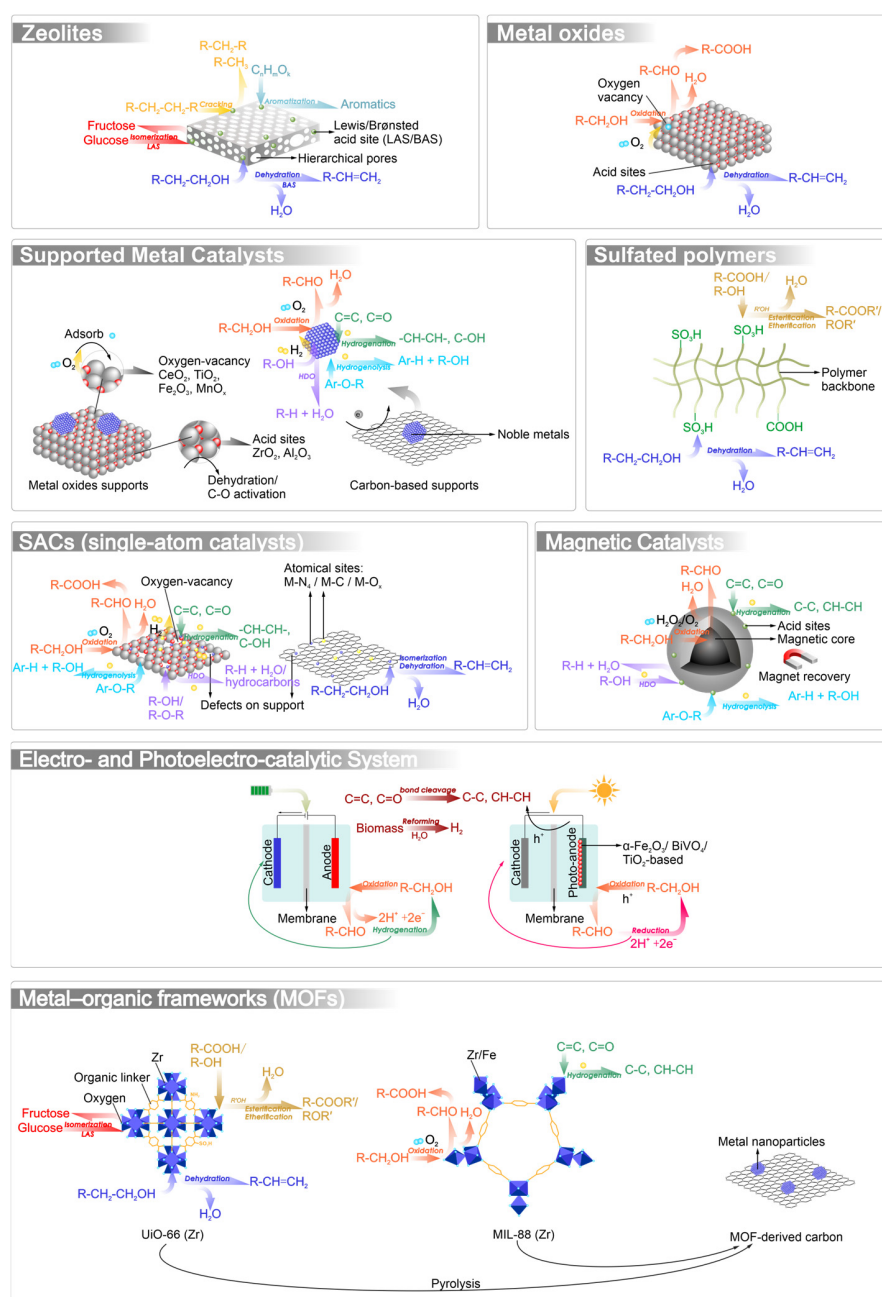


Figure 4. Overview of heterogeneous catalysts and their main catalytic pathways for biomass-derived compound conversion.

4.1. Zeolites

Zeolite catalysts are widely studied for pyrolysis or fast pyrolysis of biomass to aromatics or hydrocarbons; dehydrations of sugars to furans; alcohols to diethyl ether, ethylene, or gasoline; and cracking of heavy hydrocarbons to gasoline and olefins [260]. Zeolites are crystalline inorganic materials composed of SiO_4 and $[\text{AlO}_4]^-$ in tetrahedral shapes, forming ordered microporous structures with Brønsted or Lewis acid sites. Both characteristics allow for unique catalytic properties. Catalytic performance is governed by pore size and topology, acid-site type and density, and Si/Al ratio.

The catalytic performance of zeolites is primarily governed by the synergistic effects of acidity and pore architecture. In fast catalytic pyrolysis (450–650 °C), HZSM-5 effectively promotes cracking, deoxygenation, and aromatization of lignin-derived oxygenates into aromatic hydrocarbons such as BTX (benzene, toluene, and xylene). The medium-sized channels of HZSM-5 facilitate the formation and diffusion of BTX while restricting larger products. Its Si/Al ratio of 10– ∞ modulates acid site density, thereby balancing cracking and aromatization. Previous studies have shown that after the Si/Al ratio increased from 25 to 85, the total acidity can decrease significantly. However, excessive acidity may promote secondary condensation and coke formation. The medium pore size of 5.2–5.9 Å was reported to be most favorable for formation of aromatics. HZSM-5 can achieve high selectivity of approximately 50–70% for total aromatics and yields of 40–80% [261,262]. Zeolite catalysts also facilitate the conversion of carbohydrates, such as sugars and aldehydes, into furan compounds via triple dehydration of fructose, enabled by the action of Lewis and Brønsted acidic sites in catalysts such as H-Beta, H-ZSM-5, and $\gamma\text{-Al}_2\text{O}_3$. The HMF yield of approximately 35–40% was obtained due to secondary reactions, including rehydration to acids and polymerization to humins [263,264].

Introducing mesoporosity of 2–50 nm or creating frameworks with interconnected micro- and mesopores by demetallation, utilization of surfactants, recrystallization, steaming, etc., can increase active sites [265,266]. For example, zeolites play a crucial role in catalytic cracking of heavy hydrocarbons into gasoline-range products and light olefins. The reaction proceeds via acid-site-generated carbenium ions that drive C-C bond cleavage, while pore structure determines product distribution: large-pore Y zeolites facilitate the cracking of bulky hydrocarbons, medium-pore ZSM-5 favors the formation of light olefins and aromatics, and smaller or one-dimensional pores enhance selectivity by restricting undesired side reactions [267]. It was reported that the HMF yield can be significantly enhanced to ~70% when Beta zeolite is combined with carbon black adsorption [263].

Fine-tuning zeolite acidity is another strategy that enhances end-product yield. Patel et al. reported a 12-tungstophosphoric acid (PW_{12}) anchored zeolite HY (hydrogen-type Y) showing increased Brønsted acidity. This achieved 88% conversion and 99% selectivity to n-butyl levulinate under optimized mild conditions of 90 °C within 8 h from levulinic acid [268]. Barakov et al. studied optimization of Lewis (Zr-sites) and Brønsted (Al-sites) acid site distributions (2:5 ratio) on zeolites to achieve up to 65% HMF yield from fructose [269]. Fernandes et al. showed that H-zeolites can promote the depolymerization of β -glucan into glucose monomers. Catalytic efficiency was greatly enhanced (up to 96.9%) when reactions were carried out in the ionic liquid 1-butyl-3-vinylimidazolium bromide ($[\text{BVinIm}]\text{Br}$), promoting additional Brønsted acidity via ion exchange [270].

Zeolites generally possess good thermal stability and can often be regenerated via oxidative coke removal, although repeated treatments may alter their acidity and framework structure.

4.2. Metal Oxides

Metal oxide catalysts are widely used in biomass conversions due to their diverse catalytic functionalities, including Brønsted acidity, Lewis acidity, basicity, and redox activity. These properties enable reactions such as dehydration, esterification, acetalization, oxidation, and deoxygenation of biomass-derived compounds [271].

Metal oxide catalysts with acidic sites can promote the dehydration of carbohydrates to furans, the dehydration of biomass-derived alcohols, and the esterification of organic acids [272,273]. Combining two or more metal oxides allows tunable acidity, improved stability, and enhanced resistance to deactivation [274]. Examples of mixed metal oxides include Sn-HfO₂, SiSnPO, NbO_x/ZrO₂, and various zirconium and titanium phosphates. These catalysts are particularly useful in dehydration reactions, which convert fructose to HMF and direct the formation of HMF from glucose in aqueous solutions, where a yield of 50–76% can be achieved [275–278]. Transition metal oxides with redox properties, such as Fe₂O₃, Co₃O₄, CuO, TiO₂, MnO_x, and CeO₂, are important for the oxidation of biomass-derived platform molecules, including HMF, furfural, glycerol, and phenolics, into valued chemicals and fuels under molecular oxygen as the oxidant [279–281]. In aerobic thermal oxidation over metal oxides, the reaction often follows a Mars–van Krevelen (MvK) mechanism, in which lattice oxygen participates in substrate oxidation and the molecular O₂ is adsorbed and activated [282,283]. In addition to thermal oxidation, electrocatalysts such as NiCo₂O₄ nanowires have also been reported to efficiently oxidize HMF to FDCA under alkaline electrochemical conditions with a yield of 90% and stable performance over five cycles [284].

Compared with zeolite catalysts, metal oxides offer flexibility in tuning surface acid–base and redox properties through composition, crystal phase, defect engineering, and oxygen vacancy formation. The enhanced basicity was reported to facilitate pyrolysis vapor upgrading, promoting deoxygenation and aromatic formation [285,286]. However, metal oxides remain, tending to undergo phase transitions or leaching.

4.3. Supported Metal Catalysts

Supported metal nanoparticles, including Au, Pt, Pd, Ru, Cu, Ni, and Co, immobilized on oxide or carbon supports are used for the selective oxidation of alcohols, hydrogenation of carbonyl compounds, hydrogenolysis of C–O bonds, and HDO of biomass-derived oxygenates. Supported bi- and multi-metallic nanoparticles (e.g., Au-Pd, Pt-Bi, Au-Pd-Pt, and Au-Cu) were studied to enhance catalytic performance because the electronic modification between metals can tune oxidation activity. These catalysts are widely used in liquid-phase selective oxidation reactions [287–289].

In terms of metal oxide-supported metal catalysts, metal nanoparticles activate hydrogen, while appropriate oxide acidity facilitates selective C–O bond cleavage and prevents excessive C–C scission, leading to a more efficient deoxygenation [290]. This catalytic performance was recognized to depend not only on a metallic active phase but also on the distribution and electronic interactions between metal nanoparticles and oxide supports, as the active sites are often associated with metal–oxide interfaces [291,292]. Carbon is another important support material. The inert and porous structure, especially a hierarchical micro-mesoporous structure of char, biochar, activated carbon, or carbon nanotubes, could enhance the distribution of metal adsorption and increase the time within the active metal sites [287,289,293,294]. Supported metal catalysts are prone to coking, sintering, and leaching. While coke deposits can sometimes be removed, sintering and metal loss are difficult to reverse.

4.4. Sulfonated Polymers

Sulfonated polymers mainly include styrene-based sulfonic acid ion exchange resins and perfluorosulfonic acid-based catalysts. These materials function as strong Brønsted acids and are effectively employed in biomass conversions. Their catalytic performance is governed not only by the $\text{-SO}_3\text{H}$ groups but also by acid density and strength, pore structure, and the hydrophobic microenvironment [295]. Hydrophobic polymer backbones can help repel water generated during dehydration, thereby suppressing side reactions and improving selectivity [296]. However, these catalysts may still exhibit mass-transfer limitations and deactivation due to water or humin deposition. In addition, sulfonated polymers may lose acidic groups or structural integrity under harsh thermal or hydrothermal conditions, thereby limiting their regenerability.

Sulfonated polymers have shown promising performance in the acid-catalyzed conversion of carbohydrates. A lignosulfonate-based sulfonated polymer (LFS) was reported as a highly efficient solid acid catalyst for one-pot dehydration–etherification of fructose to 5-ethoxymethylfurfural (5-EMF) in ethanol. Under mild reaction conditions at 120 °C, the optimized LFS catalyst achieved a 5-EMF yield of 68.4% with complete fructose conversion [297]. Xue et al. [298] developed a sulfonated crosslinked polyaniline organocatalyst by introducing skeletal crosslinking followed by sulfonation with fuming sulfuric acid. This strategy enhanced the Brønsted acidity and surface hydrophobicity of the catalyst, thereby improving the catalytic dehydration of fructose to 5-HMF, with yields up to 72%. Controlled sulfonation could tune the acid properties by maximizing HMF formation under mild reaction conditions while minimizing side reactions.

4.5. Single-Atom Catalysts (SACs)

Single-atom catalysts (SACs) represent a leading candidate for highly selective biomass upgrading. Their unique structures allow nearly 100% of the metal atoms to atomically disperse and be exposed on the biomass surface, forming specific coordination structures. The atomic catalysts and ultra-small clusters of atomically dispersed metals exhibit unique catalytic selectivity that cannot be achieved with larger nanoparticles [299]. These atomic sites (usually M-N_4 , M-C , or M-O_x) can promote selective activation of C-O, C-C, and C=O bonds, thereby enabling upgrading reactions such as oxidation, hydrogenation, hydrogenolysis, and HDO [53,300].

Typical applications include using Pt_1 - and Pd_1 -based sites stabilized on oxygen-defective oxides for the selective upgrading of furan compounds, as well as isolated metal sites that cooperate with neighboring acidic or vacancy sites to promote C-O bond transformation using Sn_1 - or Mo_1 -based isolated Lewis acid sites for xylose conversion to furfural [300–303]. An emerging trend is dual-atom catalysts (DACs), which introduce adjacent multi-metal active sites with enhanced redox capability and improved stability relative to single-atom catalysts [304]. For example, Pt single-site catalysts with tailored coordination environments, such as $\text{Pt}_1\text{-N}_4$ or $\text{Pt}_1\text{-Co}_3$, have been reported for the liquid aerobic oxidation converting 5-hydroxymethylfurfural (5-HMF) to FDCA [305]. In contrast, Co dual-atoms have been shown to promote the aerobic oxidation of biomass-derived aldehydes and alcohols, where the dual-atom configuration lowers the activation barrier for oxygen adsorption and accelerates intermediate formation compared with single-Co sites [306].

Although SACs offer high activity, they often face a higher risk of metal agglomeration. Consequently, regeneration efficiency depends not only on the recovery of activity but also on the preservation of active sites.

4.6. Magnetic Catalysts

Magnetic catalysts refer to incorporating magnetic nanoparticles into various solid matrices, combining the well-established advantages of heterogeneous catalysts, especially enhanced stability and reusability, with the practical benefit of magnetic separation [307].

Designing magnetically recyclable solid acids and metal-based catalysts allows rapid catalyst separation while maintaining competitive activity. Studies developed a magnetically recyclable solid Brønsted acid catalyst, in which Fe_3O_4 served as the magnetic component, while the $-\text{SO}_3\text{H}$ surface groups anchored to the carbon molecules served as the catalytic component. Chen et al. [308] reported a magnetic cellulose-derived carbonaceous solid acid catalyst (MCC- SO_3H) through Fe salt impregnation, carbonization, and subsequent sulfonation. Catalytic testing showed that MCC- SO_3H achieved a maximum 5-ethoxymethylfurfural (EMF) yield of 63.2% from fructose and retained good recyclability, with the EMF yield decreasing only slightly to 58.5% after six cycles.

Magnetic catalysts facilitate separation and recycling, but metal leaching and loss of magnetism may compromise their long-term performance. Yuan et al. [309] developed sulfonic acid-functionalized magnetic core-shell Fe_3O_4 @carbon microstructures via interfacial polymerization, followed by controlled carbonization and vapor-phase sulfonation, to generate stable, graphitized carbon shells rich in $-\text{SO}_3\text{H}$ groups as recyclable solid acid catalysts, achieving 69% benzaldehyde conversion. Recyclability testing over nine cycles showed minimal loss in activity, down to 64.8%. This indicates promising recyclability with minimal loss in activity, but aggregation, iron leaching, and reduced magnetization remain significant drawbacks [310].

4.7. Electrocatalytic (EC) and Photo-Electrocatalytic Systems (PEC)

Electrocatalytic (EC) and photo-electrocatalytic (PEC) systems represent notable approaches for biomass valorization by utilizing external energy sources of electric and solar under relatively mild conditions. In EC systems, the applied potential promotes electron-transfer steps at the electrode surface; representative electrocatalysts and electrode materials include Ni-based electrodes, PbO_2 , TiO_2 , nanotubes, boron-doped diamond, carbon-supported transition metals, and noble-metal catalysts. In PEC systems, photogenerated electrons and holes further facilitate the conversion of molecules, reducing energy input requirements [311–315].

Hydrogen (H_2) is an energy carrier in fuel systems. Electrochemical conversion has been increasingly explored as an approach for upgrading biomass intermediates while co-producing hydrogen sources. For example, replacing water oxidation at the anode of an electrolysis cell with the electro-oxidation of biochemical- or thermochemical-derived intermediates enables hydrogen production under mild conditions (cell voltages below 1.23 V) [316].

Among PEC systems, $\alpha\text{-Fe}_2\text{O}_3$, BiVO_4 , and TiO_2 -based photoanodes are representative metal-oxide platforms for biomass oxidation. Their performance is often improved by cocatalyst deposition (such as NiOOH , CoOOH , CoPi , and NiFe-LDH) or engineered with oxygen vacancies, dopants, or carbon incorporation. These strategies significantly enhance charge separation, promote selective C-C or C-O bond cleavage, and suppress undesired overoxidation [313,317].

4.8. Metal–Organic Frameworks (MOFs)

Metal-organic frameworks (MOFs) have emerged as an important class of porous crystalline heterogeneous catalysts. MOFs have unique high specific surface areas (SSAs) that often reach several thousand $\text{m}^2 \text{g}^{-1}$, tunable pore architectures, and designable metal–ligand coordination environments [318,319].

Zr-based UiO-series and MIL-101 materials are two representative examples. UiO-66 and its functionalized derivatives have excellent thermal and hydrothermal stability. Besides the unsaturated catalytic Zr sites, linker functionalization (e.g., $-\text{SO}_3\text{H}$, $-\text{NH}_2$) can introduce Brønsted acidity or enhance adsorption selectivity [320–323]. Cr-based MIL-101 and Fe-based MIL-88 materials have also been explored due to their larger pores and abundant active centers [324,325]. Metal nodes connected by organic linkers provide catalytic sites within the framework, making MOFs attractive for upgrading biomass-derived carbohydrates and lignin-derived platform molecules, such as glucose isomerization, fructose dehydration, levulinic acid esterification, and vanillin HDO. For example, MOF-based catalysts have been widely applied in biodiesel production, where the conversion of oils, fats, and fatty acids can achieve high yields above 90% under mild conditions of 40–50 °C [326]. A bimetallic MOF-derived catalyst can achieve more than 99% conversion of vanillin to 2-methoxy-4-methylphenol (MMP) [327]. Additionally, MOFs can serve as sacrificial self-templates for generating metal nanoparticles via pyrolysis, thereby creating more stable materials for high-temperature conversions [328,329]. The long-term stability of MOFs can be limited by framework degradation, particularly under hydrothermal, strongly acidic, or strongly alkaline reaction conditions.

5. Major Chemical Transformations and Value-Added Products

5.1. Biomass-Derived Biofuels and Liquid Fuels

Biomass can serve as a sustainable feedstock for producing biofuels and liquid fuels, offering an alternative to fossil fuels. Depending on conversion pathways and molecular structures, biomass-derived liquid fuels can be categorized into first-generation biofuels (bioethanol and biodiesel) or second-generation biofuels (sugar- and starch-based biomass, vegetable oils and animal fats, and wood-based biofuels) [330].

One typical example of biomass-derived biofuels is the transesterification of triglycerides, which are abundant in vegetable oils, non-edible oils, and waste cooking oils. This process, typically involving methanol, converts triglycerides to diglycerides and monoglycerides, which yields fatty acid methyl esters (biodiesel) and glycerol as valuable byproducts [331]. Second-generation biofuels utilize lignocellulosic biomass through thermochemical and biochemical routes, enabling higher-quality liquid fuels, including cellulosic ethanol, biomass-to-liquid (BTL) fuels, and renewable diesel and bio-gasoline. Cellulosic ethanol is a key second-generation biofuel that can supply large volumes of sustainable liquid transportation fuel [332], but it requires deep decarbonization, and the core challenges are thermochemical pretreatment and enzymatic hydrolysis [333]. BTL conversion routes include gasification to syngas followed by FT synthesis, fast pyrolysis, bio-oil upgrading, hydrolysis, and fermentation [334]. Some innovative methods were integrated into the FT process, such as solid oxide co-electrolysis, improved carbon utilization, and reduced electricity requirements [335]. Integration of a gasification process model was proposed to produce drop-in jet fuel [336], a promising approach for producing ultra-clean liquid fuels [337].

Beyond traditional biodiesel, catalytic routes enable the synthesis of advanced liquid fuels. Furan-based fuels represent emerging advanced biofuels, which are derived from biomass platform molecules, such as furfural (FUR) and HMF, by catalytic hydrogenation and HDO, electro-catalytic and heterogeneous catalytic routes, and metal-catalytic routes for reducing reaction energy consumption, improving selectivity, and minimizing byproducts, and producing 2-MF and DMF [338]. They are superior to first-generation biofuels, having higher energy density, detonation resistance, and compatibility with existing fuel systems [338]. The efforts aim to do more than just burn biomass for energy or produce simple ethanol. As the use of biomass-derived bio-oils and syngas is limited due to their high

oxygen content, low stability, and poor compatibility with existing fuel infrastructure [339], the focus is increasingly on producing higher-quality, more energy-dense liquid fuels that can directly substitute for fossil-derived transportation fuels [340,341].

5.1.1. Catalytic Upgrading of Bio-Oils

Key upgrading steps for bio-oil include HDO, esterification, catalytic cracking, acetalization, and reforming, which are used to reduce oxygen content, improve energy density, and enhance storage stability [342,343]. Acetalization offers a mild upgrading pathway by stabilizing the reactive carbonyl compounds in bio-oil. HDO is among the most effective approaches for producing stabilized refinery intermediates and hydrocarbon-rich liquid fuels under an H_2 pressure, removing oxygen primarily as water while preserving carbon efficiency [344]. However, its industrial application is constrained by factors such as the requirement for high-pressure equipment, high hydrogen consumption, and catalyst deactivation.

In contrast to HDO, catalytic esterification is an effective, mild upgrading method for reducing the acidity of bio-oil by converting organic acids into esters. Solid acids, including zeolites, sulfonated resins, and acidic metal oxides, can promote esterification reactions while offering potential advantages regarding catalyst separation and recovery. HZSM-5, one of the commonly used catalysts, can promote esterification of acidic components and cracking of heavy fractions and was reported to reduce the vacuum distillation residue from ~38% in crude bio-oil to ~15% after upgrading [345]. However, the water naturally present in bio-oil may alter the reaction equilibrium and inhibit acidic sites, thereby limiting ester formation.

Acetalization is the process in which reactive aldehydes or ketones react with alcohols or polyols under acid catalysis to form acetals. By reducing the concentration of reactive carbonyl compounds, this pathway enhances the stability of bio-oil and mitigates its tendency to polymerize during storage [346,347]. However, as acetalization is a reversible reaction that produces water, its actual effectiveness depends on the nature of the carbonyl components, the properties of the acid sites, alcohol availability, and the extent of water removal.

Another way to upgrade bio-oil is catalytic cracking, which converts the large oxygen-containing molecules of bio-oil into smaller, more stable hydrocarbons and aromatic compounds, and can be performed under simpler conditions, such as without external hydrogen and at atmospheric pressure [348]. Catalytic cracking directly improves bio-oil fuel quality by producing hydrocarbon-rich liquids, while catalytic reforming converts bio-oil into syngas or H_2 -rich gas for downstream fuel production and chemical synthesis. Light oxygenates, such as ethanol and acetic acid, can achieve higher hydrogen yields at lower temperatures than heavier fractions during reforming [349]. These upgrading methods are not mutually exclusive: esterification is for mild stabilization, and catalytic cracking is for partial deoxygenation, HDO, and reforming, which can achieve deep oxygen removal. These methods enable flexible strategies for upgrading bio-oil.

5.1.2. Catalytic Upgrading of Bio-Syngas

Bio-syngas, primarily composed of H_2 , CO, CO_2 , CH_4 , and light hydrocarbons, is commonly produced by biomass gasification, bio-oil reforming, and combustion processes. However, catalytic upgrading is required because raw syngas typically has low H_2/CO ratios and higher CO_2 and CH_4 contents that limit its application [350,351]. Strategies are needed to improve reaction selectivity, decrease carbon deposition, and achieve sustainable syngas compositions for downstream conversion. Conditioned syngas can be converted into long-chain hydrocarbon fuels through the routes of FT syn-

thesis and methanol production [352]. FT synthesis generally requires H_2/CO ratios of around 2 [350,353], whereas methanol synthesis requires higher ratios. Jahangiri et al. [352] compared two primary FT catalyst systems: iron-based and cobalt-based. Iron catalysts are lower in cost and tolerate low H_2/CO ratios and water–gas shift (WGS) activity, while cobalt catalysts are more expensive but offer higher activity and a longer lifespan. Advanced metal catalysts supported on Al_2O_3 , CeO_2 , or ZrO_2 improve the efficiency of the syngas upgrading process. Upgrading bio-syngas via combined steam- CO_2 reforming over Rh/Al_2O_3 catalysts was reported to improve syngas composition, with the H_2/CO ratio increasing by up to ~95% and the CO/CO_2 ratio decreasing by ~60% [354].

5.2. Biomass-Derived Molecules and Value-Added Chemicals

C_5 and C_6 sugars are fractionally broken down from lignocellulosic biomass, which involves hemicellulose and cellulose. They act as key intermediates for the generation of furan-based, organic acid, and polyol platforms. One crucial downstream transformation is the conversion of glucose to fructose via isomerization. Lewis acid catalysts are Sn-, Ti-, or Zr-containing zeolites that typically achieve fructose yields of 30–40% in aqueous media via a hydride-shift mechanism, but their relatively high cost limits their large-scale applications [355]. Beyond Lewis acid catalysts, base catalysts represent another important route for glucose isomerization. Fructose can yield up to ~31–32% at 100 °C with the use of organic amines, but the selectivity is only 54–63% [356]. Base-catalyzed glucose isomerization uses aqueous conditions of 80–120 °C with yields of 30–35%; however, catalyst deactivation can occur due to adsorption of organic side products and partial neutralization of basic sites [357]. One study combined ethanol solvent with Mg/Al hydrotalcite catalysts and achieved fructose yields up to 56% and ~80% selectivity at 393 K by shifting the reaction equilibrium and stabilizing base-catalyzed pathways [358].

Converting sugars into key intermediates through dehydration, such as transforming fructose and glucose into HMF [359] and xylose into furfural [360], can then be further converted into fuels and chemicals. Trioses such as dihydroxyacetone (DHA) and glyceraldehyde (GLA) can be dehydrated to pyruvaldehyde (PAL), which is a precursor to lactic acid (LA) and alkyl lactates [361,362]. Multiple catalytic upgrading routes can be accessed depending on the targeted product, such as oxidative reactions to convert HMF into FDCA, a key monomer for bio-based polymers [363]. Reductive reactions transform HMF or furfural into fuel-related molecules such as dimethylfuran (DMF) and 2-methylfuran (2-MF) [364]. Glycerol- and sugar-based intermediates can be selectively converted to polyols, aldehydes, or organic acids depending on the catalyst design [365].

Organic acids are top-value-added chemicals from biomass [366], and LA, succinic acid, and itaconic acid (IA) have shown potential for producing bio-based polymers. LA is recognized as a common bio-based plastic monomer, a key monomer industrially manufactured via anaerobic fermentation [367], and is widely used in biodegradable polymers, food, pharmaceuticals, cosmetics, and chemicals [368]. FDCA is an important bio-based plastic monomer for furan-based polyesters, which could be a promising alternative to polyethylene terephthalate (PET) due to its barrier properties, high mechanical strength, and thermal stability [369]. Succinic acid, in combination with bio-based diols, can generate poly(butylene succinate) (PBS) or poly(butylene succinate-co-adipate) (PBSA) as biodegradable polyesters exhibiting high crystallinity and stiffness, as well as improved processability and ductility for packaging, agricultural films, and degradable products [370,371]. IA is produced from carbohydrate-rich biomass via microbial fermentation, owing to its vinyl groups and two carboxyl functional groups, which form unsaturated dicarboxylic structures that can be used to synthesize polyesters, polyamides, polyurethanes, etc., for polymer

applications [372,373]. Many organic acids can also serve as bifunctional monomers for producing polyesters, polyamides, and advanced plastics [366].

In addition to sugar-derived platform molecules, lignin is a complex aromatic component of lignocellulosic biomass and is a rich source of high-value aromatic compounds [374,375]. Through selective depolymerization and cleavage of linkages, particularly ether linkages, lignin can yield phenolic monomers and aromatic oxygenates such as phenol, benzaldehyde, and related aromatic acids. By selectively cleaving its robust ether bonds, lignin can also be transformed into valuable chemicals, such as aromatic aldehydes and acids, derived from lignin macromolecules [376]. 2-phenoxy-1-phenylethanol is a representative lignin dimer and a model compound; a study reported that β -O-4 ether linkages of 2-phenoxy-1-phenylethanol can undergo radical-mediated β -scission, yielding aromatic fragments such as benzaldehyde under photochemical conditions [377]. Furthermore, phenol is a major monomeric derivative obtained from lignin depolymerization and can be selectively hydrogenated to produce KA (mixture of cyclohexanone (K) and cyclohexanol (A)) oil over catalysts. It is another important chemical intermediate for nylon-6 and nylon-66 [378,379]. These bio-based high-value chemicals reflect a shift in strategies for biomass high-value valorization, accelerating the transition to a bio-based chemical industry.

5.3. Catalytic Conversion of Biomass to Value-Added Materials for Energy Storage Devices

Catalytic conversion of biomass into biomass-derived carbon has become a strategy for upgrading carbon-based electrode materials for energy storage devices [380]. HTC with catalysts is a main route, producing hydrochars that can be further converted into hard carbons for battery electrodes [381,382]. In sodium- and potassium-ion batteries, biomass-derived hard carbons obtained via catalytic routes exhibit turbostratic ordering and expanded interlayer spacing, which are essential for balancing capacity and overcoming the limitations of graphite for Na^+ and K^+ intercalation [383,384]. For energy storage systems with higher power demands, such as lithium-ion batteries (LIBs), biomass-derived carbons could also function as anodes or conductive frameworks, improving reversible capacity, cycling stability, and charge transport [385]. Transition-metal catalysts, including Fe, Co, Ni, and bimetallic systems, are used in catalytic carbonization, activation, and catalytic hydrothermal treatments for producing porous graphitic structures, accelerating carbon reordering, and contributing to electrical conductivity, ion transport, and surface stability of biomass-derived carbons [386,387].

Practical challenges still exist in the application of biomass for energy storage devices [388]. Most biomass-based carbon electrodes exhibit good gravimetric performance only at low mass loadings, whereas high mass loadings are essential for real-world supercapacitors. This excessive microporosity and insufficient electrical conductivity would diminish charge transfer and electrolyte penetration. An optimal method of combining a hierarchical porous biomass-derived carbon electrode with in situ heteroatom doping was proposed by Zhang et al. [389], which achieved stable ion transport and electrical conductivity at ultra-high mass loadings. Further optimization of catalyst selection, pore structure, heteroatom doping, and electrode-scale integration remains necessary to fully utilize biomass-derived carbons in practical applications.

6. Practical Challenges and Future Perspectives

6.1. Process and Catalyst Practical Challenges

The economic competitiveness of biomass valorization processes against established fossil fuel industries faces significant challenges. Although catalytic biomass conversion processes can reduce energy consumption, they still require high temperatures, controlled

atmospheres, and extended residence times, placing high demands on processing equipment. For example, catalytic graphitization requires temperatures above 1000 °C, which are easy to control precisely at the laboratory scale but challenging during scale-up, leading to high energy consumption and costs. Moreover, the economic viability is also influenced by pretreatment, hydrogen and solvent consumption, catalyst replacement, and downstream product separation.

Catalyst-related issues pose another major challenge for practical biomass valorization, including catalyst stability, selectivity, and recovery. During the use of transition metal catalysts for biomass conversion, aggregation and sintering occur at high temperatures, resulting in catalyst deactivation and reduced metal utilization efficiency [390]. Although heterogeneity provides theoretical advantages in terms of separation and reuse, successful examples of complete recovery and recycling without appreciable loss of performance remain limited [391]. Developing cost-effective recovery and recycling strategies for catalysts remains an important direction for the future.

Moreover, catalyst deactivation caused by thermal degradation and sintering is often irreversible, making long-term recycling especially challenging. Furthermore, severe reaction conditions, such as hydrothermal environments and oxygen-involved electrochemical conditions, can induce instability and cause ion leaching or dissolution from solid catalysts [392,393], thereby compromising their long-term performance. These challenges are even more pronounced for single-atom catalysts (SACs), where the isolated metal atoms are often coordinatively unsaturated and prone to migration or aggregation. Under hydrothermal or aqueous conditions, insufficient metal–support interactions may also promote metal leaching. Hydrothermal and aqueous environments strongly promote metal leaching and loss of atomic dispersion [394]. Although some advanced catalytic systems, such as PEC systems, have been developed, decreased energy consumption and the high cost of noble metals, which are often employed directly, often impact large-scale deployments. The issues of catalyst stability still need to be addressed to ensure long-term performance and minimize leaching.

6.2. Limitations of Biomass Feedstock

In addition to process challenges, the inherent complexity of biomass feedstocks further hinders large-scale applications. Its properties vary depending on source, growth conditions, and seasonal availability, resulting in differences in chemical composition, moisture content, and structure. This adds to processing complexities in process design and control, complicating process design, scale-up, and condition control.

The structural and chemical complexity makes it challenging to achieve precise cleavage of specific chemical bonds without introducing side reactions such as repolymerization, char and coke formation, or undesired oxygenated byproducts. As a result, many reported studies in biomass conversion have used model compounds to simplify reactions and elucidate fundamental catalytic mechanisms [108,395]. Catalyst performance generally becomes less predictable as studies progress from model compounds to biomass-derived intermediates, pretreated biomass, and raw biomass. Compared with model systems, real feedstocks contain multiple reactive components, minerals, moisture, and catalyst poisons that may alter selectivity, accelerate deactivation, and increase separation requirements. Although these model systems provide valuable insights into reaction pathways, the relationships between the catalyst and its activity do not fully capture the heterogeneous nature and limitations of the catalyst. There is still a great gap between laboratory-scale experimental understanding and practical-scale real-world applications. Enhancing selectivity from catalytic aspects is needed to produce desired products with high purity from complex

biomass feedstocks. Future efforts must focus on novel catalyst and process design, as well as developing a strategy that considers feedstock selection and pretreatment.

Moreover, current biorefinery processes cannot yet fully replace petroleum refinery processes on a large scale. One significant difference is the inherent energy density of the feedstocks. Lignocellulose has a lower energy density compared to crude oil and natural gas due to its high moisture content and oxygen-rich chemical structure [396–398]. Typical heating values also reflect this difference. Dry wood biomass has a higher heating value (HHV) in the range of $\sim 16\text{--}21\text{ MJ kg}^{-1}$, whereas crude oil and natural gas have higher energy densities of $\sim 42\text{ MJ kg}^{-1}$ and $\sim 50\text{+ MJ kg}^{-1}$, respectively [399]. Lower energy density not only reduces the energy efficiency of biomass conversion but also increases other costs, such as transportation and storage. Overall, these process-, catalyst-, and feedstock-related limitations continue to hinder the industrial implementation of biomass valorization.

6.3. Future Directions for Biomass Valorization

Catalyst development should prioritize selectivity, long-term stability, resistance to poisoning and leaching, regeneration, and the use of earth-abundant elements. More studies should move beyond model compounds toward representative biomass-derived mixtures and real feedstocks under industrially relevant conditions. Feedstock pretreatment, processing, and in situ product separation should also be explored to improve carbon utilization and reduce energy and purification requirements. Techno-economic and life-cycle assessments will be essential for comparing emerging technologies and guiding their scale-up and industrial implementation.

Beyond the continuous optimization of existing conversion technologies, future progress may require a re-examination of the fundamental framework for the high-value utilization of biomass. Many current processes attempt to handle compositionally complex biomass within relatively rigid conversion platforms, often needing drastic component separation, deep deoxygenation, and subsequent molecular restructuring. Rather than pursuing a single “universally optimal” route, flexibly adapting catalysts and conversion pathways to regional feedstock characteristics may offer greater practical value.

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