

Research progress on catalytic pyrolysis of biomass for aldehyde and ketone production

WANG Hengwei¹, QIU Li¹, GE Zefeng², YUAN Xinhua³, HUANG Pu¹, CUI Dongxu¹, LI Jinjin¹, CHEN Dengyu^{1,*}

¹ College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China;

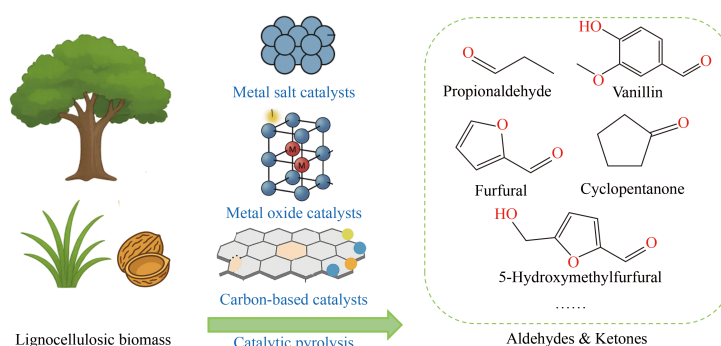
² School of Energy and Environment, Southeast University, Nanjing 210096, China;

³ Institute of Energy Power Innovation, North China Electric Power University, Beijing 102206, China

Abstract: Aldehydes and ketones, valuable oxygen-containing organic intermediates, play a fundamental role in the synthesis of fine chemicals, fuels and materials. Renewable carbon resources, represented by lignocellulosic biomass, enable the green production of platform carbonyl compounds such as furfural, 5-hydroxymethylfurfural, and low-molecular-weight aliphatic ketones via pyrolysis. This approach is of great

significance for mitigating dependence on fossil resources and reducing carbon emissions. This review provides a systematic overview of recent progress in the catalytic pyrolysis of biomass for aldehyde and ketone production. First, the structural features, types, and biomass-derived origins of typical carbonyl platform molecules are summarized. Second, the decomposition pathways and intermediate evolution behaviors of cellulose-rich, hemicellulose-rich, and lignin-rich biomasses under non-catalytic pyrolysis conditions are compared, clarifying the influence of multicomponent synergistic effects on aldehyde and ketone formation. On this basis, particular emphasis is placed on the mechanistic roles and dominant reaction pathways of metal salts, metal oxides, and carbon-based catalytic systems in regulating key steps such as dehydration, decarbonylation, C–O/C–C bond cleavage, and skeletal rearrangement. Finally, the main challenges in biomass catalytic pyrolysis toward aldehydes and ketones are analyzed, including unclear catalyst structure-activity relationships, inadequate active site stability, and limited product selectivity. Future perspectives are proposed regarding the rational design of multilevel structured catalysts for efficient and controllable conversion, the integration of *in situ* characterization with multiscale simulation to elucidate reaction mechanisms, and the development of green scale-up and process integration strategies. This work aims to provide a systematic theoretical reference and research guidance for the high-value utilization of biomass and the conversion of renewable carbon resources.

Key words: biomass pyrolysis; aldehydes and ketones; catalyst regulation; reaction mechanism; selective conversion



The continuous growth of the global population and the depletion of fossil resources have intensified the global energy and environmental pressures, including greenhouse gas emissions, climate change, and exhaustion of natural resources. As the most abundant renewable carbon resource on earth, lignocellulosic biomass is produced at an annual

scale exceeding 180 billion tons, offering substantial potential for the generation of biofuels and high value-added chemicals^[1–3]. Among biomass-derived products, aldehydes and ketones such as furfural and 5-hydroxymethylfurfural (HMF) combine high chemical reactivity with excellent molecular tunability. These

Received: 2025-10-30; Revised: 2025-12-05

Foundation items: Supported by the National Key Research and Development Program of China (2024YFB4206201).

* Corresponding author. E-mail: chendy@njfu.edu.cn.

DOI: 10.1016/S1872-5813(26)60650-0 CSTR: 32157.14.2097-213X.2026.JFCT.0005

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>)

carbonyl compounds can be upgraded into fuel components, solvents, resin monomers, and fine chemicals. They are widely regarded as key platform molecules that bridge biomass resources, liquid fuels, and high value-added chemicals^[4–5]. Carbon peaking and carbon neutrality (dual-carbon) targets drive the construction of bio-based fuel and chemical systems. In this context, achieving the direct conversion of lignocellulose to aldehydes and ketones with high selectivity and carbon efficiency has emerged as a prominent research focus at the interface of fuel chemistry and renewable energy^[6–7].

Industrial production of aldehydes and ketones relies predominantly on acid-catalyzed dehydration of refined sugars and on petrochemical routes such as carbonylation, oxidation, and syngas conversion^[4–5]. In contrast, noncatalytic pyrolysis of lignocellulose avoids deep pretreatment, shortens the conversion pathway, and can co-produce furfural, HMF, and small aliphatic ketones under suitable temperature and residence-time conditions^[6,8]. During pyrolysis, cellulose, hemicellulose, and lignin undergo highly parallel multistep reactions, including depolymerization, dehydration, bond cleavage, and condensation. As a result, the volatile product distribution is broad and dispersed, leading to low carbon yields and poor selectivity of the desired carbonyl products. Extensive condensation, polymerization, and char formation further complicate downstream separation^[6,9–10]. Thermogravimetry coupled with infrared spectroscopy and pyrolysis gas chromatography-mass spectrometry (TG-IR and Py-GC/MS) reveals distinct pathways. Cellulose mainly undergoes depolymerization-dehydration to form anhydrosugars and furanic intermediates, hemicellulose preferentially produces furfural *via* dehydration and rearrangement, and lignin decomposes into phenolics accompanied by limited amounts of aromatic aldehydes and ketones^[9–11]. Multistep pyrolysis studies and multicomponent kinetic models confirm that platform carbonyl compounds are difficult to effectively enrich under noncatalytic conditions^[6,11–13].

These limitations can be addressed by catalytic pyrolysis using heterogeneous catalysts with tailored acid-base and redox functionalities, thereby reconstructing the local reaction microenvironment at the molecular scale and directing complex pyrolysis networks toward convergent formation of carbonyl platform molecules^[8,14–16]. Metal salts (e.g., ZnCl_2 , AlCl_3 , FeCl_3) provide Lewis and Brønsted acid sites that promote sugar dehydration, isomerization, and partial decarboxylation, enhancing the selective formation of furfural and HMF while suppressing condensation and coking to a certain extent^[17–18]. Metal oxides (e.g., Al_2O_3 , ZrO_2 , TiO_2 , CaO) use surface acid-base and redox sites to promote the selective cleavage of C–O and C–C bonds and to direct intermediate rearrangements, thereby stabilizing furanic species, ketones, and aromatic carbonyl intermediates^[9,11,19]. Carbon-based catalysts, including activated carbons, layered carbons, heteroatom-doped carbons, as well as metal-N-C systems, offer tunable

surface functional groups and metal-support interfaces. These enable mild upgrading or selective preservation of carbonyl platform molecules, and in some cases, also impart favorable microwave absorption capability^[6,10]. Collectively, these studies demonstrate that coordinated tuning of acid-base strength, active-site nature, and spatial distribution of catalysts can effectively narrow the product spectrum, and suppress side-reactions such as condensation, polymerization, and charring. Consequently, the selectivity and carbon yields of target carbonyl compounds including furfural, HMF, and small ketones can be markedly enhanced^[17,20].

Against this backdrop, this paper provides a systematic overview of recent advances in biomass catalytic pyrolysis for the production of aldehydes and ketones. The review focuses on key carbonyl platform molecules represented by furfural, HMF, and typical small aliphatic ketones (e.g., acetone, butanone), with particular emphasis on studies published over the past three years (2023–2025). First, the structural diversity of lignocellulosic biomass and the pyrolytic decomposition pathways of its main constituents (cellulose, hemicellulose, and lignin) are introduced, and then the progress and common bottlenecks of noncatalytic pyrolysis routes toward carbonyl platform compounds are summarized. Next, the influence of feedstock characteristics and major catalyst families (metal salts, metal oxides, and carbon-based catalysts) on bond cleavage, dehydration, and molecular rearrangement during catalytic pyrolysis is discussed. Finally, the opportunities and challenges associated with scaling up these processes are assessed and the critical role of biomass catalytic pyrolysis in efficiently exploiting renewable carbon resources and building a sustainable bio-based chemical industry is highlighted.

1 Aldehydes and ketones as platform carbonyl compounds

Aldehydes and ketones occupy a central role as “platform molecules” in the development of bio-based chemicals and fuels. They serve directly as feedstocks for fine chemicals such as resins, solvents, plasticizers, and fragrances, and also act as key precursors for renewable fuels and functional polymer monomers. Industrial production of furfural from agricultural and forestry residues has reached several hundred thousand tons annually. Derivatives of furfural, including furfuryl alcohol, 2,5-furandicarboxylic acid and various bio-based solvents and fuel additives, have established relatively mature application chains. HMF, levulinic acid, and several small ketones are widely recognized as bio-based platform compounds; their hydrogenated, oxidized, and condensed products show strong potential as precursors for polyesters and nylons, as well as for high energy-density fuels.

Compared to conventional synthetic routes based on refined sugars or fossil resources, biomass pyrolysis and catalytic pyrolysis processes use lignocellulose as the

carbon source, thereby directly exploiting abundant agricultural and forestry residues. Studies indicate that, with optimized catalysts and process conditions, yields of furfural, HMF, and representative small ketones can reach 30%–60% or 20%–40%, depending on the specific carbon source and target product. This underscores the considerable potential of biomass pyrolysis and catalytic pyrolysis for large-scale production of aldehyde and ketone platform compounds.

1.1 Furfural

Furfural is a biomass-derived platform compound that occupies a pivotal position in green chemistry and sustainable energy systems due to its renewability and versatile reactivity. It is produced mainly from pentose-rich fractions of hemicellulose, such as xylose and arabinose, which undergo acid-catalyzed hydrolysis followed by dehydration and cyclization under hydrothermal or pyrolytic conditions to form furfural. This pathway represents one of the most important routes for the high-value utilization of biomass^[21–25]. Furfural formation proceeds primarily *via* two routes (Figure 1). The first is the “pentose route”, involving the hydrolysis of hemicellulose to xylose, isomerization to xylulose under Lewis-acid catalysis, and dehydration in an acidic medium, with the removal of three water molecules to yield furfural^[26]. The second is the “cellulose route”, where cellulose is hydrolyzed to glucose and subsequently converted into furfural through a sequence of depolymerization, isomerization, and net C1-removal steps. However, this route is more challenging to control in terms of kinetics and selectivity^[22]. Structurally, furfural consists of a furan ring

bearing an aldehyde group, combining the high reactivity of aldehydes with the rigidity and conjugation of a heteroaromatic scaffold. This combination enables a wide range of downstream transformations such as hydrogenation, oxidation, rearrangement, and condensation. Typical derivatives include furfuryl alcohol, 2,5-furandicarboxylic acid, and furoic acid, which find extensive use in fine chemicals, polymer materials, and alternative fuels^[27].

1.2 5-Hydroxymethylfurfural

HMF is a prototypical bio-based platform compound formed by the dehydration of hexoses. It is widely employed in the synthesis of levulinic acid, 2,5-dimethylfuran, 2,5-diformylfuran and 2,5-furandicarboxylic acid, which serve as high value-added fuel intermediates and functional monomers^[4–5,28–29]. HMF also plays a foundational role in renewable fuels, polyester materials, and fine chemicals. The molecular structure of HMF comprises a furan ring backbone bearing a hydroxymethyl ($-\text{CH}_2\text{OH}$) group and an aldehyde ($-\text{CHO}$) group, forming a multifunctional “furan ring + hydroxymethyl + aldehyde” motif. This combination imparts high reactivity and structural tunability in a broad range of transformations, including oxidation, hydrogenation, condensation, and polymerization. HMF is mainly formed through thermal cleavage and *in situ* dehydration of C6 sugar fragments originating from cellulose, hemicellulose, and lignin-carbohydrate complexes (LCC) (Figure 2). In the temperature range of 300–350 °C, cellulose first undergoes depolymerization and intramolecular dehydration to produce levoglucosan and other anhydrosugars, together with small amounts of C6 oligosaccharides.

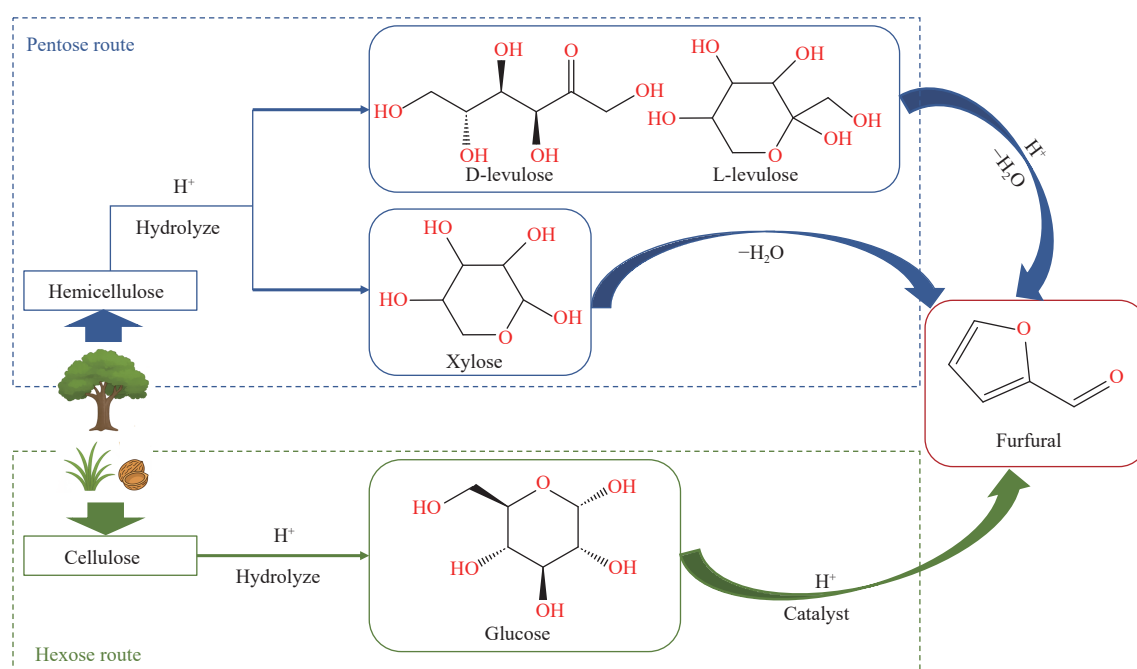


Fig. 1 Schematic diagram of the furfural formation pathway

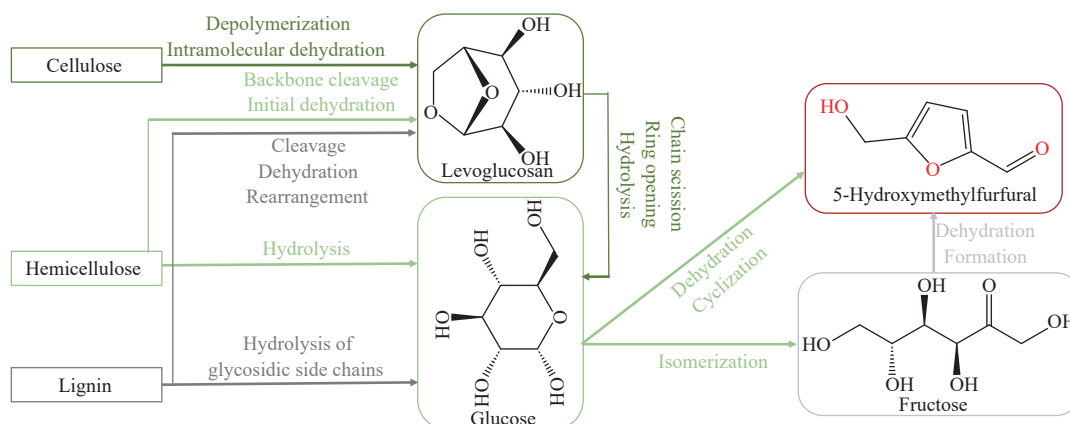


Fig. 2 Schematic diagram of HMF formation pathway

These intermediates subsequently undergo chain scission, hydrolysis, and ring opening to generate hexose monomers such as glucose, mannose, and galactose. These hexoses are partially converted to fructose *via* aldose-ketose isomerization under mildly acidic conditions, providing suitable precursors for high-selectivity dehydration to HMF^[6,9–10,12]. C6 units in hemicellulose and glycosyl side chains in LCCs decompose and hydrolyze preferentially at 220–320 °C, thereby replenishing the pool of C6 monosaccharides and anhydrosugars. Simultaneously, the release of acetic acid and other small organic acids establishes an *in situ* acidic microenvironment that promotes hexose isomerization and subsequent dehydration and rearrangement^[9,30–31].

On this basis, hexoses and their fructose-type intermediates are converted into HMF *via* multi-step dehydration and ring-closure rearrangement under intermediate temperatures of 300–350 °C, short residence times, and mildly acidic gas-solid interface conditions. Aldoses such as glucose first undergo ring opening and proton transfer to form ketose intermediates, followed by the removal of three water molecules and construction of the furan ring to yield HMF. The fructose route is generally considered more favorable for selective HMF production^[26,32]. Fast pyrolysis and two-step pyrolysis studies reveal that, in cellulose/hemicellulose-rich systems operated at intermediate temperatures and short residence times, the volatile fraction contains anhydrosugars, furanic species, and small amounts of HMF. As the temperature increases from 350 to 450–500 °C, the contents of furans, ketones, and other oxygenated small molecules increase markedly^[6,9–10,12]. However, HMF is highly susceptible to secondary reactions at high temperatures and long residence times, including rehydration to organic acids, ring opening, condensation, and carbonization. These reactions drive its further conversion into small gases, deeply deoxygenated products, and inert char^[12–13]. Biphasic solvent extraction, rapid quenching, and ionic liquids or deep eutectic solvents are commonly employed to simultaneously promote HMF formation and retention, thereby enhancing HMF selectivity and mitigating over-conversion. Overall, HMF exhibits substantial diversity in molecular structure, formation

pathways, and subsequent functionalization routes, and serves as a critical molecule linking biomass resources to a wide array of oxygen-containing organic compounds.

1.3 Other small-molecule aldehydes

Typical small-molecule aldehydes produced in biomass pyrolysis include formaldehyde, acetaldehyde, and acrolein, which share the structural feature of a short carbon chain with a terminal carbonyl (–CHO) group. These aldehydes have two contrasting roles in pyrolysis systems. On the one hand, they readily undergo condensation and polymerization, contributing to the instability and aging of bio-oil. On the other hand, they serve as valuable intermediates in conventional chemical production: formaldehyde is a key feedstock for many resins and plastics, acetaldehyde is widely used in the manufacture of acetic acid and polymers, and acrolein is a crucial precursor for acrylic acid and its esters. Small aldehydes are mainly generated from the thermal decomposition of lignocellulosic biomass. Cellulose and hemicellulose can form acetaldehyde and acrolein *via* depolymerization, retro-aldol cleavage, and partial dehydration of sugar intermediates^[33]. In parallel, terminal chain scission and demethoxylation reactions, especially the cleavage of lignin aromatic side chains, are important pathways for formaldehyde formation. As small aldehydes are both key contributors to bio-oil instability and potential platform chemicals, process design must achieve a balance between suppressing their detrimental effects and enabling their selective production and efficient capture. Related analytical techniques and process-stabilization strategies will be discussed in an integrated manner in subsequent sections on process control and catalytic systems.

1.4 Ketones

Ketones are characterized by a carbonyl group (–C=O–) bonded to two carbon atoms. Compared with aldehydes, ketones generally exhibit higher molecular stability under thermal and oxidative conditions, while retaining substantial reactivity toward condensation, cyclization, and

hydrogenation^[34]. Bio-based ketones can be broadly categorized into aliphatic ketones (e.g., acetone, methyl ethyl ketone), cyclic and enone-type ketones (e.g., hydroxyacetone, 2-cyclopentenone, 3-methyl-2-cyclopentenone, levoglucosenone), and aromatic ketones (e.g., acetophenone, 4-hydroxyacetophenone, vanillin acetone). The formation pathways of these ketones are closely related to the nature of the carbon source. Carbohydrates yield a variety of aliphatic and cyclic ketones through retro-aldol fragmentation, dehydration, and cyclization during pyrolysis, whereas cleavage and selective oxidation of lignin side chains lead to the formation of aromatic ketones. Applications of ketones span both bulk and fine chemical sectors: acetone and methyl ethyl ketone are widely used industrial solvents, cyclohexanone is a key intermediate for caprolactam production (the monomer for nylon 6), and enones and aromatic ketones serve as core scaffold precursors for fine chemicals and pharmaceuticals^[35–36].

1.5 Aromatic carbonyl compounds

Aromatic carbonyl compounds are characterized by the conjugation of an aromatic ring with a carbonyl group ($-\text{CHO}$ or $-\text{C}=\text{O}-\text{R}$), often bearing hydroxyl or methoxy substituents inherited from lignin. These substituents confer enhanced reactivity and broad functionalization potential^[37]. As high-value target products that retain both the aromatic ring and carbonyl functionality, their formation pathways are closely linked to lignin structural evolution^[38]. Under non-oxidative pyrolysis, cleavage of linkages such as $\beta\text{-O-4}$ yields a variety of phenolic monomers, which can undergo further side-chain scission to yield aryl-alkyl ketones (e.g., vanillin acetone, and 4-hydroxyacetophenone) and minor amounts of aromatic aldehydes (e.g., benzaldehyde and

anisaldehyde). Under moderately oxidative conditions, certain phenolics can be selectively transformed into aromatic aldehydes such as vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde. Aromatic carbonyl compounds mainly comprise aromatic aldehydes (e.g., vanillin, syringaldehyde, *p*-hydroxybenzaldehyde, benzaldehyde, anisaldehyde) and aromatic ketones (e.g., acetophenone, 4-hydroxyacetophenone, vanillin acetone). Vanillin and syringaldehyde are important flavor and fragrance molecules; acetophenone derivatives are key intermediates in pharmaceuticals and fine chemicals; and vanillin acetone is a promising precursor for polymers and specialty chemicals. Thus, aromatic carbonyl compounds are not only high value-added products of lignin-directed conversion but also core platform molecules for developing bio-based aromatic chemicals and their associated value chains.

2 Biomass pyrolysis

Lignocellulosic biomass comprises natural organic matter derived from woody plants (e.g., trees), herbaceous plants (e.g., cereal crop straw), and nutshells (e.g., rice husk, coconut shell, peanut shell). Its primary structural components are cellulose, hemicellulose, and lignin (Figure 3). In typical lignocellulosic feedstocks, cellulose accounts for 40%–60%, hemicellulose for 20%–40%, and lignin for 10%–25%^[39–40]. The relative proportions and structural features of these three biopolymers jointly determine biomass reactivity. Cellulose provides a crystalline framework of glucose units, hemicellulose contributes amorphous and more reactive glycosyl side chains, and lignin imparts aromatic stability and hydrophobicity. Consequently, biomass exhibits intrinsically complex and heterogeneous decomposition behavior during pyrolysis and catalytic conversion.

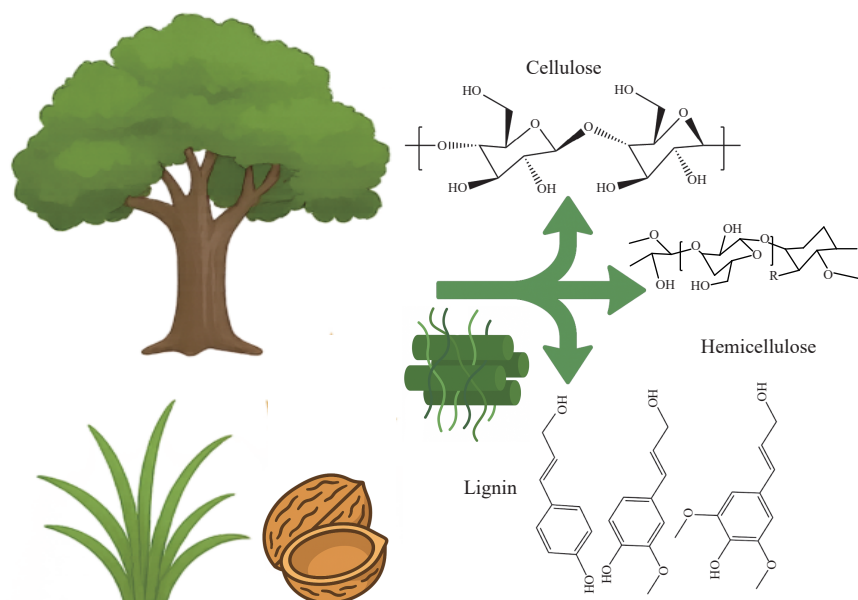


Fig. 3 Chemical structure of lignocellulosic biomass

Biomass pyrolysis typically proceeds through three stages^[41]. At low temperatures, moisture is removed through evaporation. Between 200 and 400 °C, primary decomposition of the organic matrix becomes dominant. At higher temperatures, secondary reactions generate relatively stable gaseous, liquid and solid products. Within this framework, cellulose, hemicellulose, and lignin display distinct decomposition windows and pathways. Hemicellulose decomposes first, mainly in the range of 200–280 °C. It initially undergoes deacetylation to generate acetic acid, accompanied by partial decarboxylation and CO₂ release. Subsequent cleavage of glycosidic bonds liberates pentose monomers, which then undergo consecutive dehydration and cyclization in acidic environments to yield furfural and other small aldehydes. Cellulose decomposes rapidly at slightly higher temperatures, typically between 250 and 400 °C. Transglycosylation reactions generate oligosaccharides and anhydrosugars, which then undergo retro-aldol fragmentation, C–C and C–O bond cleavage. Subsequent decarbonylation and decarboxylation produce glycolaldehyde, hydroxyacetone, acetaldehyde, and a portion of HMF. Lignin degrades more slowly over a broader temperature range of roughly 300–550 °C. Cleavage of ether linkages such as beta-O-4, beta-scission of aliphatic side chains, and selective oxidation of the phenylpropane side chain, combined with decarbonylation and decarboxylation, gradually release phenolic species and aromatic aldehydes and ketones such as vanillin and acetophenone. These transformations are accompanied by substantial char formation^[42]. Fast pyrolysis and Py-GC/MS studies indicate that, in the absence of added catalysts, the total yield of aldehydes and ketones from typical crop straw and sawdust, including small aldehydes, aliphatic and cyclic ketones, and furanic aldehydes, is about 3%–8%. For cellulose- and hemicellulose-rich feedstocks, the yields of carbonyl compounds are typically one to two times higher than those of lignin-rich feedstocks. These baseline distributions and yields provide a quantitative reference for subsequent catalytic strategies aimed at concentrating and upgrading aldehyde and ketone platforms.

2.1 Cellulose-rich biomass

Cellulose-rich biomass, exemplified by cotton stalks, bast fibers, and cereal straws, is dominated by highly crystalline cellulose composed of linear glucan chains connected by beta-1,4-glycosidic bonds. These chains are organized into a polymer network with high crystallinity and interspersed amorphous domains through intra- and intermolecular hydrogen bonding^[41,43–44]. During the pyrolysis of cellulose-rich biomass, aldehydes and ketones are mainly formed through three major pathways associated with anhydrosugars, retro-aldol reactions, and enediol rearrangements^[42,45]. In the anhydrosugar pathway, cellulose first undergoes depolymerization and transglycosylation to

form oligosaccharides and anhydrosugars. These intermediates then undergo 1,2-enolization followed by multistep dehydration and cyclization, producing HMF, levoglucosenone, and other furanic species and cyclic ketones. Subsequent fragmentation coupled with partial decarbonylation and decarboxylation releases small aldehydes and ketones such as acetaldehyde. In the retro-aldol pathway, random chain scission combined with C2–C3 or C3–C4 retro-aldol reactions generates C2–C3 dicarbonyl fragments such as glyoxal and methylglyoxal. These fragments subsequently undergo decarbonylation, decarboxylation, and rearrangement to form products such as acetaldehyde and hydroxyacetone. In the enediol rearrangement pathway, glucose and fructose intermediates isomerize and rearrange through enediol intermediates, directly yielding dicarbonyl compounds such as glyoxal and hydroxyacetone.

Recent *in situ* infrared spectroscopy and multistep kinetic modeling studies indicate that these three pathways correspond to distinct temperature regimes of cellulose pyrolysis^[30]. In the activation stage at 150–300 °C, hydrogen bonds are partially broken, accompanied by limited dehydration and glycosidic bond cleavage, leading to the formation of active and partially dehydrated cellulose^[30]. In the depolymerization stage at 300–390 °C, anhydrosugars and intermediate sugars are produced on a large scale, serving as the main carbon sources for subsequent furanic and dicarbonyl compounds^[46–47]. In the charring stage at approximately 390–650 °C, anhydrosugars and furanic species undergo ring opening and C–C bond cleavage, gradually transforming into aliphatic aldehydes, ketones, and carboxylic acids, accompanied by the formation of irregular char structures^[30,46]. These pathways often operate concurrently in the presence of inherent minerals and collectively determine the distribution of aldehydes, ketones, and furanic products. Anhydrosugars are the principal intermediates in cellulose pyrolysis, with yields of 20%–60% and typically peaking around 400 °C. At higher temperatures, they undergo consecutive dehydration and C–C and C–O bond cleavage, and are further converted into furans such as furfural and HMF, together with small aldehydes and ketones^[41,48].

Alkali metals, especially potassium, can significantly modify this behavior. Potassium weakens hydrogen bonding, lowers cellulose crystallinity, and suppresses anhydrosugar formation. Furthermore, it promotes ring opening, retro-aldol cleavage, and furan formation. Consequently, the carbon flux shifts from an “anhydrosugar-cyclic ketone” route toward a route dominated by lighter carbonyl compounds such as furfural^[30,49]. *In situ* DRIFTS and TG-MS measurements demonstrate that potassium accelerates dehydration and activation at low temperature by attacking hydrogen bonds in crystalline domains. Potassium also interacts with carbonyl groups in intermediates to form C–O–K structures. This interaction suppresses anhydrosugar formation and promotes rearrangement toward furans and

linear ketones and aldehydes. It also enhances the thermal stability of certain carbonyl species at higher temperatures, enabling linear aldehydes and ketones to be released over an extended high-temperature range^[30].

These mechanistic insights suggest several effective strategies for promoting aldehyde and ketone formation. Control of medium-temperature pyrolysis in the range of 300–400 °C, careful adjustment of residence time, acid-washing to remove alkali metals, and introduction of acidic catalysts can all markedly increase the yield and selectivity of aldehydes and ketones such as HMF and furfural. Quantitative studies using staged and two-step pyrolysis further support this view. In segmented pyrolysis between 250 and 550 °C, about 78.6% of cellulose-derived bio-oil is generated at 350 °C, and the products at this stage are predominantly anhydrosugars, ketones, aldehydes, and other light oxygenated organics^[12]. In two-step pyrolysis systems, increasing the combined cellulose and hemicellulose content leads to a pronounced increase in the relative contents of aldehydes, ketones, furans, and acids in both steps, whereas lignin-rich fractions mainly contribute phenolics and hydrocarbons^[9].

Real cellulose-rich fibers, such as flax fibers and pine needles, exhibit similar behavior. Py-GC/MS analyses indicate that, within the contraction window of 335–400 °C, furans and ketones are strongly enriched with increasing temperature, forming key families of carbonyl compounds in the volatile fraction^[10–11]. For high-ash crop residues subjected to anaerobic digestion, slow, fast, and microwave pyrolysis processes typically yield about 35%–46%, 36%–40% and 8%–27% bio-oil, respectively. Although cellulose and hemicellulose are partially degraded, substantial amounts of aldehydes, ketones, and phenolics persist in the resulting bio-oils, indicating that residual cellulose still plays an important role in constructing the aldehyde and ketone pool^[50]. Under typical fast pyrolysis conditions, cellulose-rich feedstocks deliver total yields of anhydrosugars, furans, and small aldehydes and ketones of several% up to more than 10%. In contrast, lignin-rich

feedstocks under similar conditions generate only minor amounts of aldehydes, ketones, and furans, with phenolics and aromatic hydrocarbons predominating in the bio-oil^[9,12,46].

Overall, in cellulose-rich biomass, cellulose undergoes depolymerization and transglycosylation to form anhydrosugar and glucose intermediates. These intermediates converge into a furanic pool and a C2–C3 dicarbonyl pool through enediol rearrangements, successive dehydration and cyclization, and retro-aldol cleavage. Subsequent ring opening, beta-scission, and decarbonylation/decarboxylation convert these intermediates into small aldehydes and ketones. In parallel, competing deep deoxygenation and condensation pathways divert part of the carbon flux into acids, gases, and char or aromatic products. This network of reaction pathways, summarized schematically in Figure 4, provides a mechanistic foundation for designing catalytic strategies to steer cellulose pyrolysis toward targeted aldehyde and ketone platform molecules.

2.2 Hemicellulose-rich biomass

Hemicellulose-rich biomass, including hardwoods, herbaceous plants, and agricultural crop residues, is dominated by xylan. It consists mainly of pentoses (xylose and arabinose) with smaller amounts of hexoses (glucose and mannose). The structure is amorphous and highly branched, with a relatively low degree of polymerization. Consequently, its thermal stability is significantly lower than that of cellulose and lignin, and it enters the main pyrolysis stage at approximately 220–320 °C^[10,15,50–53]. Multicomponent kinetic analyses, together with thermogravimetric measurements coupled to infrared and chromatographic detection, indicate that mass loss in hemicellulose-rich systems involves four parallel volatilization events, namely pseudo-drying, hemicellulose, cellulose, and lignin.

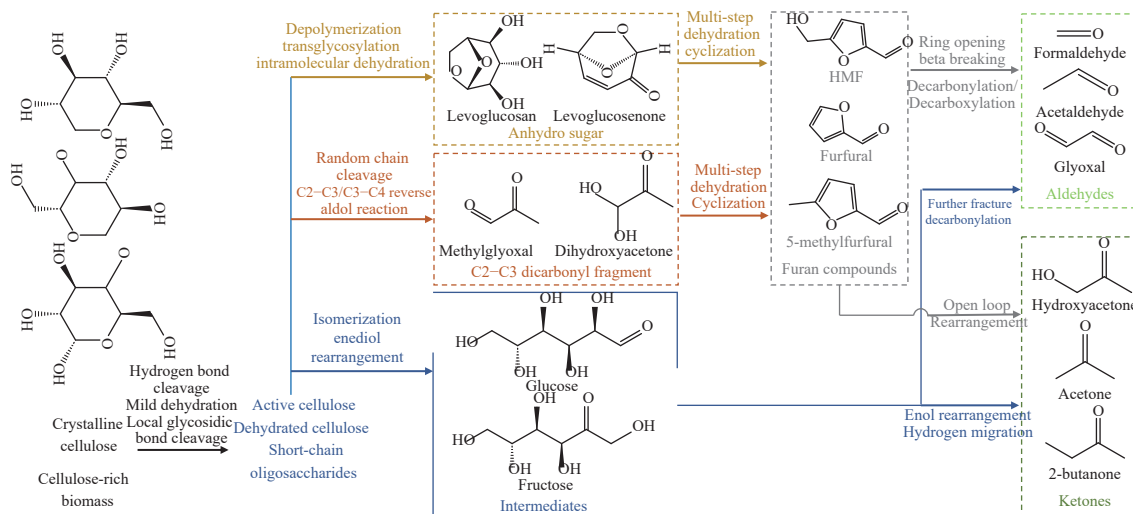


Fig. 4 Schematic reaction pathways for aldehyde/ketone carbonyl compound formation from cellulose-rich biomass pyrolysis

The apparent activation energy associated with the hemicellulose event is slightly lower than that of cellulose, at about 160 kJ/mol. Thus, hemicellulose is the primary contributor to early exothermic behavior and release of small oxygenated products^[50,53]. At the molecular level, hemicellulose pyrolysis begins with cleavage of acetyl groups and decarboxylation, generating acetic acid and releasing CO₂. This simultaneously creates an *in situ* acidic environment that promotes subsequent dehydration and cyclization of pentoses. Subsequent cleavage of glycosidic bonds along the xylan backbone produces pentose monomers and low-molecular-weight oligosaccharides. Under acid catalysis, these pentoses isomerize and undergo consecutive dehydration and cyclization, followed by rearrangement to yield furfural and other pentose-derived furanic aldehydes. Minor hexose units follow a similar route, producing HMF and 5-methylfurfural^[9–10,52]. With increasing temperature, the furan ring and residual sugar moieties undergo retro-aldol cleavage and random C–C bond scission. These reactions generate C2–C3 dicarbonyl compounds such as glyoxal and hydroxyacetone, along with small aldehydes and ketones. At higher temperatures, hemicellulose, cellulose, and lignin act synergistically. Intermediates from hemicellulose and lignin can react with H and OH fragments supplied by cellulose, promoting ring opening and formation of linear C5 and C6 structures and cyclopentanone-type compounds^[9,11].

In situ micro-Py-GC/MS measurements reveal that hemicellulose-rich biomass undergoes considerable shrinkage in the range of 335–370 °C. This contraction is strongly correlated with the peak release of furans and ketones, indicating that hemicellulose-dominated backbone rearrangement and carbonyl formation are closely linked to macroscopic structural deformation^[10]. In nitrogen-enriched systems and in co-pyrolysis with plastics, hemicellulose-derived aldehydes, ketones, and furans serve as key precursors to nitrogen-containing heterocycles and long-chain hydrocarbons. In calcium-assisted nitrogen-enriched pyrolysis, conversions of aldehydes, ketones and furans reach approximately 92%, 71% and 100%, respectively, underscoring their central role as intermediates in nitrogen-heterocycle formation^[49]. During co-pyrolysis with polyethylene, high-temperature radical processes promote carbonyl cleavage and deoxygenation. Hemicellulose-derived phenolics and saccharides are further hydrogenated to hydrocarbons, while hemicellulose inhibits the conversion of certain esters^[54].

Product distributions and quantitative data demonstrate that hemicellulose-rich biomass has a strong tendency to form furfural and small carbonyl compounds. In two-step pyrolysis systems, the first, lower-temperature step predominantly forms ketones, acids and alcohols, whereas the second, higher-temperature step yields more hydrocarbons. As the combined cellulose and hemicellulose content increases, the relative contents of aldehydes, ketones, furans, acids and alcohols in the first step increase. In the second step, aldehydes, ketones, and acids also increase, while phenolics and hydrocarbons decrease. This

indicates that hemicellulose and cellulose jointly control the abundance of early-stage oxygenated liquids^[9]. Kinetic-process simulations of fast pyrolysis combined with multivariate statistical analysis further reveal that, across sixty different biomass feedstocks, hemicellulose and cellulose contents are strongly positively correlated with aldehydes, ketones and anhydrosugars such as levoglucosan in the resulting bio-oils. They exhibit a negative correlation with phenolics and aromatic fragments that are characteristic of lignin-rich feedstocks. Therefore, hemicellulose and lignin mainly govern the distribution of functional groups in biomass-derived oils^[6]. In model mixtures, appropriate cellulose to hemicellulose ratios, such as 2:1, significantly enhance the yields of small “hydrogen-storage-type” carbonyl compounds such as glyoxal and hydroxyacetone. Conversely, excessive hemicellulose content suppresses the formation of these small molecules and favors the generation of gaseous and solid products, particularly char^[11].

For hemicellulose-rich agricultural and forestry residues such as flax fibers and mallow stalks, Py-GC/MS and TG-FTIR analyses confirm that ketones and aldehydes, together with phenolics and hydrocarbons, constitute the main energy-containing components in the volatiles. The volatilization peak associated with the hemicellulose–cellulose fraction accounts for a large share of these species^[10,50,53]. It is reported that xylan and hardwood core tissues can yield about 5%–15% furfural under medium temperatures of 220–320 °C, rapid heating, and short residence time. Moreover, the combined carbonyl yield of furfural plus HMF is substantially higher than the roughly 1%–5% typically observed for cellulose-rich or lignin-rich feedstocks^[6,9,51–52]. Taken together, these results indicate that hemicellulose is the predominant carbon source for furfural and related pentose-derived carbonyl platform molecules. These mechanistic and quantitative insights provide clear guidance for process design with the objective of producing aldehydes and ketones from hemicellulose-rich biomass. Priority should be given to maintaining the temperature window within 220–320 °C, shortening gas-phase residence time, and combining de-ashing or acidification pretreatments with careful adjustment of inorganic mineral composition; these steps can maximize the formation of furfural and C2–C3 small carbonyl compounds in the medium-temperature regime. At the same time, excessive cracking and condensation in the high-temperature regime should be minimized in order to avoid loss in selectivity^[6,9,11,53–54].

In summary, hemicellulose in hemicellulose-rich biomass undergoes three competing pathways during pyrolysis. First, chain scission generates pentose monomers and low oligomers through dehydrative condensation. Second, the resulting monosaccharides undergo dehydration and cyclization to produce furanic or pyranic carbonyl compounds, such as furfural. Finally, fragmentation of these ring structures yields small oxygenated compounds. The distribution of these reaction pathways is illustrated in Figure 5.

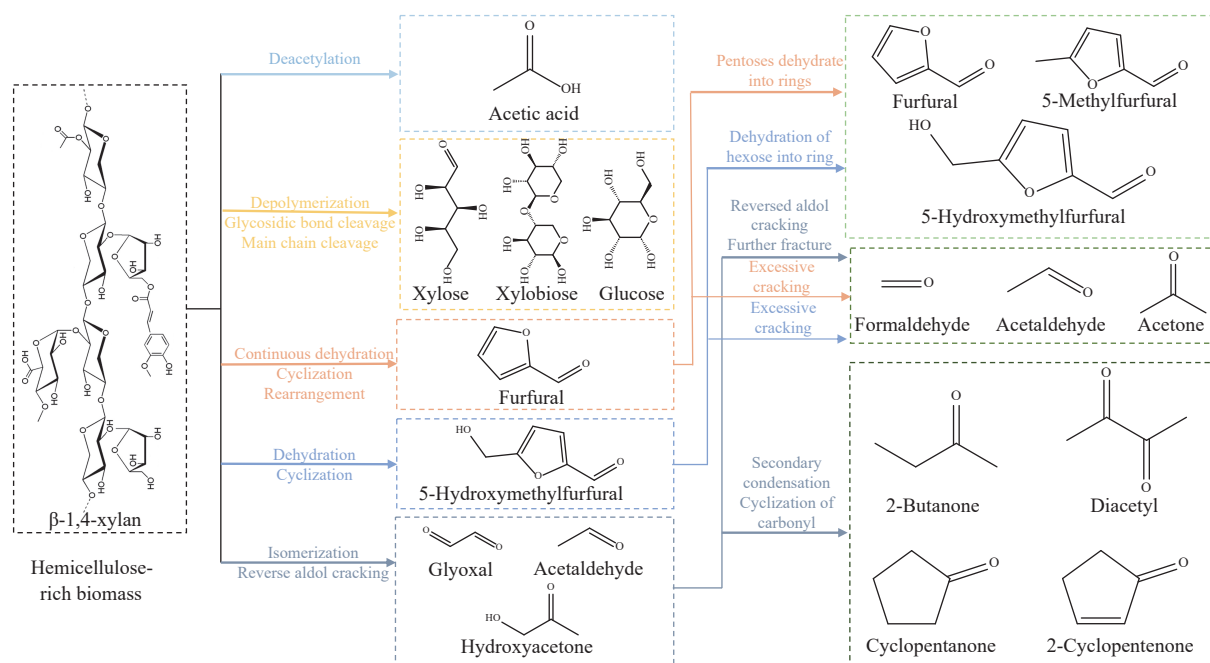


Fig. 5 Schematic reaction pathways for aldehyde/ketone carbonyl compound formation from hemicellulose-rich biomass pyrolysis

2.3 Lignin-rich biomass

Lignin-rich biomass, such as softwoods, bark, nutshells and urban pruning residues with a high fraction of bark and leaves, is composed of highly crosslinked aromatic phenylpropane units (H, G and S units). It is characterized by abundant phenolic hydroxyl, methoxy, and side-chain carbonyl groups and exhibits a broad pyrolysis temperature window of about 250–600 °C. Under inert atmospheres, lignin-rich feedstocks preferentially produce phenolic compounds and other aromatic species, accompanied by aromatic aldehydes, ketones, and char^[3,9–10,55–56]. Mechanistic studies indicate that, below 400 °C, lignin pyrolysis is dominated by cleavage of ether linkages such as beta-O-4 and by dehydration or scission of aliphatic side chains. These reactions release guaiacol, phenol, ortho- and para-methoxyphenols, and aromatic carbonyls such as vanillin, vanillin acetone, and syringaldehyde. When the temperature exceeds 400 °C, further cleavage of O–CH₃ and side-chain C–C bonds occurs, and aromatic rings undergo decarboxylation, decarbonylation and condensation, driving phenolic intermediates toward polycyclic aromatic hydrocarbons and char-like structures^[10,19,56–57].

In real lignin-rich biomass, depolymerization of LCC, together with hydrolysis, dehydration and cyclization of glycosyl units on side chains and embedded carbohydrate fragments, can generate furanic aldehydes such as furfural and HMF. In subsequent decarboxylation and C–C bond cleavage steps, these aromatic aldehydes, ketones and dicarbonyls yield low-carbon-number aliphatic aldehydes and ketones. As a result, although phenolics and char remain the dominant products, lignin-rich systems co-produce a non-negligible fraction of aldehyde and ketone compounds^[10–11,57–58]. Stepwise and segmented pyrolysis

studies reveal that, in the initial stage between 250 and 350 °C, lignin-derived phenolics and aromatic carbonyls are preferentially enriched. Further heating to 350–550 °C enhances aromatization and condensation of these intermediates, converting part of the carbonyl species into more stable aromatic and carbonaceous structures^[9,12].

Quantitative analyses confirm that lignin-rich feedstocks predominantly form phenolic and aromatic fragments, whereas aldehyde and ketone carbonyls are formed only at low levels. For example, wood residues with a lignin mass fraction of about 11% subjected to slow fixed-bed pyrolysis at 290–480 °C yield a bio-oil in which phenolics and other aromatic compounds account for more than 50% of the organic peak area. The combined content of aliphatic and aromatic aldehydes and ketones is about 2% and that of acids is about 3.5%, both clearly lower than the phenolic fraction^[17]. Leaves and bark from urban pruning trees such as Liquidambar styraciflua, with lignin contents of approximately 28% and 45%, show similar behavior under micro-scale fast pyrolysis at 600 °C, where mono-phenols and polyphenols dominate and only small amounts of acids, aldehydes, and ketones are detected^[56]. Py-GC/MS analysis of lignin isolated from coffee husk residues likewise reveals that, although twenty-six oxygenated intermediates including acids, aldehydes, and ketones can be identified, aromatic compounds remain the main components in bio-oils^[58]. Kinetic modeling and multivariate statistical analysis across sixty different feedstocks further demonstrate that lignin content correlates strongly and positively with phenolics and aromatic species (“pyrolytic lignin”). In contrast, aldehyde and ketone carbonyls correlate positively with cellulose and hemicellulose and negatively with lignin^[6]. Thus, compared with carbohydrate-rich feedstocks, lignin-rich biomass exhibits a characteristic high-phenolic, low-carbonyl product distribution.

In component co-pyrolysis systems, H and OH fragments and small aldehydes and ketones derived from cellulose and hemicellulose promote lignin side-chain cleavage and formation of aromatic carbonyls. At the same time, these highly reactive aldehydes and ketones readily undergo condensation and then deposit on lignin-derived char surfaces, increasing char yield and consuming free carbonyl species^[9,11,19]. Under oxygen- or nitrogen-containing atmospheres, saturated aldehydes, ketones, and carboxylic acids can be further oxidized or aminated to anhydrides or nitrogen-containing heterocycles. Conversions of these species can reach 70%–90%, further reducing the proportion of detectable aldehydes and ketones in the final liquid products^[13,49].

Available data indicate that, under inert atmospheres at 350–500 °C, fast or staged pyrolysis of typical lignin-rich feedstocks yields total phenolics and aromatic carbonyls such as vanillin, vanillin acetone, and acetophenone at about 10%–20% of the feed. In contrast, small carbonyl compounds such as furfural, HMF and low-carbon-number aliphatic aldehydes and ketones remain below about 1%–3%^[6,10,12,17,58], significantly lower than the aldehyde and ketone yields observed for cellulose- and hemicellulose-rich feedstocks^[6,11]. To enhance the yield and selectivity of aldehydes and ketones in lignin-rich biomass while retaining the advantageous production of phenolics, it is beneficial to operate in the medium to high temperature range of 350–500 °C with relatively high heating rates or staged pyrolysis in order to suppress condensation and charring. These thermal conditions can be combined with feedstock de-ashing, co-pyrolysis with carbohydrates, and introduction of appropriate alkali metals or acidic catalytic sites, to promote beta-O-4 bond cleavage and side-chain carbonyl retention, thereby maximizing the formation of aromatic and small-molecule aldehydes and ketones.

Overall, in lignin-rich biomass, phenylpropane units and LCC structures undergo cleavage of beta-O-4, related linkages and side-chains in the range of 250–400 °C. These processes are accompanied by dehydration and cyclization of glycosyl fragments, benzylic oxidation, and

decarboxylation and decarbonylation. They generate aromatic aldehydes and ketones including vanillin, vanillin acetone, and acetophenone, together with small amounts of furanic aldehydes and aliphatic small carbonyl species derived from embedded sugar chains. At higher temperatures and longer residence times, these pathways compete with condensation to char. The distribution of these reaction pathways is schematically illustrated in Figure 6.

2.4 Multicomponent biomass

Extensive experimental and modeling studies on the pyrolysis of multicomponent biomass demonstrate that product distributions in systems containing cellulose, hemicellulose, and lignin deviate markedly from the theoretical values predicted by mass-weighted superposition of the individual components. The deviation is most pronounced for aldehydes, ketones, and related oxygenated intermediates, which display strong synergistic effects^[9]. In two-step pyrolysis systems, comparisons between single-component samples and ternary mixtures reveal that, increasing the combined cellulose and hemicellulose content (i.e., the carbohydrate fraction) enhances the yields of aldehydes, ketones, furans, acids and alcohols in the first step, while reducing phenolic formation. In the second, higher-temperature step, the contents of aldehydes, ketones, and acids continue to rise with increasing carbohydrate content, whereas phenolics, hydrocarbons, and alcohols decrease further. These trends indicate that carbohydrate enrichment promotes the formation of small oxygenated molecules, particularly aldehydes and ketones, while suppressing the lignin-dominated aromatic phenolic pathway^[9]. Fast pyrolysis simulations and cluster analyses across diverse biomass feedstocks further show that high-cellulose and high-hemicellulose feedstocks, such as crop straws, correlate strongly with anhydrosugars, aldehydes, and ketones in the resulting bio-oils. In contrast, high-lignin feedstocks, such as softwoods and bark, correlate with phenolics and aromatic fragments.

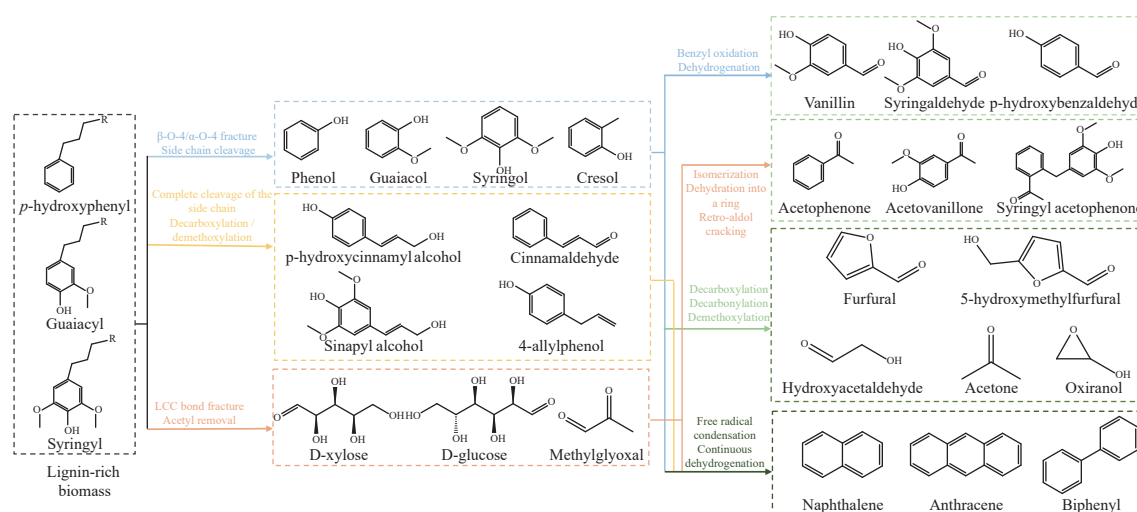


Fig. 6 Schematic reaction pathways for aldehyde/ketone carbonyl compound formation from lignin-rich biomass pyrolysis

Statistically, these two extremes define a continuous tunable spectrum ranging from carbohydrate-driven aldehydes, ketones and anhydrosugars to lignin-driven phenolics and aromatics^[6]. Multicomponent co-pyrolysis therefore alters not only the relative yields of individual functional groups but also the overall balance among aldehydes and ketones, phenolics, and aromatic char. Consequently, the total carbonyl yield and composition of real systems differ significantly from a simple linear superposition of single-component behavior^[6].

In the carbohydrate fraction, the cellulose-to-hemicellulose ratio has a decisive influence on synergistic effects. Studies on model mixtures of cellulose, hemicellulose and lignin show that a ratio of about 2:1 produces the strongest synergy in ring opening of the carbohydrate backbone and in retro-aldol cleavage. Under these conditions, enhanced C2–C3 and C3–C4 retro-aldol scission and acetic acid decarboxylation yield high levels of small aldehydes, ketones and acetic acid. Further increase in the hemicellulose fraction, however, strongly promotes gas and char formation while suppressing aldehydes and ketones in the volatile fraction. This behavior represents a general trend in which a moderate cellulose plus hemicellulose content produces positive synergy, while excessive hemicellulose leads to negative synergy^[11]. Two-step pyrolysis studies confirm that increasing the carbohydrate fraction enriches aldehydes, ketones, furans, and acids in the first-step volatiles. This effect highlights the positive influence of a higher carbohydrate fraction on the formation of aldehydes, ketones, and acids during the second pyrolysis step of the solid residue, compared to the corresponding lignin-rich reference or additive expectations^[9]. Statistical analyses for real biomass indicate that, under comparable fast pyrolysis conditions, cellulose and hemicellulose-rich feedstocks typically yield 5%–15% of furfural, HMF and small aldehydes and ketones, whereas aldehyde and ketone yields from lignin-rich feedstocks are usually in the range of 1%–5%^[6,50]. These results imply that by adjusting the cellulose-to-hemicellulose ratio, both the window and the upper bound for aldehyde and ketone formation in multicomponent systems can be tuned in an endogenous manner, without relying exclusively on external catalysts.

In systems closely resembling real lignocellulosic fibers, multicomponent synergy is strongly related to the evolution of fiber microstructure and porosity. Pyrolysis studies on coniferous and herbaceous fibers, such as pine needles, flax fibers, and wood chips, indicate that, between 300–500 °C, the volatiles contain anhydrosugars, furans, ketones, and small aldehydes such as formaldehyde and acetaldehyde. The contents of ketones and furans increase significantly with temperature^[10,17,50]. For flax fibers, rapid shrinkage of fiber length and cross section is observed in a narrow temperature window around 335–370 °C. This structural contraction corresponds to the release peaks of furans and ketones detected by Py-GC/MS, indicating that internal structural collapse and pore rearrangement are strongly

related to the enrichment of aldehydes and ketones^[10]. Two-step and sequential pyrolysis studies further show that, when cellulose, hemicellulose, and lignin are present as an integrated ternary framework, cellulose and hemicellulose mainly control primary volatiles and the formation of aldehydes, ketones, furans and anhydrosugars. In contrast, lignin dominates the formation of char and phenolics. Moreover, through its thermal properties and structural rearrangement, lignin indirectly controls the temperature and time window for the formation and release of oxygenated small-molecule intermediates^[10,50]. These observations indicate that, in real three-component systems, structure, composition, and product distribution are interrelated. The evolution of porous structure affects heat and mass transfer and amplifies either positive synergy or competitive consumption among components in both space and time.

At the mechanistic level, multicomponent synergy is mainly governed by three processes: formation of *in situ* acidic microenvironments, radical reactions and hydrogen transfer, and interactions between volatiles and the char phase. Hemicellulose, with low thermal stability and abundant acetyl groups, typically decomposes first, releasing acetic acid, CO₂, and light oxygenated molecules^[9–11]. This establishes an acidic and mobile microenvironment inside particles and at gas–solid interfaces, which catalyzes depolymerization, dehydration, and cyclization of cellulose-derived oligosaccharides and anhydrosugars. It further accelerates their conversion into furfural, HMF and small aldehydes and ketones. By modifying local polarity and pH value, it also affects the residence time and secondary reactions of sugar intermediates. Thus, a pronounced positive synergy is produced for small carbonyl intermediates such as glycolaldehyde and hydroxyacetone under medium temperature and short residence conditions^[11]. Concurrently, lignin softens and partially melts in the range of 300–550 °C, forming a viscous aromatic matrix. Phenoxy radicals and phenolic fragments released from lignin capture sugar-derived radicals and participate in hydrogen transfer. At moderate lignin levels, this radical sink and hydrogen donor function inhibits excessive crosslinking and condensation of cellulose and hemicellulose fragments, thereby reducing char formation. It also stabilizes reactive carbonyl intermediates and facilitates the release of light aldehydes and ketones from the viscous phase^[9]. However, at excessive lignin fraction or temperature, this radical network shifts toward aromatic condensation and heavy tar formation, directing aldehydes and ketones into deep deoxygenation and aromatization pathways^[13].

In real biomass, the three major components are not simply physically mixed but are tightly interconnected through LCC, ether linkages, and hydrogen bonds^[10,49–50]. This connectivity imparts distinct structural and spatial characteristics to multicomponent synergy. When LCC are cleaved, aromatic and polysaccharide fragments enter the same reaction zone within very short time and length scales.

This strongly enhances *in situ* acid-catalyzed dehydration, radical scavenging, and hydrogen transfer^[57]. Sequential pyrolysis studies reveal significant cross-deposition and cracking between volatiles derived from cellulose or lignin and char formed from the other component. At 350 °C, cellulose-derived volatiles, particularly aldehydes, condense with lignin char to form oxygen-rich carbonaceous deposits, thereby increasing char yields and consuming part of the aldehydes and ketones. At 650 °C, the same volatiles are more likely to undergo catalytic cracking on the opposite char, which removes aliphatic structures and promotes aromatization of the char phase^[57]. Under oxidizing atmospheres, carboxylic acids, aldehydes, and saccharides in multicomponent systems are preferentially oxidized, broadening the product spectrum toward phenolics and polycyclic aromatic char^[13]. Collectively, these findings demonstrate that volatile-char interactions govern the competition between retention of light aldehydes and ketones and conversion into char or deeply deoxygenated products; these interactions are highly sensitive to temperature and redox conditions^[13,19,57].

At the process control level, regulation of aldehyde and ketone content by multicomponent synergy is a soft-control strategy based on functional division among components, local microenvironment engineering, and rearrangement of competing kinetic pathways. Cellulose and hemicellulose are the main carbon sources for aldehydes, ketones, and anhydrosugars, and generate primary oxygenated molecules such as HMF, glycolaldehyde, acetaldehyde, and hydroxyacetone. Hemicellulose additionally provides furfural through pentose dehydration and releases acetic acid to create an acidic environment. Lignin acts as both a tunable reservoir of radicals and hydrogen donors and as an aromatic matrix. While determining the degree of condensation, charring, and phenolic formation, lignin also regulates the partitioning of sugar-derived intermediates between aldehydes and ketones on one hand and char or heavy tars on the other, through radical scavenging and hydrogen transfer^[13,19,56–57]. Within a medium temperature window of 350–480 °C, under relatively high heating rates, short gas-phase residence times, and efficient quenching, multicomponent synergy can maximize the retention of furfural, HMF and small aldehydes and ketones generated from cellulose and hemicellulose, while suppressing further cracking and deep deoxygenation. Smaller particle sizes and improved heat transfer further amplify these positive synergies^[11]. Available data indicate that, under similar pyrolysis conditions, cellulose- and hemicellulose-rich feedstocks can achieve total aldehyde and ketone yields (including anhydrosugar-derived carbonyls) in the range of 5%–15%, whereas lignin-rich feedstocks typically yield 1%–5%^[6]. Real multicomponent biomass often exhibits positive deviations from these linear superposition values due to synergy. Consequently, a mechanistic understanding of multicomponent interactions, combined with rational adjustment of feedstock composition and operating conditions, enables targeted control of aldehyde and ketone

formation in noncatalytic biomass pyrolysis. Furthermore, it provides a theoretical basis and design guidance for high-selectivity, high-carbon-efficiency pyrolytic biorefinery processes.

3 Biomass catalytic pyrolysis

3.1 Metal salt catalysts

3.1.1 Regulation of aldehyde and ketone product distributions by metal salt type

Metal salts with different cation-anion combinations can direct the product spectrum of biomass pyrolysis toward either oxygenate families or deeply deoxygenated products. Eutectic chloride mixtures containing ZnCl₂ are prototypical systems that promote platform molecule formation. Molten chlorides such as ZnCl₂/KCl/NaCl in the range of 350–450 °C strongly suppress the formation of levoglucosan and complex anhydrosugars and compress the volatiles from carbohydrate-rich feedstocks (e.g., cellulose, straw, pine) into a simplified spectrum dominated by furfural and acetic acid. In the liquid phase, the combined yield of C5 furfural and C2 acetic acid increases sharply^[18,20]. Molten-salt pyrolysis under these conditions therefore functions as an upstream step that selectively generates furfural and acetic acid, which can then be upgraded along aldehyde- and ketone-centered platform routes.

Iron and nickel salts mainly regulate the internal composition of the carbonyl pool by changing the relative proportions of different subclasses. A systematic comparison of Fe(NO₃)₃, FeCl₂, FeCl₃ and Fe₂(SO₄)₃ shows that iron chlorides produce bio-oils in which ketones dominate the volatile fraction, whereas iron sulfates yield bio-oils enriched in carboxylic acids. Iron nitrates primarily promote char graphitization and increase hydrogen content of the gas phase, while exerting only a minor influence on carbonyl distribution^[59]. Similar trends are observed for nickel salts. Among Ni(NO₃)₂, NiSO₄, NiCl₂ and Ni(CH₃COO)₂, nickel chloride favors ketone-rich oils, nickel sulfate promotes phenolic enrichment, and nickel acetate significantly increases furan yields, whereas nickel nitrate has only a weak overall impact^[60]. For a given metal cation, a clear pattern emerges: chlorides favor ketones, sulfates favor acids and phenolics, and carboxylates favor furanic products.

On solid supports, metal chlorides can be combined with tailored porosity to achieve finer control over product distributions. For example, distinct selectivity patterns can be achieved by loading FeCl₃, MnCl₂ or NaCl on hydrochloric-acid-activated peanut shell biochar as a support. FeCl₃-modified biochar shows the highest selectivity toward phenolics and aromatic hydrocarbons in the oil phase. MnCl₂ combines strong decarboxylation activity with high phenolic and aromatic hydrocarbon yields. NaCl does not display pronounced selectivity for any

single product family, but delivers relatively high yields of aromatic hydrocarbons at low loadings^[61]. These results indicate that combinations of alkali metal and transition metal chlorides on mesoporous-microporous carbons can modulate the relative proportions of oxygenated products by tuning acidity, basicity, and pore structure. This, in turn, determines whether aldehyde and ketone intermediates are preserved as platform molecules or are driven further along deoxygenation pathways^[61].

On solid supports, metal chlorides can be combined with tailored porosity to achieve finer control over product distributions. For example, distinct selectivity patterns can be achieved by loading FeCl₃, MnCl₂, or NaCl on hydrochloric-acid-activated peanut shell biochar as a support. FeCl₃-modified biochar shows the highest selectivity toward phenolics and aromatic hydrocarbons in the oil phase. MnCl₂ combines strong decarboxylation activity with high phenolic and aromatic hydrocarbon yields. NaCl does not display pronounced selectivity for any single product family, but delivers relatively high yields of aromatic hydrocarbons at low loadings^[61]. These results indicate that combinations of alkali metal and transition metal chlorides on mesoporous-microporous carbons can modulate the relative proportions of oxygenated products by tuning acidity, basicity, and pore structure. This, in turn, determines whether aldehyde and ketone intermediates are preserved as platform molecules or are driven further along deoxygenation pathways^[61].

Composite catalysts in which metal salts serve as precursors to Ga, Zn, or Ni oxides supported on ZSM-5@SBA-15 represent a contrasting, deep-deoxygenation-oriented strategy. In catalytic pyrolysis, Ga/Zn-ZSM-5@SBA-15 markedly increases selectivity toward aromatic hydrocarbons and phenolics while sharply reducing the contents of carboxylic acids and other carbonyl species in the bio-oil^[62]. In such strong-acid-metal composite systems, aldehydes and ketones are not enriched as the main targets, but function instead as transient intermediates rapidly converted to hydrocarbons. A bifunctional acid-base catalyst consisting of K₂CO₃ and Cu(NO₃)₂ co-loaded on hydrothermally carbonized activated carbon has been applied to liquid-phase esterification and transesterification^[63]. Although not designed for pyrolysis, this system illustrates the broader concept that metal salts can be used to arrange acid-base sites with high precision on biomass-derived carbons, offering a blueprint for future carbon-based bifunctional catalysts tailored to gas-phase transformations of aldehydes and ketones.

Overall, these studies show that appropriate selection and pairing of metal cations and anions enables navigation between several distinct catalytic regimes. Molten chloride salts can be used to selectively generate furfural and acetic acid as upstream platform products. Iron and nickel chloride systems enrich ketones. Sulfate- and carboxylate-based systems favor acids, phenolics, and furans. Deeply deoxygenating metal oxide-zeolite composites and carbon-based bifunctional catalysts drive aldehydes and ketones

further toward hydrocarbons. This spectrum of options provides a multidimensional toolbox for either amplifying or consuming aldehyde and ketone intermediates, underpinning the design of biorefinery flowsheets that place aldehyde and ketone platform molecules at the core of biomass catalytic pyrolysis.

3.1.2 Key mechanisms governing aldehyde and ketone formation and transformation in metal-salt-catalyzed pyrolysis

In metal-salt-catalyzed biomass pyrolysis, aldehydes and ketones are not incidental side products. They serve as critical platform intermediates between sugar-unit dehydration and cleavage on one side and deep deoxygenation and aromatization on the other. Their formation and content are governed by several catalytic factors acting simultaneously. Overall, metal salts reorganize the formation, enrichment, and subsequent fate of aldehydes and ketones through four interconnected mechanistic pathways: coordinated Brønsted and Lewis acidity, which activates C–O bonds and cleaves sugar units; transition-metal redox cycling and hydrogen transfer, which regulate the extent of deoxygenation; anion-controlled hydrolysis, oxidation and decarboxylation chemistry; and restructuring of heat and mass transfer and secondary reaction networks by molten salt phases and porous structures.

The first key mechanism is the combined action of Brønsted and Lewis acidity in C–O bond activation and sugar-unit cleavage. Most metal salts establish local acidic environments that govern dehydration, retro-aldol cleavage, and ring opening, thereby determining whether aldehydes and ketones are formed and retained as intermediates. In molten chlorides, Zn²⁺ acts as a strong Lewis acid and coordinates with glycosidic and ring oxygen atoms. This coordination significantly lowers the barriers for cellulose and hemicellulose depolymerization and dehydration, enabling the sugar backbone to bypass the conventional route through anhydrosugars and subsequent chain condensation. Instead, the carbon flux rapidly converges into a limited set of channels dominated by furfural, acetic acid, and a few other platform molecules^[18,20]. By contrast, Fe and Ni sulfates provide stronger Brønsted acidity, enhancing decarboxylation and deep deoxygenation. Under these conditions, carbonyl species evolve from the aldehyde and ketone stage toward acids and phenolics, rather than accumulating as aldehydes and ketones^[59–60]. In essence, the density and strength of Lewis acid sites determine whether the carbon backbone is intercepted at the aldehyde and ketone platform or driven toward more deeply deoxygenated products.

The second key mechanism is the control of deoxygenation extent by transition-metal redox cycles and hydrogen transfer. Transition-metal cations such as Fe²⁺/Fe³⁺ and Ni²⁺ are transformed in situ during pyrolysis

into nanoscale oxides, carbides, or nitrides. Through redox cycling and hydrogen transfer, these species jointly control bond cleavage, deoxygenation degree, and char formation. Iron oxides and carbides generated from iron salts promote cracking and partial deoxygenation of large oxygenated molecules, and simultaneously induce graphitization of the char phase and enhance H_2 evolution^[59]. In nickel systems, Ni–H species can stabilize radicals and transfer hydrogen to unsaturated oxygenated intermediates. This behavior determines whether aldehydes and ketones are further hydrogenated and condensed, or whether they proceed *via* decarboxylation and decarbonylation toward gases and aromatic hydrocarbons^[60]. Under microwave heating, the high dielectric loss of nickel salts creates local hot spots inside particles, which markedly accelerates radical generation and hydrogen transfer, intensifying these pathways^[60]. By tuning metal oxidation states and the kinetics of hydrogen transfer, a suitable balance can be achieved between retaining aldehydes and ketones and sacrificing them to deeper deoxygenation^[59–60].

The third key mechanism involves anion-governed hydrolysis, oxidation, and decarboxylation chemistry. For a given metal cation, the coordinated anion governs the local acidity, oxidizing strength, and decarboxylation tendency, thereby indirectly controlling the size and composition of the aldehyde and ketone pool. In molten salts and $FeCl_x$ and $NiCl_2$ systems, chloride readily undergoes hydrolysis to release HCl, establishing a strongly acidic gas-solid interface. This environment promotes sugar dehydration, cyclization, and formation of small aldehydes and ketones, while also facilitating chlorination reactions^[59–60]. Nitrate (NO_3^-) combines coordinating ability with oxidizing power. Its decomposition produces NO_x , which favors early oxidation and graphitization of the carbon framework and shifts the system toward deep deoxygenation and char formation, thereby weakening the selectivity toward aldehyde and ketone families^[59–60]. Sulfate forms surface sulfates that strengthen Brønsted acidity and decarboxylation tendencies, and drive carbonyl species from the aldehyde and ketone stage toward acids and eventually aromatic phenols^[59–60]. Acetate readily participates in decarboxylation and dehydration and directs the product distribution toward furanic species, which consumes upstream aldehyde and ketone fragments^[60]. Collectively, these phenomena indicate that the anion defines the boundary conditions of local acidity, oxidizing power, and decarboxylation propensity for any given metal cation^[59–60].

The fourth key mechanism involves the way molten salt phases and porous structures reshape heat and mass transfer, as well as the networks of secondary reactions. Molten salts and porous supports modify heating rates, temperature uniformity, and vapor residence time, thus reconfiguring the secondary pathways of aldehyde and ketone intermediates. Molten chlorides provide Lewis acidity while simultaneously acting as ionic heat-transfer media, markedly increasing heating rates and homogenizing temperature fields. Under

these conditions, sugar-derived intermediates undergo targeted dehydration and cleavage within very short timescales. Then, rapid quenching locks primary products such as furfural into the condensed oil, suppressing subsequent cascade reactions^[18,20]. In contrast, biochars impregnated with metal salts generally exhibit high surface areas and abundant mesopores. Synergy between micropores and mesopores enhances adsorption of volatiles and prolongs their residence time. Phenoxy and related intermediates can then undergo further rearrangement and aromatization within the pore network, reducing aldehyde and ketone accumulation while enhancing the formation of aromatic hydrocarbons and phenolics^[59,61]. Hierarchically porous Ga/Zn/Ni-ZSM-5@SBA-15 catalysts, prepared from metal salt precursors, combine strong acidity and dehydrogenation activity in a micro-mesoporous framework. This structure facilitates the evolution of aldehydes and ketones along sequential decarboxylation and decarbonylation, aromatization, and coking pathways^[62]. Through coordinated design of the metal cation, anion, support or matrix, and the temperature window and residence time, the reaction network can be carefully shifted between regimes where aldehydes and ketones are enriched as platform molecules and regimes where they are almost completely converted into fuel-range hydrocarbons and aromatic chemicals.

Overall, metal salt catalysts for biomass pyrolysis rely primarily on tunable Lewis and Brønsted acidity and on the redox properties of transition metals. Under medium- to high-temperature fast pyrolysis or co-pyrolysis conditions (typically 350–600 °C in fixed-bed or molten-salt configurations), they lower the depolymerization and dehydration barriers of cellulose and hemicellulose. Consequently, complex intermediates are compressed into a narrow-spectrum carbonyl platform centered on furfural, HMF, and small ketones and acids. Under stronger acidity and longer residence times, the same systems promote further decarboxylation, condensation, and aromatization, thereby converting the aldehyde and ketone pool into gaseous products and aromatic hydrocarbons^[29,64]. From the perspective of suppressing side reactions and extending catalyst lifetime, moderate attenuation of Brønsted acid strength and careful control of molten-salt viscosity and mass transfer help inhibit humin formation and irreversible coking, while maintaining the generation of platform molecules such as furfural. In practical terms, halide salts (e.g., $ZnCl_2$, $FeCl_3$ and $NiCl_2$) and sulfates of Fe and Ni show distinct advantages in enhancing yields of furfural and related platform molecules. By contrast, mineral salts of K, Na and Ca in biomass ash mainly create local acidic and basic microenvironments *in situ*. Their active-site types and side-reaction windows are more diffuse and difficult to define, yet they complement metal halides and sulfates in controlling deep deoxygenation and char formation.

Despite these advantages, metal salt catalysts face challenges related to salt corrosion and volatilization, the cost of separation, recycling, and reuse, and difficulties in

precisely controlling local acidity and mass transfer. For applications targeting aldehyde and ketone platforms, metal salts are most suitable as upstream fractionation and enrichment units. Promising strategies include immobilizing or confining salts on thermally stable porous supports, combining staged feeding with on-line regeneration, and coupling these units with robust solid acids, solid bases, or hydrogenation catalysts. These approaches can enhance resistance to sintering and loss while exploiting the strong directing power of metal salts over aldehyde and ketone formation, thereby providing a more controllable route to aldehyde- and ketone-centered biorefinery schemes.

3.2 Metal oxide catalysts

3.2.1 Regulation of aldehyde and ketone product distributions by metal oxide type

In metal oxide-based systems, tuning acidity, basicity, and redox properties allows the balance to be shifted between retaining aldehyde and ketone products and driving them to deep deoxygenation. Thus, the distributions of ketones, aldehydes, acids, phenolics, furfural, and related oxygenated families in bio-oil can be reshaped. Basic CaO and Ca-Al solid bases are among the most typical examples. Acetic-acid-modified CaO significantly increases the density of strong basic sites while preserving the CaO framework. In straw pyrolysis, this modification increases the relative fraction of ketones in the oil from about 27% to about 43%. This indicates that the cleavage pathways of carbohydrate components are effectively locked at the ketone platform stage rather than progressing further toward gases or aromatic hydrocarbons through deep deoxygenation^[65]. In fast pyrolysis of pine sawdust, both CaO and CaO-Ca₁₂Al₁₄O₃₃ (CaAl-3) increase the yields of phenolics and ketones. In particular, CaAl-3 balances deoxygenation ability with structural stability and can act as a long-lived basic generation bed producing intermediate oils enriched in phenols and ketones^[66]. In plastic-biomass co-pyrolysis, the strong basicity of CaO pushes carbonyls further along the reaction network by promoting carbonyl cleavage and hydrogen transfer. During co-pyrolysis of waste masks and Moringa seed cake, the contents of aldehydes, ketones, and acids in the oil decrease significantly, whereas the proportions of alkanes, alcohols, and methyl-containing groups increase, suggesting that carbonyls are increasingly consumed in the form of fuel-type components^[67]. Collectively, these results indicate that the same class of CaO and CaAl basic oxides can be operated in two distinct modes, one that enriches ketones as a platform and another that drives ketones toward complete deoxygenation into fuel-range hydrocarbons^[65–67].

In acidic metal oxides and acid-support-metal oxide systems, complex carbonyl pools are often simplified and directed toward specific platform molecules. Studies on Al₂O₃-loaded dolomite porous ceramics reveal that

increasing Al₂O₃ loading markedly decreases the contents of acids and ketones in the pyrolysis oil, while significantly increasing phenolics and aromatic hydrocarbons. This results in an overall pattern of phenolic enrichment and ketone suppression^[68]. In another acid-metal cooperative system, Pd-PdO/ZnSO₄ channels carbonyl species efficiently into furfural. Under flash pyrolysis at 400 °C, furfural yields reach 74%–82% from C6 cellulose and monosaccharides and up to 96% from C5 xylan. For practical feedstocks such as bagasse and corncobs, furfural yields of 23%–33% are achieved^[27]. ZnSO₄ provides dehydration and isomerization sites, while Pd/PdO selectively cleaves C–C bonds. As a result, carbon that would otherwise distribute over multiple C6 carbonyl platforms such as HMF and levoglucosenone is redirected into a single C5 aldehyde, namely furfural^[27]. In lignin-first cascade utilization, NiMo/Al₂O₃ first performs mild hydrodeoxygenation of lignin oils and then catalyzes pyrolysis of the remaining cellulose-rich residues. In this scheme, about 10% of feed carbon enters hydrocarbons, 8% enters furfural-type compounds, and 9% enters other alternative fuels^[14]. Thus, in acidic and acid-metal systems, aldehydes and ketones, especially furfural, function as designed platform intermediates that can either be collected as final products or upgraded to phenolics, aromatic hydrocarbons, or fuel-range hydrocarbons, depending on the downstream configuration^[14,27,68].

In transition metal oxide systems coupled to gas-phase utilization, metal oxides not only increase liquid yields but also convert part of the carbonyl pool into gaseous reducing agents or precursors for downstream hydrogenation. For example, when Fe₃O₄ nanoparticles catalyze slow pyrolysis of corncobs, the bio-oil yield reaches 55.9% at 450 °C with 2 g of catalyst. The oil contains various light oxygenates, including alcohols, esters, aldehydes, phenolics, ketones, and heterocycles. This indicates that Fe₃O₄ promotes cleavage of lignocellulosic macromolecules into low-carbon-number carbonyls and related species while maintaining moderate deoxygenation^[69]. CuO supported on porous carbon is more often applied in post-treatment of pyrolysis oils. Using methanol as a hydrogen source, it converts aldehydes and ketones in the oil into diols and cyclic alcohols with high selectivity, achieving total yields of about 81%–82%. In this process, carbonyls are converted into more stable and more polar alcohol-type fuel components^[70]. In reduction systems for waste LiCoO₂, CO-rich gases generated by pyrolysis of cellulose-rich, low-lignin biomass can almost completely reduce LiCoO₂ to CoO and Li₂CO₃ within 1 h at 500 °C. Simultaneously, LiCoO₂ and CoO surfaces exhibit deoxygenation activity toward gaseous oxygenates, promoting the formation of monocyclic aromatics^[71]. In these integrated systems, carbonyls and their upstream functional groups are not treated primarily as liquid-phase targets but are deliberately converted into CO, syngas, and sources of reducing equivalents that can be exploited in coupled thermochemical processes^[69–71].

3.2.2 Key mechanisms governing aldehyde and ketone formation and transformation over metal oxide catalysts

In metal-oxide-catalyzed biomass pyrolysis, aldehydes and ketones occupy an intermediate position between sugar-unit dehydration and cleavage at one end and deep deoxygenation and aromatization at the other. Their generation, enrichment, or further consumption is mainly governed by four classes of mechanisms: basic sites and metal oxygen bond structures; cooperation between acid and metal sites; redox cycling and gas phase coupling; and control of residence time and secondary reactions by pore structure and phase state. Together, these four dimensions act as regulatory valves in the reaction network and determine where carbonyl species are intercepted and in what form they exit the system.

Basic sites and Ca–O structures dictate whether carbohydrate cracking stops at the ketone platform stage or proceeds beyond it. In CaO, H–CaO and CaAl systems, the density of strong basic sites and the Ca–O bond length directly influence the adsorption of sugar-derived intermediates on the surface and the barriers for dehydration and decarbonylation. Acetic-acid-modified H–CaO elongates Ca–O bonds and greatly increases the density of strong basic sites. Under these conditions, primary products from cellulose and hemicellulose are readily captured and undergo directed dehydration and decarbonylation. Density functional theory calculations confirm that energy barriers for ketone formation are lowered, while thresholds for further aromatization and complete cracking are elevated. Consequently, the reaction network tends to stabilize at the ketone platform level, leading to ketone enrichment^[65]. In CaO–Ca₁₂Al₁₄O₃₃ solid bases, incorporation of Ca₁₂Al₁₄O₃₃ improves sintering resistance and thermal stability, allowing basic sites to remain active at high temperatures. These sites promote ring opening and carbonyl formation while mitigating structural collapse^[66]. However, when the basic strength or loading is excessively high, or when these oxides participate in plastic co-pyrolysis, these strong basic sites promote decarboxylation, hydrogen transfer, and C–C and C–O bond cleavage. Aldehydes and ketones are then rapidly consumed in secondary reactions, yielding alkanes and alcohols^[67]. By tuning the Ca–O structure and basic strength, this family of basic oxides can switch between two extreme roles: generators that enrich ketones at the platform level or scavengers that drive ketones to complete deoxygenation.

Cooperation between acid and metal sites determines whether specific carbonyl platforms are selectively retained or driven toward deeper upgrading. Acidic oxides and acid-support-metal oxide systems rely on the spatial coupling between Lewis or Brønsted acid sites and metal sites to determine whether carbonyls remain as aldehydes and ketones or are transformed into phenolics, aromatic hydrocarbons, or fuel-range hydrocarbons. For example,

when Al₂O₃ introduces acid sites on dolomite ceramics, it promotes dehydration, rearrangement, and aromatization of acids and ketones in the oil, driving them toward phenolics and aromatic hydrocarbons while partially depleting ketones already at the oil-formation stage^[68]. In the Pd–PdO/ZnSO₄ system, ZnSO₄ provides dehydration and isomerization sites that convert C6 sugars into furfural precursors. The PdO shell on PdO(101) facets selectively performs Grob-type cleavage of the C6 formaldehyde side chain and reforms the released HCHO *in situ* into H₂ and CO. The Pd⁰ core then catalyzes the final dehydration step to yield furfural. As a result, carbon that would otherwise distribute over multiple C6 carbonyl platforms such as HMF and levoglucosenone is funneled into a single C5 aldehyde, strongly suppressing the accumulation of C6 byproducts^[27]. In NiMo/Al₂O₃, Ni and Mo metal sites provide hydrogenation and hydrodeoxygenation functions, while Al₂O₃ supplies acid sites. Upstream, this catalyst performs mild hydrodeoxygenation to convert lignin oils into hydrocarbons. Downstream, it directs cracking of cellulose-rich residues into furfural-type compounds and light hydrocarbons, thereby creating a continuous channel from furfural outlet to fuel inlet within a single catalytic system^[14]. In such acid-metal systems, the balance between acid and metal functions determines which carbonyl families are retained as platforms and which are sacrificed to deeper upgrading.

Redox cycling and gas phase coupling transform carbonyls and their precursors into H₂ and CO or recombine them into alcohols. Metal oxides with pronounced redox activity exploit reversible oxidation states and oxygen vacancies to convert aldehydes, ketones, and upstream oxygenates into gaseous reducing agents or stable liquid products. In Fe₃O₄, the Fe²⁺/Fe³⁺ redox cycle and surface oxygen vacancies promote cleavage of lignocellulosic macromolecules, breaking multifunctional oxygenates into low-carbon-number aldehydes, ketones, and related light oxygenates while achieving partial deoxygenation. This process yields a carbonyl intermediate pool that is easier to control in subsequent upgrading^[69]. In CuO/porous carbon systems, methanol undergoes etherification and reforming on CuO surfaces, generating H₂ and CO₂. Cu²⁺ is reduced *in situ* to Cu⁺ and Cu⁰, which continuously supply surface hydrogen atoms in the catalytic cycle. Aldehydes and ketones in the bio-oil are converted into the corresponding alcohols through one or two hydrogenation steps, enabling carbonyl-to-alcohol transformation without external high-pressure hydrogen^[70]. In systems employing biomass pyrolysis gas to reduce LiCoO₂, CO-rich syngas generated by directed cleavage of carboxyl, carbonyl, ether, and ester groups in cellulose-rich biomass can almost completely reduce LiCoO₂ to CoO and Li₂CO₃ within 1 h at 500 °C. At the same time, LiCoO₂ and CoO surfaces promote deoxygenation of gaseous oxygenates and formation of monocyclic aromatic hydrocarbons^[71]. In these integrated systems, carbonyl fragments are redistributed into H₂ and CO as reducing equivalents and into aromatic products in

the gas phase, shifting carbonyls from liquid-phase platforms to tunable reservoirs of reducing power.

Metal oxide catalysts use tunable basic and acidic sites, metal-oxygen structures, and redox cycling to regulate aldehyde and ketone formation, enrichment, and deep conversion in pyrolysis (400–600 °C) and oil-upgrading (150–350 °C) regimes. Mineral-based oxides such as dolomite and olivine provide stable Ca-Mg-Si-O frameworks with weak acid-base sites that buffer uncontrolled cracking and coking. In contrast, synthetic oxides obtained by impregnation or precipitation allow precise tuning of site density and strength, and can be tailored to select aldehyde and ketone platforms. Basic CaO and CaO-Ca₁₂Al₁₄O₃₃ enrich ketones with moderate deoxygenation and suppress over-cracking and humin formation. Together with acidic zeolites such as Zn/ZSM-5, they function as upstream beds for phenol and ketone generation^[65–67]. Alumina and acid-support-metal oxides such as Pd-PdO/ZnSO₄ and NiMo/Al₂O₃ funnel dispersed carbonyl intermediates into furfural or aromatic platforms. Redox-active oxides such as Fe₃O₄ and CuO cleave and partially deoxygenate oxygenates, converting carbonyl fragments into H₂, CO, or alcohol products. Some challenges remain, such as sintering, carbonation, coking, and poorly controlled local acid-base environments. These issues highlight the need for synergistic design with engineered pore structures and staged reactors such as basic-acid dual beds. Stability and regenerability under long-term cycling can be enhanced by incorporating high-melting-point frameworks (Ca₁₂Al₁₄O₃₃, Al₂O₃, ZrO₂), strong metal-support interactions, and reversible carbonate and redox cycles.

3.2.3 Regulation of aldehyde and ketone product distributions by carbon catalyst type

Compared with metal salts and metal oxides, carbon-based catalysts provide a multifunctional platform integrating Brønsted acidity, Lewis acidity or basicity, tunable metal active centers, and a designed pore environment. During biomass pyrolysis and upgrading, this integration enables stage-specific control of aldehydes, ketones, and adjacent oxygenate families such as furfural, furfuryl alcohol, cyclic ketones, and levulinic acid^[72]. A representative strategy is the preparation of carbon-derived solid acids directly from biomass. By modulating the balance between Brønsted and Lewis acid sites during in situ carbonization, hemicellulose- and cellulose-derived intermediates can be directed toward either furfural or carboxylated ketone type platforms.

This approach is exemplified by a magnetic carbon solid acid obtained by pyrolysis and sulfonation of tobacco stalk, which contains carboxylic Brønsted acid sites (5.04 mol/mg) and a higher density of Lewis acid sites (21.16 mol/mg). In a gamma-valerolactone-water medium, it enables whole-feed conversion of tobacco stalk to furfural, with a

maximum furfural yield of 46.68% at 190 °C for 120 min^[22]. Brønsted acidity drives dehydration of pentose and hexose sugars and their ketose isomers, while Lewis acidity promotes isomerization and stabilizes furanic intermediates, thereby concentrating the carbonyl pool toward furfural^[22]. A complementary example is provided by Mo-doped carbon microspheres obtained through one-pot hydrothermal carbonization of amorphous cellulose with phosphomolybdic acid. Mo₂C and Mo⁶⁺ species act as strong Lewis acid sites that promote glucose to fructose isomerization, while carboxyl groups on the carbon framework provide Brønsted acidity. This combination facilitates dehydration and subsequent hydration pathways to levulinic acid, yielding about 33.02% levulinic acid from corncob at 195 °C for 90 min^[43]. These results highlight a clear design lever. Heteroatom and polyoxometalate-derived motifs embedded into carbon frameworks allow tuning of Brønsted and Lewis acidity, enabling carbon flow to be steered between furfural and levulinic acid platforms^[22,43].

Carbon also plays a distinct role when used as a support for non-noble metals. It promotes high dispersion of metal nanoparticles and simultaneously shapes the local acid-base environment. These combined effects rewire the hydrogenation and rearrangement network linking furfural, furfuryl alcohol, 2-methylfuran, and cyclic ketones. In an integrated molten-salt process, ZnCl₂-containing chloride melts generate furfural-rich volatiles from pine wood. Downstream gas-phase hydrodeoxygenation over Cu/activated carbon at 400–500 °C achieves up to 92% selectivity for furfural to 2-methylfuran. The corresponding 2-methylfuran yield is about 10.3% based on dry pine wood^[73]. Relative to Cu/SiO₂, Cu/activated carbon provides higher Cu loading and dispersion and a milder acidic environment, thereby suppressing side pathways toward cyclic ketones and favoring the route from furfural to furfuryl alcohol and then to 2-methylfuran^[73].

MOF-derived metal-carbon composites widen the range of controllable product outcomes. A CuNi alloy supported on N-doped porous carbon (Ni-Cu-NPC) converts furfural to cyclopentanone with yields above 88.7% in water. Alloy sites catalyze hydrogenation of C=O and C=C, while pyrrolic N in the carbon matrix generates locally acidic motifs such as OH–Ni–N–H⁺ that promote furan-ring rearrangement and intramolecular dehydration, shifting selectivity toward five-membered cyclic ketones^[35]. In contrast, carbon-coated Cu/CuO_x@C derived from Cu-BTC favors the alcohol endpoint. In a formic-acid transfer hydrogenation system at 170 °C, it delivers 99.1% furfural conversion with 98% selectivity toward furfuryl alcohol. The Cu⁰ to Cu⁺ balance and the mild acidity of the carbon shell facilitate C=O hydrogenation while suppressing furan-ring hydrogenation and C–O hydrogenolysis^[74]. These examples highlight a second design lever. Metal identity and alloying determine hydrogenation functions, while N-doped carbon chemistry dictates whether the network terminates at alcohols or proceeds toward cyclic ketones.

For lignin-derived aromatic aldehydes, N-doped carbon

supports can maintain high activity while mitigating over-hydrogenation of the aromatic ring. Ni@CN obtained by pyrolysis of Ni-ZIF at 425 °C contains small Ni particles with high Ni⁰ exposure, which achieves 99.5% vanillin conversion with 98.3% selectivity toward vanillyl alcohol at 80 °C. Electronic interactions between Ni and the N-doped carbon raise the barrier for further hydrogenolysis, maintaining selectivity at high conversion^[75]. Similar acid-base principle applies to furfural hydrogenation. In 33ZrO₂/NC_750 prepared from chitosan, Zr⁴⁺ provides Lewis acid sites, while N species on the carbon and O²⁻ contribute Lewis basicity. Their cooperation promotes transfer hydrogenation in 2-propanol, resulting in 93% furfural conversion and 96% furfuryl alcohol selectivity, while minimal Brønsted acidity suppresses condensation and over-hydrogenation^[23]. A Co-NC/MXene composite obtained by co-carbonizing ZnCo-ZIF with MXene further strengthens this interface control. Co nanoparticles embedded in N-doped carbon are anchored on MXene sheets, and cooperate with MXene surface functionalities to deliver 98.7% furfural conversion and 100% selectivity toward furfuryl alcohol in water at 333 K and 2 MPa H₂^[76]. Collectively, N-doped carbon and carbon-MXene interfaces provide a third design lever. They tune metal dispersion and valence, local acid-base microenvironments, and adsorption strength, thereby shifting distribution equilibria across furan aldehyde, furan alcohol, 2-methylfuran, cyclic ketones, aromatic aldehydes, and aromatic alcohols^[23,35,73–76].

3.2.4 Key mechanisms governing aldehyde and ketone formation and transformation over carbon-based catalysts

In carbon-based catalytic systems, selectivity is jointly governed by the acid-base characteristics of the carbon framework, structure of metal-N-C interfaces, compatibility with a given hydrogen source, and coupling of the catalyst to upstream pyrolysis or hydrolysis. These factors determine whether furanics and aromatic carbonyls are retained as platform molecules or proceed toward alcohols, cyclic ketones, and fuel-range products. Prior work can be organized into four coupled mechanistic pathways.

Acid-site engineering on carbon frameworks controls the convergence of sugars to a narrow platform pool, most notably furfural and levulinic acid. In magnetic carbon solid acids, carboxyl groups supply Brønsted acidity and oxygenated groups while residual metal nodes provide Lewis acidity. Their spatial proximity on porous carbon lowers barriers for hydrolysis, isomerization, and dehydration, enabling direct furfural production from tobacco stalk in gamma-valerolactone and water with yields up to 46.68%. Kinetic fitting indicates an apparent activation energy of about 30 kJ/mol, consistent with stabilization of oxonium-type intermediates at the carbon surface^[22]. In Mo-doped carbon microspheres, Mo₂C and Mo⁶⁺ increase Lewis acidity, while carboxyl groups provide

Brønsted acidity. As a result, isomerization is accelerated and downstream hydration and fragmentation are promoted. This suppresses HMF accumulation and funnels carbon to levulinic acid with yields up to 33.02%^[43]. In ZrO₂/NC, Zr⁴⁺ Lewis acid sites and pyridinic N based Lewis basicity form effective site pairs that favor MPV-like hydride transfer to furfural C=O, delivering about 96% selectivity toward furfuryl alcohol while minimizing condensation and over-hydrogenation^[23]. The central design principle here is the Brønsted to Lewis balance and its spatial pairing, which determines whether the reaction network terminates at furfural or proceeds toward levulinic acid type platforms.

Metal-N-C interface chemistry governs cascade selectivity by integrating hydrogen activation with local rearrangement chemistry. In Ni-Cu-NPC, a CuNi alloy embedded in a pyrrolic N rich carbon matrix forms adjacent hydrogenation and Lewis-acidic motifs in water. This enables a controlled pathway from furfural to furfuryl alcohol and then to cyclopentanone with yield of 88.7%^[35]. In Cu/CuO_x@C, tuning the Cu⁰ to Cuⁿ⁺ balance creates interfacial sites that generate hydrogen from formic acid *via* formate species and polarize furfural C=O, enabling near-quantitative conversion to furfuryl alcohol under transfer hydrogenation^[74]. Ni@CN maintains strong aldehyde hydrogenation activity for vanillin but suppresses deeper hydrogenolysis, sustaining vanillyl alcohol selectivity above 98%^[75]. Co-NC/MXene demonstrates interface regulation, where electronic and acid-base effects lower the H₂ dissociation barrier and stabilize adsorption geometries, achieving nearly complete conversion with 100% selectivity toward furfuryl alcohol at 333 K and 2 MPa H₂^[76]. The key design knob is interfacial coordination and electronic structure, which dictate competitive adsorption and hydrogenation order of C=O relative to aromatic motifs.

Hydrogen-source matching closes the loop between platform formation and selective upgrading. Gamma-valerolactone and aqueous systems provide strong solvation and high proton activity, enabling furfural or levulinic acid formation without external hydrogen donors when combined with acidic carbons^[22,43]. In 2-propanol transfer hydrogenation, ZrO₂/NC couples Lewis acid-base functions to activate the alcohol and polarize furfural C=O within an MPV-type cycle, reducing dependence on high-pressure H₂. With formic acid, Cu/CuO_x@C-450 prioritizes hydrogen generation through formate pathways while maintaining favorable furfural adsorption, achieving above 99% conversion and 98% selectivity toward furfuryl alcohol. Under direct H₂, N-doped carbon and MXene tuning lower H₂ activation barriers and maintain moderate adsorption, allowing hydrogenation to target C=O rather than furan or aromatic rings^[35,76]. The design parameter is therefore not only the catalyst but also the hydrogen donor, since each donor requires distinct site pairing and microenvironments.

Process-level coupling determines whether carbon-based catalysts function as upstream fractionation units or downstream upgrading modules. In molten-salt hydropyrolysis of pine wood, ZnCl₂-KCl-NaCl media

funnel primary vapors toward furfural-rich intermediates, while a downstream Cu/AC bed leverages high surface area and hierarchical porosity to disperse Cu and control vapor residence time. This configuration mitigates undesired chlorinated byproducts and selectively converts furfural to 2-methylfuran in a continuous gas-phase step^[73]. In liquid-phase pretreatment, acidic carbons fractionate native biomass into furfural and levulinic acid platforms^[22,43], which can then be routed over carbon-based hydrogenation catalysts to produce furfuryl alcohol, cyclopentanone, and related fuel intermediates^[23,35,74,76]. The design knob at this level is reactor staging and coupling, which govern the construction and consumption of the platform pool.

Overall, carbon-based catalysts offer a versatile toolbox for building and upgrading aldehyde and ketone platforms under mild conditions (80–220 °C), using gamma-valerolactone, alcohols, formic acid, water, or H₂ as the reaction medium and hydrogen source. Tunable site density, hydrophilicity, and pore architecture suppress acetalization, condensation, and coke deposition while preserving high chemoselectivity. Some persisting challenges include synthesis complexity for MOF-derived and heteroatom-doped carbons, risks of metal sintering and leaching, and mass-transfer limitations in viscous bio-oil environments. Future progress will likely rely on stronger anchoring motifs (e.g., N and P), confinement-enabled architectures, mesopore-rich hierarchical porosity, and regeneration-aware process windows, together with integrated optimization of active sites, hydrogen source, solvent, and reactor configuration.

3.3 Catalytic design principles and process integration toward aldehyde and ketone platforms

Biomass pyrolysis targeting aldehyde and ketone carbonyls requires catalysts capable of sustaining a complex cascade of dehydration, bond scission, and deoxygenation at the carbonyl platform level. The reaction network should neither stall at anhydrosugars and heavy tars, nor be driven prematurely toward deep deoxygenation endpoints such as syngas and aromatics. Therefore, effective solutions require coordinated design across active sites, nanoscale interfaces, transport environments, and process configurations rather than optimization of a single material property.

Acid-base functionality serves as the primary retention point for carbonyl intermediates. Moderately strong, spatially organized Brønsted and Lewis acid sites lower barriers for depolymerization, isomerization, and selective dehydration, thereby channeling carbon from cellulose and hemicellulose into a limited set of furanic and low-molecular-weight aldehyde and ketone platforms^[18,20,59,73]. Basic or amphoteric sites should then be tuned to provide partial deoxygenation capacity while avoiding conditions that drive carbonyls toward excessive cracking, aromatic formation, or hydrocarbon formation^[22,43,65–67,73]. Suppression of humin formation, condensation and coking

should be integrated into the same design logic by controlling site strength and proximity. The practical design variables are the type, strength, density, and spatial pairing of acid-base sites, which collectively determine stabilization of the carbonyl pool within the reaction network.

Selectivity and stability are further controlled at nanoscale interfaces where hydrogen activation and carbonyl transformation are coupled. Metals or mixed-valence centers that activate H₂, formic acid, or alcohol dehydrogenation should be positioned near acid or base sites that polarize C=O bonds and direct dehydration, rearrangement, and mild deoxygenation^[23,27,63,75–76]. This proximity promotes localized hydride transfer, favoring selective hydrogenation of aldehydes and ketones while limiting over-hydrogenation and deep deoxygenation. Strong anchoring through metal-support interactions or metal-N-C coordination reduces sintering and leaching under thermal and redox cycling. The main design parameter is interface architecture, which governs the relative rates among hydrogen activation, carbonyl hydrogenation, rearrangement, and further deoxygenation.

Transport and phase environments provide a subtle yet equally powerful control lever by setting residence time and secondary chemistry. Upstream molten salts or ionic phases enable rapid and uniform heating and promote directed dehydration under strong Lewis acidity. Rapid condensation then transfers narrow-spectrum carbonyls, such as furfural, into the liquid phase, thereby mitigating repolymerization and over-cracking^[18,20,59,73]. Downstream hierarchical micro- and meso-porous supports balance contact and diffusion resistance, facilitating upgrading through controlled hydrogenation, mild aromatization, or redistribution while limiting pore coking and full deoxygenation^[23,74–75]. The main design variable is the residence-time window established by phase choice and pore hierarchy, which governs whether carbonyls are retained or consumed.

Hydrogen source and solvent must be matched to catalyst functionality rather than selected independently. Gamma-valerolactone and water provide a polar and proton-active medium that supports selective formation of furfural and levulinic acid over moderately strong solid acids^[22,43]. Transfer hydrogenation using 2-propanol relies on Lewis acid-base site pairs that enable MPV-like hydride transfer, while formic-acid systems require mixed-valence metal centers that favor the formate pathway and stabilize carbonyl adsorption and polarization^[74]. Direct H₂ hydrogenation requires electronic tuning of metals through oxide, carbon, or nitrogen coordination to facilitate H₂ activation while controlling adsorption strength to prioritize C=O reduction^[23,35,74–76]. The key design variable is hydrogen-source choice, which must be co-optimized with the metal-acid-base ensemble responsible for hydrogen supply and transfer.

Process integration is best implemented as functional zoning across stages rather than through a single universal catalyst. Upstream units should compress raw biomass into a controllable carbonyl platform pool using acidic salts,

strong solid acids, or selected oxides under fast pyrolysis or solvolysis conditions^[14,22,43,73]. Midstream units can employ mildly basic or amphoteric oxides to achieve gentle deoxygenation and to tune aromaticity and acidity without erasing platform identity^[65–66,68]. Downstream units can deploy carbon-based and metal-N-C catalysts to convert carbonyl platforms into fuels and fine chemicals under transfer hydrogenation or mild hydrogenation conditions, with representative products including furfuryl alcohol, 2-methylfuran, cyclopentanone, levulinic acid derivatives, and aromatic alcohols^[14,35,74]. Mineral-based catalysts are suitable for upstream operation where heat load and coke stress are high, while structurally refined synthetic catalysts can be reserved downstream for selective upgrading. Across all configurations, stability constraints such as sintering resistance, coking resistance, and regenerability should be evaluated alongside activity and selectivity using multi-cycle testing and in situ characterization. The overall design principle is staged, target-driven integration that ensures carbonyl fragments are formed at the appropriate node, stabilized, and then converted into the desired products.

4 Conclusions and outlook

This review consolidates progress in biomass catalytic pyrolysis toward aldehydes and ketones, and highlights the coupling among feedstock composition, operating conditions, and catalytic function. Across representative systems, cellulose, hemicellulose, and lignin populate different intermediate pools during thermal conversion, including furanic species, cyclopentanone type oxygenates, and phenolic fragments. With an appropriate catalytic microenvironment, these intermediates can be redirected toward targeted carbonyl platforms through depolymerization, dehydration, decarbonylation, and rearrangement. The central objective is to maintain carbon flow at the carbonyl platform level rather than allowing accumulation as anhydrosugars and heavy tars, or diversion toward deeply deoxygenated endpoints.

Metal salts, metal oxides, and carbon-based catalysts are the primary tools for reshaping reaction networks and product distributions. Selectivity is governed by the balance of acid-base functionality, redox capability, and local coordination environments that regulate the formation and evolution of key intermediates. Basic oxides promote carbon coupling routes such as aldol-type chemistry, while acidic sites accelerate dehydration and skeletal rearrangement. Controlled integration of these functions can increase selectivity toward desired oxygenates. Hierarchical porosity and bifunctional architectures that incorporate multiple active motifs within a single scaffold are especially attractive because they enable efficient one-pot upgrading while reducing secondary losses. A key design variable is the spatial pairing and strength matching of acid-base and redox functions, which determines whether carbonyl intermediates are retained, upgraded, or over-converted.

Looking ahead, catalyst development should prioritize

multilevel structures that integrate acid-base and redox functions, while maintaining stability under high temperature pyrolysis. Operando and in situ measurements, including time-resolved infrared or Raman spectroscopy coupled with mass spectrometry, together with multiscale simulation and kinetic modeling, are essential for tracking active-site dynamics and intermediate lifetimes under realistic conditions. These tools can clarify the influence of oxide cluster size, defect chemistry, and feedstock heterogeneity on pathways and selectivity. Data driven modeling, especially automated machine learning, can subsequently map relationships among feedstock descriptors, reactor parameters, catalyst features, and product slates. Such models allow inverse screening of catalyst composition and operating windows for predictable carbonyl-centered outcomes. The critical design variable is a closed-loop workflow that links operando evidence to model-guided optimization.

Durability must be an equally important target as activity and selectivity. Thermomechanical robustness and sintering resistance can be improved by using high-melting inorganic frameworks, confined nanostructures, and stronger metal-support interactions that suppress migration, aggregation, and volatilization. Carbon-based catalysts deserve special attention because they combine low cost with high tunability and can host acidic, basic, and metal coordination sites within a single scaffold, including anchored nanoparticles or single atoms. Under alternative energy inputs such as microwave assistance, carbon materials can enhance local heating and accelerate key bond scission and oxygen removal steps while maintaining structural integrity. The key design principle is stability by construction, which can be achieved through confinement, anchoring, and regenerability engineered from the outset.

Finally, process intensification should combine catalytic pyrolysis with continuous operation and online separation to create integrated schemes of continuous pyrolysis, staged upgrading, and real-time fractionation. Multi-zone temperature control, staged feeding, and adjustable gas-solid contact times can reproduce at scale the favorable regime of moderate temperature and short residence time, which facilitates capture of transient carbonyl intermediates. Emerging energy-delivery modes such as microwave heating and nonthermal plasma expand the operating space for selective bond activation and partial redox chemistry. In practice, catalyst classes should be deployed by function: upstream units form a controllable carbonyl intermediate pool, while downstream units selectively hydrogenate, rearrange, or couple that pool under milder conditions to produce fuels and fine chemicals. Life-cycle assessment, techno-economic analysis, and carbon-footprint accounting should be applied across catalyst manufacture, operation, and regeneration to identify routes with true industrial potential. The overarching design principle is coupled catalyst-reactor design that locks carbonyl intermediates at the appropriate node and converts them along an efficient and sustainable pathway.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] DAS N, MAHESHWARI D K, PANDEY P. Energy crop-based rhizoremediation and lignocellulosic biomass production as sustainable bioeconomy-driven solution for biofuel generation and waste mitigation[J]. Prog Energy Combust Sci, 2024, 103: 101161.
- [2] CHEN Z, CHEN L, KHOO K S, et al. Exploitation of lignocellulosic-based biomass biorefinery: A critical review of renewable bioresource, sustainability and economic views[J]. Biotechnol Adv, 2023, 69: 108265.
- [3] LI J, GE J, ZHAO Y, et al. Lignin-tailored fabrication of Ni single atom catalyst with Ni-N₃ active site for efficient and selective catalytic transfer hydrogenation of lignin-derived aldehydes[J]. Chem Eng J, 2024, 496: 154315.
- [4] XU S, LI Q, CHEN Z, et al. A composite catalyst of sugarcane-derived N-doped biochar and Fe(NO₃)₃ for improved electron transfer in stepwise oxidation of 5-hydroxymethylfurfuran under air[J]. Surf Interfaces, 2024, 46: 103966.
- [5] FENG Y, GUO H, SMITH R L, et al. Electrocatalytic oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid *via* metal-organic framework-structured hierarchical Co₃O₄ nanoplate arrays[J]. J Colloid Interface Sci, 2023, 632: 87–94.
- [6] MOTTA I L, MARCHESAN A N, GUIMARES H R, et al. Exploring the impact of biomass composition on high-value bio-oil components: Insights from fast pyrolysis kinetic simulation and multivariate analysis[J]. Chem Eng Tran, 2024, 109: 145–150.
- [7] YE L, REN X, LIU X, et al. Study on energy characteristics and pyrolytic principles of typical fruit tree pruning in northern China[J]. J Forest Eng, 2025, 10(1): 97–104.
- [8] CHEN B, YANG S, SHANG L, et al. Catalytic pyrolysis of biomass to aromatics over bifunctional Ni/ZSM-5 catalysts assembled on rice husk-derived silica platform[J]. Chem Catalysis, 2024, 4(4): 100958.
- [9] ZHANG L, LIU J, ZHANG Z, et al. Research of the two-step pyrolysis of lignocellulosic biomass based on the cross-coupling of components by Py-GC/MS[J]. Biomass Convers Biorefinery, 2023, 13(13): 11789–11802.
- [10] DHAHAK A, CÉZARD L, BAUMBERGER S, et al. Kinetic, products and shrinkage for the pyrolysis of flax fibers[J]. J Anal Appl Pyrolysis, 2024, 180: 106538.
- [11] XIE W, ULLAH F, LU Y, et al. Interactions of biomass constituents and the effect on the hydrogen storage molecules during fast pyrolysis[J]. Energy, 2025, 328: 136428.
- [12] LI C, LI Y, JIANG Y, et al. Staged pyrolysis of biomass to probe the evolution of fractions of bio-oil[J]. Energy, 2023, 263: 125873.
- [13] GAO G, HU X, SHAO Y, et al. Distinct responses of feedstocks of varied origin in oxidative pyrolysis[J]. Energy, 2024, 312: 133489.
- [14] QIAN Q, LUO Z, MIAO F, et al. Experimental study and process evaluation of a graded utilization strategy for woody biomass: Integration of reductive catalytic fractionation, hydrodeoxygenation, and catalytic pyrolysis[J]. Energy, 2025, 322: 135574.
- [15] TULER G V, GUIMARES T, MARAL M T, et al. Thermochemical conversion of lignocellulosic biomass for sustainable bioproducts[J]. Biomass Convers Biorefinery, 2025, 15(12): 18187–18200.
- [16] CUI D, HU X, LIU X, et al. Evaluation of municipal solid waste conversion to dimethyl ether *via* gasification and electrochemical upgrading system based on Aspen Plus simulation[J]. Energy Environ Pro, 2025, 39(3): 167–175.
- [17] ELHENAWY Y, FOUAD K, MANSI A, et al. Experimental analysis and numerical simulation of biomass pyrolysis[J]. J Therm Anal Calorim, 2024, 149(19): 10369–10383.
- [18] SRIDHARAN B, GENUINO H C, JARDAN D, et al. Novel route to produce hydrocarbons from woody biomass using molten salts[J]. Energy Fuels, 2022, 36(20): 12628–12640.
- [19] HU L, LI T, JING Y. Thermal pyrolysis behavior and decomposition mechanism of lignin revealed by stochastic cluster dynamics simulations[J]. J Phys Chem C, 2024, 128(9): 3832–3838.
- [20] ESTRADA LEON A, PALA M, HEERES H J, et al. Micro-pyrolysis of various lignocellulosic biomasses in molten chloride salts[J]. J Anal Appl Pyrolysis, 2022, 168: 105739.
- [21] YE Q, LI Y, ZHONG Z, et al. Investigation on the synthesis of furfural *via* pyrolysis utilizing metal-loaded solid acid catalysts[J]. J Anal Appl Pyrolysis, 2024, 181: 106656.
- [22] ZHANG Z, LU L, XU H, et al. A magnetic carbon-based solid acid catalyst derived from tobacco stalk for efficient valorization of tobacco stalk to furfural[J]. Ind Crop Prod, 2025, 227: 120816.
- [23] ZHU X, LIU Z, HU Z, et al. Chitosan-derived NC support zirconia as highly efficient catalyst for the catalytic transfer hydrogenation of furfural to furfuryl alcohol[J]. Appl Catal A: Gen, 2025, 706: 120492.
- [24] YOGITA, ANJANA P N, KUMAR P M, et al. Studies on cobalt nano particles supported on nitrogen-doped carbon catalysts for selective hydrogenation of biomass derived furfural[J]. Catal Lett, 2025, 155(4): 137.
- [25] CHEN H, DUAN J, YIN S, et al. Investigation into the pyrolysis mechanism of α -D-galactose to furfural and furan[J]. J Fuel Chem Technol, 2025, 53(9): 1385–1398.
- [26] ZHONG Y, LIU Y, WANG S, et al. Incorporation of tin oxide nanoparticles on sulfonated carbon microspheres as a bifunctional catalyst for efficient conversion of biomass-derived monosaccharides to 5-Hydroxymethylfurfural and furfural[J]. Ind Crop Prod, 2024, 208: 117913.
- [27] ZHOU Q, GU J, WANG J, et al. High production of furfural by flash pyrolysis of C₆ sugars and lignocellulose by Pd-PdO/ZnSO₄ catalyst[J]. Nat Commun, 2023, 14(1): 1563.
- [28] ZHAO M, LI Z, SI F, et al. Synergistic interaction between Cu single atoms and Cu nanoclusters boosting the selective oxidation of 5-hydroxymethylfurfural[J]. Chem Eng J, 2024, 492: 152284.
- [29] XU X, JING C, CHEN Y. Bimetallic MOF-74 and derivatives: Fabrication and efficient electrocatalytic biomass conversion[J]. Chin J Inorg Chem, 2025, 41(8): 1545–1554.
- [30] ZHAO D, FENG H, WANG Y, et al. Influence mechanism of K on cellulose pyrolysis by stepwise isothermal method in-situ DRIFTS method[J]. Fuel, 2024, 360: 130601.
- [31] DECHAO W, JIE Z, XIN L, et al. Enhancing the catalytic activity of Au/TS-1 in cellulose pyrolysis *via* alkali metal modification: A comprehensive study[J]. Renewable

- Energy, 2025, 251: 123471.
- [32] HAMEED S, PAN X, GUAN W, et al. Co-N-C catalyst with single atom active sites for base-free aerobic oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid under mild conditions[J]. Mol Catal, 2024, 569: 114616.
- [33] SUN Z, YANG X, ZHANG B, et al. Product-oriented thermodynamic function construction of wheat straw and thermodynamic analysis for rapid pyrolysis[J]. Fuel, 2024, 358: 130285.
- [34] PRABHUDESAI V S, YERRAYYA A, GURRALA L, et al. Hydrodeoxygenation of mixtures of biomass-derived model compound oxygenates over Pt/HY catalysts[J]. Chem Eng Sci, 2024, 288: 119800.
- [35] CAI Z, ZHANG Z, QI Y, et al. Selective conversion of furfural to cyclopentanone over the N-doped CuNi alloy carbon materials derived from porphyrin-based bimetallic metal-organic frameworks[J]. Fuel, 2024, 371: 131898.
- [36] HU Z, XIE A, CHEN C, et al. Facile synthesis of N, P co-doped carbon encapsulated Ni catalyst for green production of cyclopentanone from biomass derivative furfural[J]. Fuel, 2022, 319: 123815.
- [37] CHEN L, HUANG F, WU L, et al. CO₂ boost aromatic-rich bio-oil production in biomass catalytic stepwise pyrolysis over Y zeolite[J]. Chem Eng J, 2025, 503: 158429.
- [38] JIANG Y, LI C, ZHANG L, et al. Impacts of acidic or basic sites on poplar sawdust on pyrolytic products and pyrolysis kinetics[J]. J Anal Appl Pyrolysis, 2023, 174: 106151.
- [39] ASHOKKUMAR V, VENKATKARTHICK R, JAYASHREE S, et al. Recent advances in lignocellulosic biomass for biofuels and value-added bioproducts - A critical review[J]. Bioresour Technol, 2022, 344: 126195.
- [40] DENG W, FENG Y, FU J, et al. Catalytic conversion of lignocellulosic biomass into chemicals and fuels[J]. Green Energy Environ, 2023, 8(1): 10–114.
- [41] SYGULA E, CIOLKOSZ D, BIALOWIEC A. The significance of structural components of lignocellulosic biomass on volatile organic compounds presence on biochar - a review[J]. Wood Sci Technol, 2024, 58(3): 859–886.
- [42] K N Y, T P D, P S, et al. Lignocellulosic biomass-based pyrolysis: A comprehensive review[J]. Chemosphere, 2022, 286: 131824.
- [43] LI X, XU H, HU W, et al. One step synthesis of Mo-doped carbon microspheres for valorization corncob to levulinic acid[J]. Ind Crop Prod, 2022, 184: 115019.
- [44] HAN X, ZHANG S, XU J, et al. Effect of the component evolution of Chinese fir sawdust on wood vinegar during hydrothermal process[J]. CIESC J, 2023, 74(10): 4311–4318.
- [45] STEFANIDIS S D, KALOGIANNIS K G, ILIOPOULOU E F, et al. A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin[J]. J Anal Appl Pyrolysis, 2014, 105: 143–150.
- [46] SUN K, GUO T, LI Y, et al. Rapid pyrolysis of cellulose: Revealing the role of volatile matter and char structure evolution[J]. J Anal Appl Pyrolysis, 2024, 182: 106704.
- [47] DEBIAGI P, PIAZZA V, PAPAGNI M, et al. Cellulose pyrolysis kinetic model: Detailed description of volatile species[J]. Proc Combust Inst, 2024, 40(1): 105651.
- [48] JIANG L, FANG Z, ZHAO Z, et al. Levoglucosan and its hydrolysates via fast pyrolysis of lignocellulose for microbial biofuels: A state-of-the-art review[J]. Renewable Sustainable Energy Rev, 2019, 105: 215–229.
- [49] BI D, HE Z, HUANG F, et al. Interaction mechanisms among Cellulose, Hemicellulose, and lignin in Nitrogen-Rich pyrolysis under K and Ca Presence: Intermediate evolution and product formation[J]. Chem Eng J, 2024, 496: 153798.
- [50] XU L, ZHANG Y, WANG Z, et al. Kinetic analysis and pyrolysis behavior of pine needles by TG-FTIR and Py-GC/MS[J]. BioResources, 2023, 18(3): 6412–6429.
- [51] RAO J, LV Z, CHEN G, et al. Hemicellulose: Structure, chemical modification, and application[J]. Prog Polym Sci, 2023, 140: 101675.
- [52] HE Y, LUO Y, YANG M, et al. High value utilization of biomass: selective catalytic transformation of lignocellulose into bio-based 2, 5-dimethylphenol[J]. Catal Sci Technol, 2022, 12(14): 4524–4534.
- [53] WANG Y, YANG S, BAO G, et al. Pyrolytic characteristics of abutilon stalk waste using TG-FTIR, Py-GC/MS, and artificial neural networks: Kinetics, thermodynamics, and gaseous products distribution[J]. J Anal Appl Pyrolysis, 2024, 178: 106403.
- [54] HE Z, LV Q, JIANG X, et al. Understanding the synergistic mechanisms of co-pyrolysis of straw and polyethylene for high-quality pyrolysis oil[J]. Renewable Energy, 2025, 246: 122923.
- [55] PATEL R, DHAR P, BABAEI-GHAZVINI A, et al. Transforming lignin into renewable fuels, chemicals, and materials: A review[J]. Bioresour Technol Rep, 2023, 22: 101463.
- [56] VALDEBENITO F, RAMÍREZ-LVAREZ R, ALEXANDRA MUOZ M, et al. Biomass characterization and solvent extraction as tools to promote phenol production from urban pruning[J]. Fuel, 2024, 362: 130830.
- [57] SHAO Y, LI C, FAN M, et al. Sequential pyrolysis for understanding specific influence of cellulose- and lignin-derived volatiles on properties of counterpart char[J]. Green Chem Eng, 2024, 5(2): 222–235.
- [58] COURA M R, DEMUNER A J, DEMUNER I F, et al. Coffee biomass residue as a raw material for cellulose production and Py-GC/MS analysis[J]. Waste Biomass Valorization, 2024, 15(1): 349–364.
- [59] XIA S, YANG H, LEI S, et al. Iron salt catalytic pyrolysis of biomass: Influence of iron salt type[J]. Energy, 2023, 262: 125415.
- [60] HU J, HE Y, ZHANG J, et al. In-situ catalytic pyrolysis of biomass with nickel salts: Effect of nickel salt type[J]. J Anal Appl Pyrolysis, 2023, 172: 106029.
- [61] LIU Z, LI P, CHANG C, et al. Influence of metal chloride modified biochar on products characteristics from biomass catalytic pyrolysis[J]. Energy, 2022, 250: 123776.
- [62] WEI X, CAO Y, LI J. Synergistic effect of acid sites and a gallium-based modified meso-/microporous catalyst for the pyrolysis of biomass[J]. Renewable. Energy, 2022, 191: 580–590.
- [63] ABDULLAH R F, RASHID U, IBRAHIM M L, et al. Bifunctional biomass-based catalyst for biodiesel production via hydrothermal carbonization (HTC) pretreatment – Synthesis, characterization and optimization[J]. Process Saf Environ Protect, 2021, 156: 219–230.
- [64] YAO Z, WANG X, MA Z, et al. Modulation of surface properties of metal organic framework-derived carbon substrates through vacancy defects for high-value biomass conversion[J]. J Colloid Interface Sci, 2025, 695: 137752.
- [65] ZHANG Y, WANG J, LUO Q, et al. Intrinsic promotion mechanism of calcium oxide on ketone production during

- catalytic fast pyrolysis of biomass via experiment and density functional theory simulation[J]. Bioresour Technol, 2024, 410: 131310.
- [66] ZHANG J, HUANG Y, SEKYERE D T, et al. Catalytic fast pyrolysis of waste pine sawdust over solid base, acid and base-acid tandem catalysts[J]. Bioresour Technol, 2024, 394: 130294.
- [67] TAMILARASAN N, SAKTHIVEL R, BALAJI K. Influence of metal oxide catalyst on co-pyrolysis of biomass and COVID-19 waste[J]. Environ Technol, 2024, 45(9): 1721–1732.
- [68] LIU Y, LIU S, LIU W, et al. Preparation of dolomite-based porous ceramics with Al₂O₃-loading as the heat carrier for biomass catalytic pyrolysis[J]. BioResources, 2021, 16(3): 5234–5247.
- [69] DIN M I, SADAF S, HUSSAIN Z, et al. Assembly of superparamagnetic iron oxide nanoparticles (Fe₃O₄-Nps) for catalytic pyrolysis of corn cob biomass[J]. Energy Sources Part A, 2024, 46(1): 8519–8527.
- [70] YANG X, SHAO S, LI X, et al. Catalytic transfer hydrogenation of bio-oil over biochar-based CuO catalyst using methanol as hydrogen donor[J]. Renewable Energy, 2023, 211: 21–30.
- [71] ZHOU F, WANG H, WANG S, et al. Balancing the components of biomass and the reactivity of pyrolysis gas: Biomass-assisted recycling of spent LiCoO₂ batteries[J]. Environ Sci Technol, 2024, 58(4): 2102–2111.
- [72] WANG L, CHEN D, ZHOU J. Surface reconfiguration of pine-based porous carbon enhanced persulfate for removing bisphenol A[J]. Energy Environ Pro, 2024, 38(2): 145–154.
- [73] LEÓN A E, ULLOA-MURILLO L M, GHYSELS S, et al. 2-Methylfuran from pinewood by molten-salt hydropyrolysis and catalytic hydrogenation of the furfural intermediate[J]. Sustainable Energ Fuels, 2024, 8(12): 2704–2717.
- [74] WANG T, SUO W, QU M, et al. Cu/CuOx@C for efficient selective transfer hydrogenation of furfural to furfuryl alcohol with formic acid[J]. J Chem Technol Biotechnol, 2022, 97(11): 3172–3182.
- [75] QIU Z, HE X, MA S, et al. Ni nanoparticles embedded in nitrogen doped carbon derived from metal–organic frameworks for the efficient hydrogenation of vanillin to vanillyl alcohol[J]. New J Chem, 2022, 46(21): 10347–10356.
- [76] DOU K, XIE D, SHI J, et al. Structural characterization of MXene-supported cobalt nanoparticle catalysts and their catalytic performance in the hydrogenation of furfural to furfuryl alcohol[J]. J Mol Struct, 2025, 1320: 139518.

生物质催化热解制取醛酮类化合物的研究进展

王恒威¹, 邱 丽¹, 葛泽峰², 袁鑫华³, 黄 浦¹, 崔东旭¹, 李津津¹, 陈登宇^{1,*}

(1. 南京林业大学 材料科学与工程学院, 江苏 南京 210037; 2. 东南大学 能源与环境学院, 江苏 南京 210096;

3. 华北电力大学 能源电力创新研究院, 北京 102206)

摘 要: 醛酮类化合物作为重要的含氧有机中间体和附加值化学品, 在精细化工、燃料与材料合成等领域具有关键基础性作用。以木质纤维素生物质为代表的可再生碳源, 通过热解过程实现糠醛、5-羟甲基糠醛及小分子脂肪酮等平台羰基化合物的绿色制备, 对缓解化石资源依赖和降低碳排放具有重要意义。本工作综述了近年生物质催化热解制备醛酮类化合物的研究进展: 概述典型醛酮平台分子的种类、结构特征及其在生物质分解中的来源; 比较富纤维素、富半纤维素与富木质素等不同类型生物质在非催化热解条件下的分解路径及中间体演化规律, 阐明多组分协同对醛酮生成的影响; 在此基础上, 重点归纳金属盐、金属氧化物及碳基催化体系在调控脱水、脱羧、C–O/C–C 断键和骨架重排等关键步骤中的作用机理及主导反应路径。分析当前生物质催化热解制醛酮研究在催化剂构效关系、活性位稳定性和选择性提升等方面面临的主要挑战, 展望面向高效可控定向转化的多级结构催化剂设计、原位表征与多尺度模拟耦合机理研究以及绿色放大与过程集成等发展方向。本研究旨在为生物质高值化利用及可再生碳资源转化提供系统的理论参考与研究借鉴。

关键词: 生物质热解; 醛酮类化合物; 催化剂调控; 反应机理; 定向转化

中图分类号: TK6; TQ517.4

文献标识码: A

作者简介:



陈登宇(1985), 博士, 教授, 研究方向为生物质热化学转化, chendy@njfu.edu.cn。