

Catalytic Transformation of Carbohydrates into Renewable Organic Chemicals by Reversing the Principles of Green Chemistry

Saikat Dutta*

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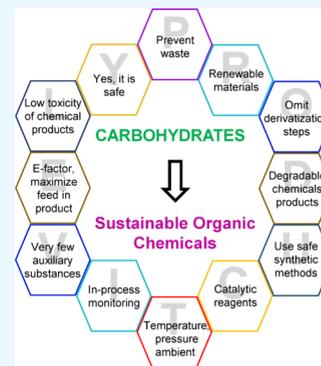
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ABSTRACT: Adherence to the principles of green chemistry in a biorefinery setting ensures energy efficiency, reduces the consumption of materials, simplifies reactor design, and rationalizes the process parameters for synthesizing affordable organic chemicals of desired functional efficacy and ingrained sustainability. The green chemistry metrics facilitate assessing the relative merits and demerits of alternative synthetic pathways for the targeted product(s). This work elaborates on how green chemistry has emerged as a transformative framework and inspired innovations toward the catalytic conversion of biomass-derived carbohydrates into fuels, chemicals, and synthetic polymers. Specific discussions have been incorporated on the judicious selection of feedstock, reaction parameters, reagents (stoichiometric or catalytic), and other synthetic auxiliaries to obtain the targeted product(s) in desired selectivity and yield. The prospects of a carbohydrate-centric biorefinery have been emphasized and research avenues have been proposed to eliminate the remaining roadblocks. The analyses presented in this review will steer to developing superior synthetic strategies and processes for envisaging a sustainable bioeconomy centered on biomass-derived carbohydrates.



1. INTRODUCTION

The abundance and affordability of carbon-based liquid transportation fuels, chemicals, and synthetic polymers, primarily sourced from petroleum, have revolutionized industrialized societies over the past seven decades or so.^{1,2} However, the accomplishments came at the steep cost of widespread environmental pollution, deriding the perception of the improved quality of life.³ Combustion of petrofuels and decomposition of petrochemicals introduce anthropogenic carbon into the biosphere, resulting in a kinetic imbalance in the carbon cycle and disastrous environmental complications (e.g., global warming).⁴ Moreover, the depleting reserves of economically retrievable petroleum feedstock grapple with the steeply increasing demand for petrofuels and petrochemicals.⁵ Therefore, serious deliberations have been made to identify commercially attractive, sustainable carbon-based feedstock to produce affordable transportation fuels and chemicals without worsening environmental distress.⁶ In this regard, biomass-derived carbohydrates, especially those present in the plant matter of terrestrial and aquatic origin, could be economically feasible and environmentally acceptable biogenic carbon to replace, at least partially, the fossilized carbon sources in producing transportation fuels, organic chemicals, and synthetic polymers.⁷ The combustion of biofuels and decomposition of biochemicals introduce CO₂ into the biosphere, which gets sequestered during photosynthesis within a reasonable time frame, thereby ensuring a circular carbon economy.⁸

Carbohydrates have received major attention as a viable feedstock because of their natural abundance in most biomass,

relatively low cost, and the presence of oxygen-containing functionalities (i.e., alcohol, aldehyde) in the parent molecules.⁹ The cellulose and hemicellulose fractions combined correspond to around 70 wt % of dry terrestrial lignocellulosic biomass. Other common carbohydrates include simple sugars (e.g., glucose, fructose, sucrose), starch, inulin, and carbohydrates in algal biomass (e.g., carrageenan, agarose). Discussion regarding the availability and choice of feedstock in a carbohydrate-centric biorefinery has been elaborated in the next section.

The carbohydrate-derived renewable bioproducts can be structurally indistinguishable from those originating from petroleum and work as the drop-in replacement of the latter.¹⁰ Biorenewable products can also be novel, structurally relatable compounds imitating the properties of existing petroleum-derived products and act as their functional substitutes.¹¹ Both classes of bioproducts have advantages and constraints. Bioproducts that are drop-in replacements of petrochemicals enjoy the prevalent infrastructure, established markets, and the availability of literature data on their toxicological properties.¹² However, there is limited scope to introduce desired changes in the molecular structure for functional efficacy and biodegradability.

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tion. On the contrary, the renewable alternatives of existing petrochemicals can be fine-tuned structurally for desired properties and functions.¹³ The challenge in this case is to compete with existing petrochemicals for market share and insufficient data on their properties, such as toxicology and recyclability. The carbohydrate molecules are starkly different from the hydrocarbons present in petroleum. The value-addition of hydrocarbons involves a series of oxidation and functionalization reactions. On the other hand, the value-addition of carbohydrates involves depolymerization, defunctionalization, and refunctionalization steps.¹⁴ Therefore, the chemical transformation of carbohydrates into organic chemicals requires a different set of reagents and reaction parameters than those practiced on the petroleum-derived hydrocarbons. Moreover, polymeric carbohydrates are available in relatively pure form in only a handful of biomasses. In most cases, the carbohydrates must be isolated from raw biomass before subjecting them to further value-addition pathways.¹⁵ The direct use of raw biomass during the value-addition of carbohydrates, though preferable from the step efficiency perspective, often decreases the activity of the catalysts and reagents employed, lowering the selectivity and yield of the desired product.¹⁶ In some cases, elaborate product purification is also warranted, increasing the operational cost and decreasing the environmental acceptability. In this regard, vegetation biomass contains small organic molecules and biopolymers of diverse molecular structures. The inorganic components include metal salts, moisture, and siliceous materials. The proportion of the organic components varies significantly depending on the species, geographic location where it is produced, seasonal parameters, storage conditions, and pretreatment processes employed.¹⁷ The major organic components in the abundant terrestrial lignocellulosic biomass are biopolymers, such as cellulose, hemicellulose, and lignin. Some biomass contains significant amounts of extractives, such as protein, triglycerides (oil seeds), and simple sugars (e.g., glucose, sucrose).¹⁸ Value-addition of carbohydrates, where the native molecular structure is not preserved in the product, can be broadly classified into thermochemical, chemocatalytic, and enzymatic pathways. Chemical-catalytic processes enjoy some of the best features of thermochemical and enzymatic processes.¹⁹ These processes are fast (seconds to hours), biomass-independent, selective, employ innocuous reagents in catalytic amounts, and work under energy-efficient conditions.^{20,21} The chemical-catalytic value addition of carbohydrates allows selective functionalization and defunctionalization steps, embracing the wide range of functionalities and structural complexities in their molecular structure. Therefore, these processes circumvent the tedious and polluting oxidation steps in synthesizing the functionalized petrochemicals from petroleum-derived hydrocarbons. The catalytic transformation of biomass-derived carbohydrates into organic chemicals of desired structural traits and properties can benefit from the wealth of knowledge of synthetic organic chemistry. Over the past three decades, several chemical-catalytic processes have been developed that promise the economically competitive production of industrially relevant organic chemicals from renewable carbohydrates. In terms of molecular compositions, majority of the renewable chemicals obtained by the catalytic transformation of carbohydrates possess oxygen-containing functionalities.²² Other elements, such as nitrogen, can be introduced during synthetic upgrading (e.g., amination) or by retaining the nitrogen atom of the nitrogen-containing carbohydrate (e.g., chitin) during catalytic

transformation.^{23,24} The transformations must be performed under reagent- and energy-economic conditions to maximize sustainability in the organic chemical industries. Substrates, reagents, solvents, and other synthetic auxiliaries are screened through multiple parameters, such as availability, cost, efficiency, ecotoxicity, and recyclability, before selecting them for any organic transformation.

The framework of “green chemistry” can help strategize the sustainable synthesis of transportation fuels, organic chemicals, and synthetic polymers from carbohydrates following the chemical-catalytic pathway under economically advantageous and environmentally acceptable conditions.²⁵ Interestingly, both green chemistry and biorefinery concepts evolved during the late 1990s.²⁶ Green chemistry ensures chemical risk reduction by eliminating hazards at the molecular level by designing inherently safe chemicals instead of the traditional risk reduction strategy of restricting exposure to hazardous chemicals. The principles of green chemistry aim to make chemical manufacturing practices increasingly more sustainable by designing products and processes that prevent generating waste. The preferential use of renewable feedstock in synthetic processes is the seventh principle of green chemistry. When using petroleum as the feedstock in the organic chemicals manufacturing industries, green chemistry practices can only ensure more efficient use of the exhaustible resource. Organic chemical industries can achieve sustainability in the true sense by employing a renewable carbon-based feedstock (e.g., carbohydrates) (Figure 1).

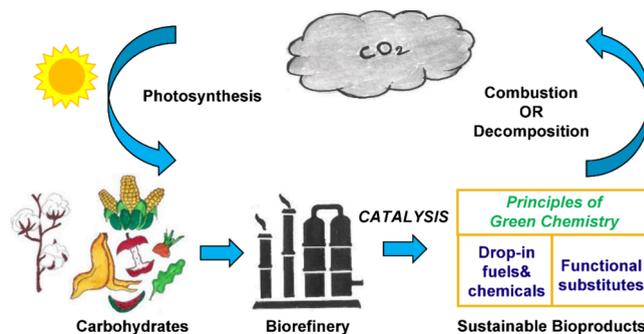


Figure 1. Sustainable bioproducts and a circular carbon economy under a carbohydrate-centric biorefinery setting.

The components required for an organic transformation are (1) reactants or starting material(s), (2) solvent and other synthetic auxiliaries (e.g., separating agent, additive), (3) reagents (stoichiometric or catalytic), and (4) reaction conditions (e.g., temperature, heating method, pressure). Sustainable synthetic practices attempt to minimize materials and energy input, such as eliminating components other than the substrate and using ambient reaction parameters during product preparation, isolation, and purification. Catalysis is an integral part of green chemistry (ninth principle) because it allows access to products starting from abundant and innocuous starting materials under eco-friendly conditions. Moreover, the selectivity toward a specific product can be tweaked using an appropriate catalyst. When solvents, reagents, and other synthetic auxiliaries cannot be averted, safer materials are deployed to supplement the problematic ones. When choosing feedstock, reagents, and products, emphasis is given to the entire life cycle assessment (LCA) of the materials, often referred to as the “cradle to grave” assessment, to make informed decisions.²⁷

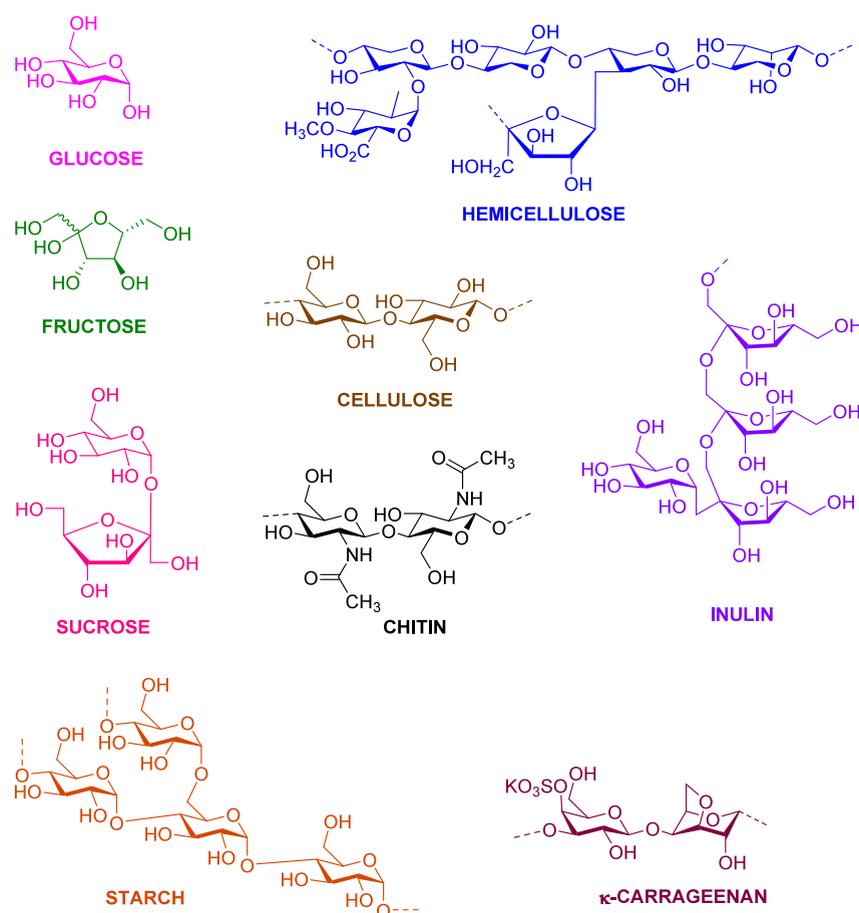


Figure 2. Molecular structure of abundant sugars and polymeric carbohydrates that may be used as feedstock in a carbohydrate-centric biorefinery.

LCA is widely used to quantify the environmental benefits of biochemicals over their life cycle.²⁸ The techno-economic analysis (TEA) of biochemicals gives qualitative and quantitative data about the technological maturity of the processes, feasibility from the economic perspective, and market readiness.²⁹ Although LCA and TEA are independent analyses, the combined data give comprehensive information and insights for maximizing societal, economic, and environmental benefits in producing biochemicals (or bioproducts in general) in a biorefinery setting.

This review elaborates on the chemical-catalytic transformations of biomass-derived carbohydrates into organic chemicals of commercial significance by revering the principles of green chemistry.

2. CHOICE OF CARBOHYDRATE FEEDSTOCK

The composition and molecular structures of various vegetation biomass components depend on the feedstock type, seasonal factors, storage conditions, and other processing parameters.³⁰ Sugars and polymeric carbohydrates comprise a major fraction of edible and nonedible terrestrial and algal biomass. For example, the terrestrial lignocellulosic biomass consists of nearly 70% (dry mass basis) carbohydrates, such as cellulose and hemicellulose. Understanding the molecular structure of carbohydrates is paramount to develop catalytic processes for their transformation in various value-added products. Cellulose is the single most abundant biopolymer in nature, and only a small fraction of its around 180 billion metric tons annual production worldwide is utilized for synthesizing organic

chemicals and materials.³¹ Many end-user products (e.g., newspapers, corrugated boxes) are also composed of cellulose-rich materials. Moreover, cellulose is a significant component in many biomass waste streams (e.g., agricultural residue, forestry waste, municipal wet waste).³² Cellulose is a linear homopolymer of D-glucose units stitched together by the hydrolytically stable β -1,4-glycosidic bonds. Natural cellulose is highly crystalline (degree of crystallinity ranges from 50 to 80%) due to the extensive hydrogen-bonding network within and between the neighboring chains formed by three –OH groups per glucose unit. These structural features in cellulose result in high mechanical strength, low water absorption, and chemical recalcitrance.³³ Even though cellulose is comparatively a tough substrate for catalytic value addition, its high abundance from nonfood sources, high productivity, low cost, and structural homogeneity (i.e., made of glucose units exclusively) make it a promising feedstock in a carbohydrate-centric biorefinery.³⁴

Starch is another abundant polysaccharide comprised of glucose units connected by the α -1,4-glycosidic bonds. Starch contains amylose (10–30%), a linear polymer of glucose that forms a spiral structure (six glucose units per turn) owing to hydrogen bonding. Starch also contains amylopectin (70–90%), where α -1,4-glycosidic connects the glucose units and α -1,6-glycosidic bonds, leading to a branched polymer.³⁵ Starch is significantly less crystalline than cellulose and more prone to hydrolysis. Many edible biomasses contain simple sugars like fructose, sucrose, and glucose. Inulin is a heterogeneous collection of fructose polymers consisting of a chain-terminating glucosyl moiety and a repetitive fructosyl moiety found in

chicory, asparagus sp., jerusalem artichoke, dahlia, etc.³⁶ Carbohydrates in marine biomass include carrageenan (from seaweeds), chitin (from the crustacean shells), alginate, and agar.³⁷

Carrageenans (κ , ι , λ) are linear, high-molecular-weight, sulfated polysaccharides, which are made up of alternating 3-linked β -D-galactopyranose and 4-linked α -D-galactopyranose or 4-linked 3,6-anhydro- α -D-galactopyranose units (Figure 2).³⁸ Chitin is a long-chain polymer of *N*-acetylglucosamine, and amide derivative of glucose.³⁹ In terms of annual production in the biosphere, chitin is only next to cellulose, with an estimated production of over 1 billion metric tons. The presence of a nitrogen atom in chitin presents an opportunity to produce nitrogen-containing platform chemicals and *N*-heterocyclic compounds from carbohydrates.²⁴ Several studies have attempted the catalytic synthesis of *N*-heterocycles starting from chitin, chitosan (produced commercially by the deacetylation of chitin under base hydrolysis), and *N*-acetylglucosamine (NAG, the monomeric unit of chitin).⁴⁰ A major challenge in sourcing nitrogen-containing compounds from chitin is to retain the amide functionality during its acid-catalyzed depolymerization.⁴¹

The selection of carbohydrate feedstock is crucial from the process economics and environmental perspectives. The processes for catalytically converting first-generation starchy food crops into biofuels and biochemicals are relatively well-explored.⁴² Bioethanol production from sugar-based or starchy feedstock, such as sugar cane and maize, has been commercialized. However, the large-scale production of these edible biomasses is geographically localized and diverting them to the chemical industries may threaten food security in vulnerable parts of the world. Moreover, the energy, land, and materials requirement (e.g., irrigation, fertilizer, pesticides) for producing the food-based biomasses raises serious concerns about whether their conversion into chemicals is truly sustainable.⁴³ In this regard, the second-generation, nonfood lignocellulosic biomasses alleviate most of the concerns faced with food-based biomasses. Terrestrial lignocellulosic biomasses are produced on marginal land and do not require significant energy and material input during their growth.⁴⁴ Moreover, they are geographically diverse and abundant and often end up in various waste streams. Significant research activities have been focused on the catalytic transformation of lignocellulosic into biofuels and biochemicals over the past two decades.⁴⁵ The third-generation biomass includes freshwater and seawater algae that grow with minimal energy and materials (e.g., nutrients) requirements.⁴⁶ More importantly, algae cultivation does not require land and proliferates faster than most lignocellulosic biomasses. Lignocellulose and algal biomass contain polymeric carbohydrates (e.g., cellulose, hemicellulose), often combined with other biopolymers (e.g., lignin), which require more elaborate technological intervention for their catalytic transformation into value-added products. Bioethanol produced by the fermentation of lignocellulose and other cellulosic wastes has significant environmental incentives over the same sourced from starchy or sugar-rich biomasses. The catalytic conversion of cellulosic biomass and wastes into targeted liquid fuels and organic chemicals can assist in the effective waste management of these materials, improve the local economy by creating jobs and revenues, and help achieve carbon emission goals.

The major technical challenges for converting carbohydrates into liquid transportation fuels and organic chemicals are (1) separation of carbohydrates from other components of crude

biomass, (2) depolymerization of carbohydrates into monomeric sugars, (3) selective deoxygenation/defunctionalization into small organics, and (4) construction of the desired carbon framework and functionalities in the targeted product. Understandably, performing all the above transformations in a single step is preferred to maximize the process efficiency. Unfortunately, in most one-pot processes, the selectivity toward the targeted product(s) remains low due to several alternative mechanistic pathways during the cascades of synthetic steps. Therefore, the steps are often performed sequentially to maximize the yield of the desired product and also simplify the purification process. However, the relative advantages and limitations of single-stage and multistage syntheses from the carbohydrate feedstock must be evaluated carefully for each bioproduct.

3. CHOICE OF CATALYST CANDIDATE

Catalysis, the ninth principle of green chemistry, satisfies many of the objectives of green synthesis. Even though organic synthesis and catalysis developed independently in the initial years, the two research fields now rely heavily on each other for future growth.⁴⁷ At present, nearly 90% of organic synthetic processes are catalytic in the industrial setting.^{48,49} Catalysts lower the activation energy of a reaction by altering the mechanistic pathway, and different catalysts preferentially allow access to different products. The catalytic activity is checked by parameters like turnover number (TON) and turnover frequency (TOF). Green metrics like atom economy (AE) and environmental factor (E-factor) are dramatically improved using catalytic reagents instead of stoichiometric reagents. Even though certain homogeneous catalysts perform excellently in the catalytic value addition of carbohydrates, this review highlights heterogeneous catalysts more due to their clear advantage in isolating and purifying products over their homogeneous counterpart. However, homogeneous catalysts typically require milder reaction conditions than their heterogeneous counterpart, have stereochemical control, and are easier to study mechanistically. Mineral acids are frequently used for the dehydration of carbohydrates into 5-(hydroxymethyl)furfural (HMF), furfural (FUR), and levulinic acid (LA).^{50,51} Similarly, alkali metal hydroxides are commonly used for Aldol and Benzoin condensation reactions involving HMF and other furanic compounds. Ruthenium and Iridium-based homogeneous catalysts in the presence of appropriate ligands have been used for the hydrogenation of HMF into partially hydrogenated products, such as 2,5-bis(hydroxymethyl)furan (BHMF) and 2,5-bis(hydroxymethyl)tetrahydrofuran.^{52,53} Attempts to oxidize HMF into maleic anhydride or 2,5-diformylfuran using homogeneous catalysts include metal nitrates, such as copper(II) nitrate, vanadium salts, and also Mn(III)-salen complexes.⁵⁴ Homogeneous metal-based catalysts have certain advantages, such as uniformity of active sites, good tunability of catalytic activity, excellent selectivity, and high atomic efficiency. However, there are serious complications in using homogeneous metal catalysts that largely outweighs the advantages, such as the use of expensive ligands, poor thermal stability, challenging recovery, and cumbersome product purification. Recent research in the catalytic value addition of carbohydrates or the platform chemicals derived from them involve heterogeneous catalysts (bulk or supported). Bulk heterogeneous catalysts are metal alloys or metal oxides that can be used for acid-catalyzed or redox reactions.⁵⁵ For example, Ni/ZnO catalysts have been used for catalytically hydrogenating carbohydrate-derived HMF

into 2,5-dimethylfuran (DMF).⁵⁶ Supported heterogeneous catalysts have received significantly more interest for their increased stability, better activity, slower deactivation, and superior recyclability. Moreover, the catalyst support sometimes provides catalytic sites for another transformation leading to bifunctional or multifunctional catalyst. For example, noble-metal NPs (e.g., Pt, Ru, Pd) supported on silica–alumina or zeolite can be used in redox reactions (catalyzed by the metal sites) and also dehydration reactions (catalyzed by the Brønsted and Lewis acid sites on the support).⁵⁷ The metal NPs chosen for hydrogenation/dehydrogenation catalysts are either noble metals or earth-abundant first transition metals. Noble metal-based catalysts are already being used in various petrorefinery operations and downstream synthetic value addition (e.g., oxidation, functionalization) pathways. The major concern regarding the noble metals are their limited reserve, high cost, poor stability, and environmental impact in their preparation (e.g., mining).⁵⁸ However, these catalysts typically show excellent activity and selectivity even under relatively mild reaction conditions, especially when the metal particles are cut down to nanosize, stabilized on the supporting material, or alloyed with other metals. The recycling strategies are relatively straightforward and efficient. Therefore, the share of cost of catalyst in the unit production cost of product remains practicable. The major push for using earth-abundant first transition metal-based catalysts as substitute for noble metals is their high abundance and low cost. Copper and nickel-based supported catalysts have been developed that work well for hydrogenation and hydrodeoxygenation reactions.⁵⁹ However, the copper or nickel catalysts often show relatively lower activity and selectivity than their noble metal counterparts, gets deactivated by coking, and must be reduced to their metal form before use as catalyst and the metal nanoparticles get easily oxidized.⁶⁰ Supported heterogeneous catalysts get deactivated in various pathways. Understanding the deactivation mechanisms of catalysts remains crucial to improving the life of catalyst, recyclability, and designing superior catalyst. A common pathway for deactivation of supported catalysts containing metal NPs is their aggregation, thereby lowering the surface area and active sites for the reaction. Fouling, where the active sites are physically blocked (e.g., coking) is another deactivation pathway. Strong chemisorption of various species used in the reaction mixture onto the catalyst surface, leaching of active centers from the support, and permanent change in the crystalline structure of the supporting material (i.e., sintering) are other deactivation pathways.⁶¹ In certain cases, the deactivation can be reversed. For example, coking of catalyst can be reversed by calcination provided no sintering happens at the calcination temperature. Chemisorption can be removed by washing with a suitable solvent, and leaching can be avoided by choosing the appropriate solvent and reactor design. Nanocatalysts and single-atom catalysts (SACs) are being developed to make the catalysts increasingly more atom efficient, stable, and selective with a uniform and tunable metal center, as well as an adjustable metal–support interaction.^{62,63} Nanocatalysts and SACs improve the atom efficiency of catalytic sites, selectivity, activity, and stability compared to bulk heterogeneous catalysts. Metal-based nanocatalysts and SACs have been used extensively over the past decade in the redox transformations (e.g., hydrogenation, hydrogenolysis, oxidation) of sugars or sugar-derived platform chemicals. The increased catalytic activity of nanocatalysts can be attributed to their enhanced surface area, convenient accessibility of the active sites, and surface defects at

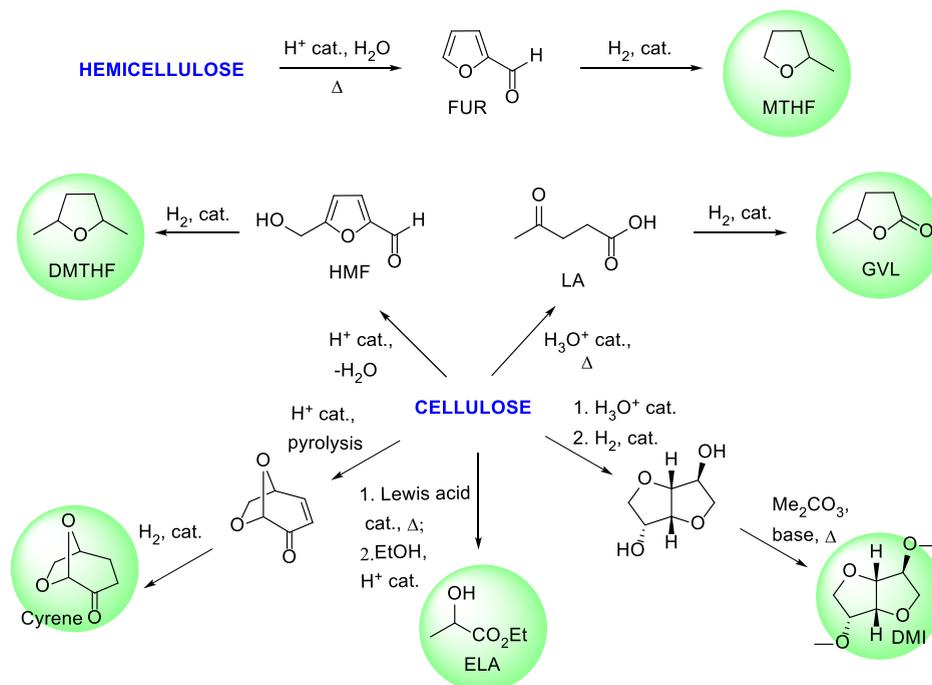
the nanoscale.⁶⁴ However, the catalytic activity and selectivity depend on the location of the metal atom in the active sites (e.g., facets, corners, and edges), which is often difficult to reproduce while synthesizing the nanocatalysts. Sintering during the reaction also changes the structure of the active sites and changes the selectivity abruptly. SACs are relatively new but show remarkably better catalytic properties than nanocatalysts. The atomic precision of the metal active sites on the catalyst's surface ensures low metal loading, high atom efficiency, high stability (e.g., thermal), and excellent selectivity. The improved activity and selectivity of SACs compared to nanocatalysts is due to the uniformity of the active sites in the former, which favors only one reaction pathway over others. For example, the use of a Ni-based SAC supported on N-doped carbon showed 9-fold higher activity (TOF = 832 h⁻¹) than that of supported Ni NPs during the catalytic transfer hydrogenation of FUR into furfuryl alcohol (FAL) in 2-propanol.⁶⁵ SACs can be seen as the heterogenization of homogeneous catalysts, thereby combining the advantages of both homogeneous and heterogeneous catalysts. The catalyst recovery and recyclability are also better in SACs than nanocatalysts, owing to stronger interaction with the support in the former. However, the cost (instrument, process) of preparing SAC by physical (e.g., atomic layer deposition) or chemical (e.g., pyrolysis) methods with high atomic precision and desired scalability requires further research.⁶⁶ Organocatalysts are also increasingly used in the value addition of carbohydrates due to their bulk availability in pure form, relatively low toxicity, high stability, and convenient recoverability compared to transitional metal salts.^{67,68} For example, the dehydration of fructose into HMF has been reported using 4-(pyridinium)butanesulfonate as an organocatalyst.⁶⁹ Similar studies examined the efficiency of various organocatalysts containing both acidic and basic groups toward the dehydration of glucose into HMF.⁷⁰ A high-yielding synthetic protocol has been reported for the synthesis of novel products by Morita-Baylis-Hillman reaction from furaldehydes and acrylates using 1,4-diazabicyclo[2.2.2]octane as the organocatalyst.⁷¹

4. CHOICE OF SOLVENT

The benefits of using solvents in synthetic organic transformations are manifold.⁷² Solvents often alter the reaction pathway by directly or indirectly participating in the reaction mechanism.⁷³ Besides, solvents help homogenize the reacting components and bring them closer to the molecular level for the bond-making or bond-breaking steps.⁷⁴ Solvents also act as heat transfer media, minimize mass transfer limitations, and assist in isolating and purifying products. Various organic solvents differing in polarity, hydrogen-bonding capability, and hydrophobicity are used, and solvent screening for the optimum yield in an organic transformation is routinely studied.⁷⁵ Not surprisingly, a notable fraction of petroleum is used to produce solvents for laboratory and industrial use. However, the use of solvents in synthetic chemistry comes with daunting issues. The use and recovery of a high volume of organic solvents substantially increase the operational cost of a process. Besides, no solvent recovery system can reach 100% efficiency, and solvent loss by decomposition or accidental release into the environment is often encountered. Contamination of the product with trace solvent(s) and its associated health hazards further complicates the issue.⁷⁶

Therefore, the attempts to reduce the use of hazardous organic solvents as synthetic auxiliaries have intensified over the

Scheme 1. Preparation Route of Some Important Carbohydrate-Derived Renewable Solvents



past two decades. The problematic solvents, such as chlorinated hydrocarbons, are replaced with greener alternatives (e.g., ethers, esters) in one strategy. Renewable replacements of petroleum-derived solvents are increasingly used in synthetic organic chemistry, including the catalytic value addition of carbohydrates. The effects of various conventional and biorenewable solvents on the conversion of biomass (e.g., pretreatment, hydrolysis, and dehydration reactions) and extraction of products (or intermediates) have been explored (Scheme 1).⁷⁷ For example, 2-methyltetrahydrofuran (MTHF) synthesized from biomass-derived FUR is a promising substitute for tetrahydrofuran (THF) as an industrial solvent. Solvents like ethyl acetate can be made entirely biorenewable by sourcing ethanol and acetic acid from biomass following enzymatic or chemical-catalytic routes. However, to estimate their true environmental impact, detailed studies must be made to compare their production cost, efficiency as a solvent, and LCA. Strict criteria, including availability, cost, stability, ecotoxicity, and biodegradability, have been set to screen green solvents from the existing list and develop new ones.^{78,79} Novel classes of compounds have been prepared, and their efficiency as a solvent/reaction medium for various organic transformations has been explored. Ionic liquid (IL), supercritical fluid (SCF), and deep eutectic solvent (DES) have immense potential as reaction media. ILs are salts that are liquid below an arbitrary temperature (ca. 100 °C). ILs have excellent chemical and thermal stability, low toxicity, and low flammability. In addition, the ILs have a large working temperature window compared to conventional organic solvents, are nonvolatile, have high solvation power for a wide range of organic and inorganic molecules, and are multifunctional (e.g., reaction media, catalyst, etc.) An extensive library of ILs has been produced by structural modifications of the cation and anion to fine-tune properties such as melting point, acidity, and chirality. The major concerns associated with using ILs on a large scale are their high cost and difficulty in purification. Recently, organic amine-based inexpensive ILs have shown

promise in the catalytic value addition of biomass.⁸⁰ At temperatures and pressures greater than the critical points, substances show no clear distinction between the liquid and gaseous phases and are called SCFs. SCFs have also been instrumental in the value addition of biomass, such as the pretreatment of lignocellulosic biomass into cellulose, hemicellulose, and lignin using supercritical carbon dioxide (scCO₂).⁸¹ Supercritical water is used for various biomass value addition pathways, including hydrolysis, dehydration, and acid-catalyzed reactions.⁸² FUR and HMF have been produced from carbohydrates and cellulosic biomasses using scCO₂ as the reaction medium or extractant.^{83,84} Esterification of LA into EL as a heterogeneous acid catalyst.⁸⁵ Steam explosion using scH₂O and scCO₂ has been employed for the pretreatment of lignocellulosic biomass. The scCO₂ penetrates the polymeric network of cellulose, decreases its crystallinity, and makes it more amenable to chemical reagents for downstream value addition pathways. Catalytic reduction of furfurals and LA into furanic products and γ -valerolactone (GVL) have been performed successfully in the scCO₂ medium.⁸⁶

Since the first paper was published in 2001, DES has quickly gained prominence as the reaction medium for sustainable synthesis.⁸⁷ Even though many of the characteristics of DES are similar to ILs, they are two different classes of compounds. DES can be described by the general formula C⁺X⁻zY, where C⁺ is an ammonium, phosphonium, or sulfonium cation, and X⁻ is a Lewis base, typically a halide anion. The complex anionic species are formed between X⁻ and a Lewis or Brønsted acid Y (z = number of Y molecules interacting with the anion).

Other than organic solvents, the catalytic value-additions of carbohydrates have also been performed in aqueous medium, ILs, DESs, solvent-free conditions, and in SCFs.⁸⁸ Interestingly, several carbohydrate-based ILs with promising properties and potential applications have also been developed.⁸⁹

ILs have been used as the nonaqueous reaction medium for the dehydration of carbohydrates in producing HMF. Acid-

Table 1. Advantages and disadvantages of different solvents used in synthetic organic transformations

Type of solvent	Advantages	Disadvantages	ref
Petroleum-based solvent (Conventional solvent)	<ul style="list-style-type: none"> • Low cost 	<ul style="list-style-type: none"> • Toxic to environment and health 	105
Biobased solvent	<ul style="list-style-type: none"> • High extraction efficiency • Known physicochemical properties 	<ul style="list-style-type: none"> • Not sustainable 	106
Ionic liquid	<ul style="list-style-type: none"> • Low toxicity • Sustainable 	<ul style="list-style-type: none"> • High production cost • Less available choices • Limited information about properties 	107
Deep eutectic solvent	<ul style="list-style-type: none"> • Properties can be tailored • No evaporative loss 	<ul style="list-style-type: none"> • High production cost • Toxicity depends on the cation and anion used • Difficult to recover and recycle 	108
Supercritical solvent (scCO ₂ , scH ₂ O)	<ul style="list-style-type: none"> • Low cost • Components can be biorenewable • Properties can be tailored 	<ul style="list-style-type: none"> • Some components may be toxic at high concentration • Highly viscous • Challenging purification 	109
Switchable solvent	<ul style="list-style-type: none"> • Nontoxic • Abundant • Easily recyclable • Polarity can be altered reversibly by CO₂ • Straightforward process 	<ul style="list-style-type: none"> • High capital and operational expenditures • The commonly employed tertiary amines are often environmentally toxic 	110

functionalized (e.g., sulfonic acid) ILs can also promote the dehydration steps.⁹⁰ DES prepared from choline chloride (ChCl) and urea have been used for the dehydration of glucose into HMF using sulfonic acid-functionalized activated carbon as a heterogeneous catalyst.⁹¹ A combination of ChCl and ethylene glycol (EG) has been used as a DES for dehydrating glucose into HMF under batch and continuous flow conditions.⁹² A three-constituent DES has also been used as a reaction media and also as reactant for 5-(chloromethyl)furfural (CMF) synthesis.⁹³ Recent reviews have elaborated on the use of ILs and DESs for the production and value addition of HMF.^{94,95} Supercritical carbon dioxide (scCO₂) and supercritical water (scH₂O) have been used as acid and reaction media for producing HMF or LA from glucose.^{96,97}

Among the above options, solvent-free synthesis is the most appealing because it avoids using solvents altogether. The reactions can be performed in a melt or under a mechanochemical process (e.g., ball-milling).⁹⁸ For example, the deacetylation of chitin into chitosan can be performed under mechanochemical process.⁹⁹ However, heat transfer and mass transfer limitations must be sorted during the process scale-up. Moreover, the isolation and purification of the product may require solvents to be used. The central idea of using water as a sustainable reaction medium for organic transformations is its abundance, innocuous nature, and versatile properties at different temperatures. The acid-catalyzed dehydration and concomitant dehydration of carbohydrates into 2-furaldehydes (e.g., FUR, HMF) and LA are routinely performed in the aqueous or aqueous–organic biphasic medium.^{51,100} The transformation of FUR or FAL into cyclopentanone (CPN) is routinely performed in the aqueous medium at elevated temperatures.¹⁰¹ Cellulose or glucose can be converted into lactic acid (LAC) in subcritical water. Condensation reactions (e.g., Benzoin, Aldol) between carbohydrate-derived platforms are frequently performed in the aqueous or IL medium.¹⁰² ILs are increasingly being used to prepare platform chemicals from carbohydrates and their synthetic value addition.¹⁰³ In some cases, ILs can act as catalysts as well as the reaction medium. For example, various sulfonic acid-functionalized ILs have been used in preparing FUR and HMF from carbohydrates. However, the high cost of most ILs and their challenging recovery from the

reaction mixture remain challenging for the process economics and scale-up.¹⁰⁴ The following table (Table 1) lists the relative advantages and disadvantages of various classes of solvents and reaction media used in the synthesis of biorenewable chemicals from carbohydrates.

5. CHOICE OF REAGENTS

There is a stark difference between biomass and petroleum components at the molecular level. Biomolecules and biopolymers are heavily functionalized and contain carbon atoms in various oxidation states, whereas petroleum primarily consists of hydrocarbons. Therefore, the synthesis of petrochemicals involves a series of synthetic steps introducing heteroatom-containing (e.g., O, N) functional groups in the hydrocarbon moiety. Incidentally, these oxidation steps using stoichiometric or catalytic reagents lead to significant waste streams that can cause pollution. On the contrary, biorefinery operations selectively remove excess functionalities from the heavily oxygenated biomolecules. One of the greatest benefits of using biomolecules as feedstock for synthesizing functionalized chemicals is the similarity of the oxidation states and pre-existing heteroatom-containing functionalities attached to the carbon atoms. Catalytic reagents are preferred over stoichiometric ones as the former requires low energy and materials input, minimizing waste formation. Innocuous oxidants are preferred for oxidation reactions, leading to innocuous byproducts like water. For example, air or purified O₂ gas is a preferred gaseous oxidant, whereas aqueous H₂O₂ is the preferred liquid oxidant.^{111,112} Oxidation processes involving the above oxidants lead to water as the sole innocuous byproduct. Molecular H₂ or a hydrogen-donor molecule is routinely used in the presence of a suitable catalyst for reducing biomolecules or biomass-derived chemical intermediates into renewable bioproducts.^{113,114} Green metrics like AE and E-factor are satisfactory for redox processes involving oxidizing and reducing agents. Metal-based catalysts are integral to the redox processes and govern their economic and environmental suitability. Comparative discussions on noble metal and earth-abundant first-transition metal catalysts have been incorporated in the previous section. Electrocatalytic value addition of carbohydrate-derived platform chemicals is getting increasingly popular because of the low cost,

good scalability, energy- and reagent-economic nature, and less waste generation.¹¹⁵ HMF has been oxidized into 2,5-furandicarboxylic acid (FDCA), a potential monomer for sustainable polymers, and has been produced by electrolysis using metal–organic framework-structured hierarchical Co_3O_4 nanoplate arrays as an electrocatalyst on nickel foam electrode surface.¹¹⁶ The reduction of HMF into BHMF has been attempted using a AgCu foam electrocatalyst.¹¹⁷ Another advantage of this process is forming two different products by removing electrons from one substrate (i.e., oxidation) and introducing those into another substrate (i.e., reduction).¹¹⁸ Chemical oxidizing and reducing reagents are not required in this process, and water in the electrolyte often acts as the reagent. The major challenge in this process is to design the electrocatalyst on the electrode surface for best selectivity and current efficiency. The stability of the electrolyte and the separation of product from the electrolyte solution must also be figured out

6. REACTOR DESIGN AND REACTION PARAMETERS

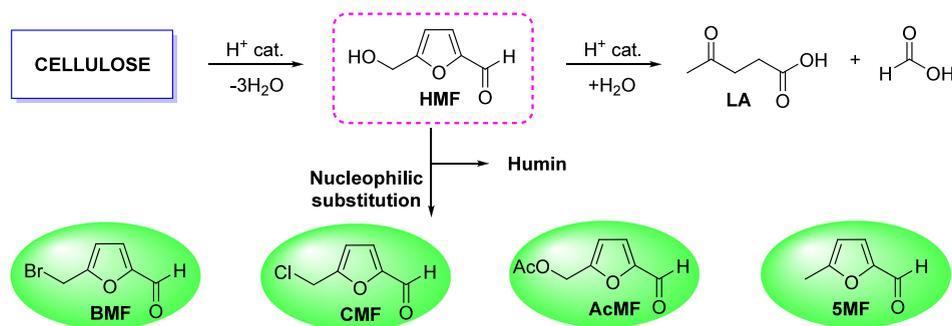
The type of reactor and the associated reaction parameters play pivotal roles in determining the process efficiency. Many of the derivative chemistry of carbohydrate-derived platform chemicals have been carried out in the laboratory scale either in a batch reactor or a small-scale continuous flow reactor. For example, HMF production has been performed in a batch as well as continuous flow reactor.¹¹⁹ Recently, the production of CMF from high fructose corn syrup has been demonstrated in a continuous flow process.¹²⁰ A major shortcoming in a batch reactor is the low concentration of product per unit volume of the reactor.¹²¹ The problem has been offset by using a fed-batch process during LA production, where additional amounts of feedstock were introduced at regular intervals leading to high concentration of LA at the end of the transformation.¹¹⁹ A few processes have been carried out in a pilot or demonstration scale in various reactor set up. For example, the *Biofine* process of LA production used a two-stage process using a plug-flow reactor (PFR) and a continuous stirred tank reactor (CSTR). The dilute H_2SO_4 catalyzed hydrolysis of cellulosic biomass first allows the carbohydrates to break down into HMF and FUR in the PFR. After removing FUR by evaporation, the HMF is rehydrated into LA in the CSTR working under slightly lower temperature and pressure but with longer residence time than the PFR. The process allows excellent isolated yields of LA compared to most processes of synthesizing LA from cellulosic biomass. The conversion of cellulosic biomass into fuels by pyrolysis have been performed in several other reactors.¹²² Traditionally, the conversion of carbohydrates into fuels and chemicals are performed under resistive heating in an oil bath or heating mantle (lab-scale) or by external heating (direct heating of reactor or secondary heating by hot air or steam stripping in the industrial scale). Inductive heating has several advantages over resistive heating in terms of process intensification, energy efficiency (minimizes heat transfer limitations), reactor setup simplification, and safer operations in radio frequency heating.¹²³ Inductive heating is getting increasing popular in organic transformations and it can certainly be used in the biorefineries.¹²⁴ Cellulose-derived LA has been converted into GVL, a potential renewable solvent and biofuel, by catalytic transfer hydrogenation using a Ru-catalyst supported on magnetic nanoparticles under inductive heating.¹²⁴ Under microwave (MW) irradiation conditions, organic reactions can be accelerated and selectivity of the product can be fine-tuned by

choosing appropriate MW parameters, while offering instantaneous heating, high temperature homogeneity, and selective heating.¹²⁵ Heating under MW irradiation is increasingly being used for the value-addition of carbohydrates through the platform chemicals.¹²⁶ MW irradiation technique has been used for the production of furanic platforms, such as HMF and 5-(ethoxymethyl)furfural directly from sugars.^{127,128} Large-scale MW reactors are now available so that this technology can be translated to industry. Ultrasound has been used as an alternative source of energy for the bond-making and bond-breaking reactions in carbohydrate value addition.¹²⁹ However, the scalability of the technology remains questionable.

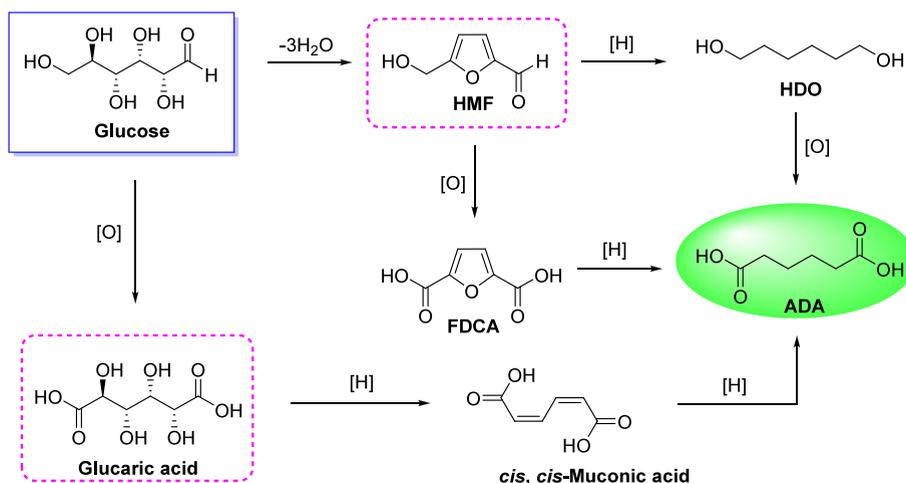
7. CARBOHYDRATE-DERIVED PLATFORM CHEMICALS

A handful of primary petrochemicals can be used as platform chemicals to synthesize virtually all bulk- and specialty chemicals and organic materials used in industrialized societies. The synthetic steps typically involve building the desired carbon framework and functionalizing the hydrocarbon moieties. The same strategy may be followed for the value-addition of carbohydrates into renewable bioproducts.¹³⁰ Synthesizing a handful of reactive and strategically functionalized molecules (known as *platform chemicals*) by the catalytic transformation of carbohydrates can lead to ready access to a wide range of products of commercial significance in a two-step process. The platform chemicals are produced selectively from minimally treated or even untreated carbohydrates in the first step. The compounds are then separated, purified, and subjected to downstream synthetic value addition pathways. In recent years, novel catalytic systems have been developed that allow the conversion of carbohydrates directly into targeted products through platform chemicals that act as a transient intermediate. These processes simplify process design, minimize waste generation, and lower operational costs. However, the catalyst(s) used in these processes must be tailor-made since they must catalyze more than one type of reaction, maintain high reactivity, and afford high selectivity. This section gives an overview of the catalytic production and downstream synthetic value-addition of some important carbohydrate-derived platform chemicals. Understanding the reactivity patterns of the platform chemicals is crucial to developing efficient synthetic processes for expanding their derivative chemistry and encompassing a wider range of products. The platform chemicals can be categorized depending on the number of carbon atoms in the skeletal framework. If there is no carbon–carbon bond-breaking reaction involved, the hexose carbohydrates (e.g., glucose, cellulose) lead to C6 platform chemicals, such as HMF, levoglucosenone (LGO), and isosorbide (IS). The acid-catalyzed dehydration of NAG, the monomeric unit of chitin, produced 3-acetamido-5-acetylfuran (AAF).¹³¹ AAF is a promising nitrogen-containing furanic platform chemical that can be converted into various derivatives of commercial value. The major challenge in the application of AAF is to produce it directly from chitin in the desired selectivity and yield under moderate conditions. The catalytic conversion of glucose involving the C–C bond-breaking process leads to C3 platform chemicals like LAC and C2 platform chemicals like EG. The removal of oxygen atoms from the glucose moiety can be done using dehydration, hydrodeoxygenation, decarboxylation, decarbonylation, and hydrogenolysis reactions. Introducing additional oxygen atoms into the glucose molecule involves oxidation reactions.

Scheme 2. Synthesis of HMF and Its Hydrophobic Analogs from Carbohydrates



Scheme 3. Biorenewable Synthesis of Adipic Acid from Glucose by Redox Chemistry without Breaking the Carbon–Carbon Bonds



7.1. 5-(Hydroxymethyl)furfural. Acid-catalyzed dehydration of hexose sugars, such as glucose and fructose, forms HMF.^{132,133} The transformation involves the sequential elimination of three molecules of water from a molecule of glucose or fructose without involving carbon–carbon bond-cleaving reactions. Therefore, the process has 100% carbon efficiency, whereas the AE stands at 70%. Moreover, 50% of the oxygen atoms in glucose are eliminated in the catalytic process in the form of water molecules and form an aromatic compound. The direct production of HMF from polymeric carbohydrates (e.g., starch, cellulose, inulin) involves a prior hydrolysis step.¹³⁴ HMF has been produced from carbohydrates using an exhaustive list of Brønsted and Lewis acid catalysts. The 150-year-old process has received renewed interest since the 1990s due to its commercial prospect in producing renewable biochemicals and increasing focus on feedstock sustainability in the chemical industries. HMF is typically obtained in good yields from fructose due to the straightforward elimination of three water molecules sequentially from its predominant fructofuranose moiety. However, since fructose originates from food biomasses and is expensive, it is unlikely to be a commercially viable feedstock for HMF production. Therefore, the focus has been shifted to producing HMF from abundant and inexpensive sugars (e.g., glucose) or from polymeric carbohydrates (e.g., cellulose).¹³⁵ Even though glucose can be converted into HMF by alternative mechanistic pathways, catalysts and reaction conditions that allow glucose to isomerize into fructose before dehydration have been developed to ensure higher yields of HMF. Over the past decade, significant

advancements have been made to convert cellulose and cellulosic biomass into HMF in acceptable yields. However, the process has yet to reach commercialization due to scalability and process economics concerns. The inherent hydrophilicity and poor stability (hydrolytic, thermal) of HMF make its isolation from the aqueous (or polar) reaction media, purification, and storage quite challenging.¹³⁶ One way to circumvent this issue is isolating HMF from the reaction mixture as a hydrophobic analog. Even though the isolation and purification of the hydrophobic analogs of HMF are relatively straightforward, their synthetic upgrading mandates recovering the stoichiometric reagent integrated in their structure (e.g., acetic acid in AcMF) (Scheme 2).

Moreover, the reactivity patterns of various HMF analogs differ significantly. Regardless, HMF and its hydrophobic analogs have a wide span of derivative chemistry encompassing all major classes of chemicals of commercial importance.¹³⁷ The principles of green chemistry play governing roles in the synthetic value addition of HMF and its hydrophobic analogs. Hydrophobic analogs of HMF that possess a halogen atom include CMF and 5-(bromomethyl)furfural.^{138,139} CMF has shown promise as a stable substitute of HMF to access the derivative chemistry of the latter.¹⁴⁰ The ester analogs of HMF includes 5-(formyloxymethyl)furfural (FMF) and 5-(acetoxymethyl)furfural (AcMF).^{141,142} Several stoichiometric reagents have been examined to produce the hydrophobic analogs of isolated HMF by nucleophilic substitution of its hydroxymethyl group. However, the two-step processes are less energy- and reagent-economic, requiring the cumbersome

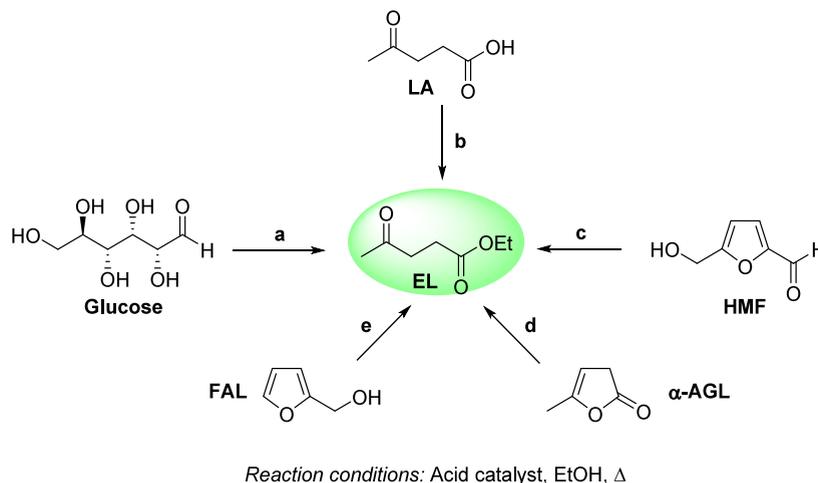
isolation of HMF. Therefore, recent studies largely focus on the one-pot production of the hydrophobic analogs of HMF. For example, CMF is produced by dehydrating sugars, polymeric carbohydrates, and cellulosic biomasses in concentrated aqueous HCl.¹⁴³ Attempts have been taken to identify the most efficient extracting solvent that safeguards the CMF in the organic layer as it forms and accumulates in the reaction mixture. Reaction engineering to retard the hydrolysis of CMF into HMF in the organic layer has been studied by artificially increasing the chloride content using a quaternary ammonium chloride phase transfer catalyst.¹⁴⁴ However, major technological and environmental complications in CMF synthesis come from using aqueous HCl as a volatile and corrosive mineral acid. Another important derivative of HMF is 5-methylfurfural (5MF), produced by partial reduction of HMF or directly from carbohydrates.^{145,146} Several recent studies have explored the possibility of using an alternative acidic reaction media containing a high concentration of chloride content. For example, metal chlorides and acidic ILs containing chloride as the counteranion have been explored.¹⁴⁷ Even though acceptable yields of CMF have been obtained using such reaction media, the processes worked well only on simple sugars (e.g., fructose) as the substrates. However, unless the processes afford satisfactory yields of CMF starting from abundant and inexpensive carbohydrates (e.g., cellulose) under economically amenable and environmentally acceptable conditions, the suitability of the processes for commercial adoption will remain questionable.

Adipic acid (ADA) is a high-volume chemical typically used as a monomer for synthesizing Nylon-6,6.¹⁴⁸ Several alternative synthetic pathways have been developed over the past decade on the biorenewable synthesis of ADA from glucose or cellulose (Scheme 3).¹⁴⁹ In terms of the chemical equation, the conversion of glucose into ADA is an overall reduction. Suppose a disproportionation reaction can be performed on the carbon atoms of glucose. In that case, each mole of glucose will require only one mole of hydrogen to be converted into a mole of ADA, along with two moles of water as the sole byproduct according to the chemical equation [$C_6H_{12}O_6 + H_2 = C_6H_{10}O_4 + 2H_2O$]. Unfortunately, no known catalyst affords the direct transformation of glucose into ADA. HMF has been used as a key intermediate to transform glucose into acrylic acid (ACA) by redox steps.¹⁵⁰ In one strategy, HMF is first reduced into 1,6-hexanediol (HDO) under a catalytic hydrogenation reaction using a suitable heterogeneous catalyst and molecular hydrogen.¹⁵¹ HDO is then oxidized to ADA by catalytic oxidation reaction.¹⁵² Alternatively, HMF is oxidized to 2,5-furandicarboxylic acid (FDCA), which is then reduced to ADA.¹⁵³ Catalytic pathways without going through the HMF intermediate involve oxidizing glucose into glucaric acid and reducing the latter into ADA by catalytic hydrogenation.¹⁵⁴ However, multiple reduction and oxidation reactions are involved in all these cases, leading to significantly more hydrogen consumption and lower AE. For example, the synthesis of ADA through the intermediacy of HDO requires five moles of hydrogen per mole of glucose. Moreover, the ease and selectivity toward the oxidation or reduction of specific functional groups still need to be improved for process economics and scale-up.¹⁵⁵ The eighth principle of green chemistry states the advantages of decreasing the number of synthetic steps and recommends removing unnecessary derivatization steps to minimize waste accumulation. In the

present scenario, the intermediacy of HMF may be avoided for the synthesis of ADA if plausible.

7.2. Furfural. The pentose sugars (e.g., xylose, arabinose) in the hemicellulose fraction undergo acid-catalyzed dehydration to form FUR.¹⁵⁶ Unlike HMF, the production of FUR has been commercialized, and there are established markets for many of its derivatives.¹⁵⁷ HMF and FUR act as nodal points for synthesizing other furanic chemicals, which can then be transformed into acyclic compounds, carbocycles, heterocycles (other than furan), and benzenoids by primarily catalytic steps.¹⁵⁸ In this subsection, the chemical-catalytic process development of some specific derivatives of FUR has been elaborated. FAL has been one crucial derivative of FUR with applications in the resin industry and as a chemical intermediate for various renewable products. FAL is produced by the selective reduction of FUR, typically achieved under the catalytic hydrogenation conditions using molecular hydrogen and a metal-based heterogeneous catalyst. Needless to say, the process is significantly better regarding process economics and environmental aspects than processes using stoichiometric chemical reducing agents, such as $NaBH_4$. Over the past decades, significant improvements in the catalytic process have been made. Highly efficient catalysts that allow the production of FAL in the desired selectivity and yield under economically attractive and environmentally acceptable conditions have been developed. Even though the commercialized process used the efficient copper chromite catalyst, more research is dedicated to designing eco-friendly catalysts for the transformation. Hydrogenation can happen to the aldehyde group and the furan ring, and hydrodeoxygenation can happen to the C–O bonds in the resulting hydroxymethyl group and tetrahydrofuran ring. The selectivity of the product depends on the catalyst used, synthetic auxiliaries (e.g., solvent), and reaction conditions (e.g., temperature, hydrogen overpressure). Hydrogenolysis of the C–OH bond in FAL leads to 2-methylfuran (MFU).¹⁵⁹ It has been found that acidic sites in the catalyst and some specific metals promote the hydrogenolysis reaction. However, the density and strength of acidic sites in the catalyst play crucial roles in MFU synthesis since strongly acidic sites trigger the polymerization of FUR or FAL. Other important derivatives obtained from FUR by hydrogenation include MTHF.¹⁶⁰ The processes are highly atom-efficient, and water is formed as the sole byproduct. The hydrogenation processes can be performed in the liquid or gas phase. In the liquid phase, the solvent plays a decisive role in the selectivity of a specific product. The catalytic decarbonylation of FUR leads to furan, which can be a renewable entry point for industrial solvents like THF. Moreover, the renewable THF can be catalytically converted into 1,3-butadiene by a dehydra-decyclization process on a suitable catalyst surface.¹⁶¹ The catalytic decarbonylation process has successfully been extended to various 5-substituted-2-furaldehydes. For example, HMF has been decarbonylated into FAL. Since HMF can be sourced from inexpensive and abundant feedstock like cellulose, the transformation of HMF into FAL can significantly improve availability and decrease the cost of the latter. These stoichiometric reagentless transformations require a suitable catalyst and produce less to no waste. FUR can be transformed into CPN by catalytic hydrogenation and Piancatelli rearrangement in the aqueous medium. Renewable synthesis of CPN from FUR allows the synthesis of carbocycles and related chemicals from carbohydrates. FUR can be transformed into angelica lactones (AGLs), LA, and levulinic acid esters by acid-catalyzed

Scheme 4. Alternative Synthetic Pathways for Ethyl Levulinate



rearrangement, hydrolysis, or alcoholysis. Interestingly, the transformation of FAL into AGL or LA is 100% atom economic.

7.3. Levulinic Acid. The rehydration of HMF followed by ring-opening leads to 4-oxopentanoic acid or LA, along with an equimolar amount of formic acid (FA). LA is often found as a minor byproduct during the preparation of HMF.¹⁶² LA can be formed directly from carbohydrates without isolating the HMF intermediate.¹⁶³ FUR can also be transformed into LA via the FAL intermediate.¹⁶⁴ Hundreds of publications have been devoted to producing LA from various carbohydrate feedstock under a variety of conditions (e.g., method of heating, batch or flow conditions, catalysts, medium). While yield remains a major factor for most processes, other bottlenecks include scalability of the technology, cost associated with the isolation and purification of LA, and recyclability of the acid catalyst employed. Since the reaction is performed in water or in polar medium where LA remains soluble, it has to be either extracted or distilled out after removing water and low-boiling components in the reaction mixture. The use of corrosive acids (e.g., H_2SO_4 , HCl) under pressurized conditions also complicates the reactor design and increases capital expenditure. Commercial strategies for producing LA from lignocellulosic biomass includes the Biofine process.¹⁶⁵ The Biofine process involves a two-stage process leading to nearly 70 mol % (based on the hexose content in the feedstock) of LA starting from cellulosic biomass. Initially, the aqueous suspension of lignocellulosic biomass is digested in dilute H_2SO_4 (3.5 wt %) in a plug flow reactor (215 °C, 25 bar, 15 s), where the feed is transformed into FUR and HMF. FUR is separated by vaporization at this stage. The mixture is then transferred into a continuous stirred-tank reactor (195 °C, 14 bar, 25 min), where HMF converted into LA. Water and FA are first distilled off, lignin and humin are filtered, and LA is then subjected to purification by vacuum distillation. In the process, FA is not isolated. The humin and lignin residues are neutralized before drying and then combusted for generating process heat.

LA has been recognized as one of the top 12 biomass-derived chemicals based on its commercial potential.¹⁶⁶ LA contains two synthetically versatile functional groups in its moiety: ketone and carboxylic acid. Moreover, the methylene and methyl group at the α -position of these two carbonyl functionalities are also activated and participate in various chemistry. The derivatives produced from LA have applications ranging from fuels to solvents to plasticizers to agrochemicals to pharmaceuti-

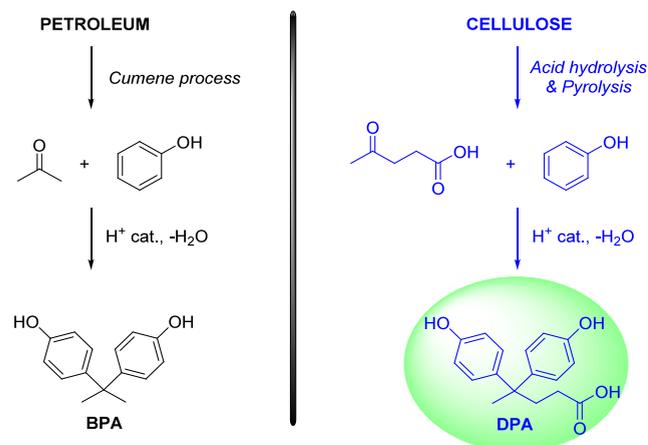
als.^{167,168} The intramolecular lactonization of LA, followed by dehydration, forms AGLs. The AGLs can exist in equilibrium between three positional isomers, where α -AGL is a predominant form. The ester and olefin group in AGLs can participate in chemistry that is not possible to access from LA.¹⁶⁹ An acid catalyst typically catalyzes the LA to AGL transformation, even though a catalyst-free synthesis has also been reported. In a typical process, LA (bp 252 °C, at 1 bar) is mixed with the acid catalyst and heated to around 160 °C under a controlled vacuum so that AGL (bp 170 °C, at 1 bar) gets distilled off from the reaction flask as it forms (along with the water byproduct) into the collection flask.¹⁷⁰ Earlier processes used homogeneous mineral acids (e.g., H_3PO_4) as catalysts. Even though satisfactory yields of AGL were obtained, the corrosivity and recovery of the homogeneous acid catalyst remain the bottlenecks. Heterogeneous acid catalysts with moderate acidity, especially silica-rich catalysts (e.g., zeolite and montmorillonite clay), have shown high activity and selectivity toward AGL. The next advancement in this catalytic process could benefit from developing a catalyst (preferably heterogeneous) that allows the reaction to work under lower temperatures, improving the energy efficiency and simplifying the separation of AGL.

Ethyl levulinate (EL) has received significant interest recently as a potential diesel additive, green solvent, and renewable chemical for downstream synthetic value addition.¹⁷¹ EL can be produced from several different carbohydrate-derived chemical intermediates (Scheme 4). While such feedstock versatility is appreciated for a synthetic process, the alternative synthetic pathways can be evaluated from the vantage point of green chemistry principles. EL can be produced by the Fischer esterification of isolated and purified LA. The process typically uses an acid catalyst of some sort in excess ethanol to favor the equilibrium toward the EL side.¹⁷² In this strategy, the prior purification of LA and the removal of excess ethanol by distillation are two energy-intensive steps. Ethanolysis of isolated HMF forms EL and ethyl formate in equimolar quantities, then separated by fractional distillation.¹⁷³ However, the process relies on the scalable and high-yielding preparation of HMF from inexpensive carbohydrates. The high-yielding preparation of HMF from inexpensive carbohydrates and its challenging purification remain the key challenges for the process.¹³⁶ Glucose or cellulose can be directly converted into EL in the ethanolic medium using a suitable acid catalyst.^{174,175}

In this strategy, the requirement of isolating HMF or LA as an intermediate is averted. However, the process requires more demanding conditions (e.g., pressure reactor), longer duration, and excess ethanol. Moreover, the loss of ethanol as diethyl ether and other side products cannot be avoided for most acid catalysts employed. EL can be produced by reacting α -angelica lactone (α -AGL), produced by the acid-catalyzed intramolecular dehydrative lactonization of LA, with ethanol.¹⁷⁶ EL is formed irreversibly without forming water as the byproduct in this reaction. However, the preparation of α -AGL from LA is an energy-intensive process. The alcoholysis of FAL, produced by the partial hydrogenation of hemicellulose-derived FUR, also forms EL.¹⁷⁷ However, the process involves more synthetic steps, and FAL is sourced from less abundant carbohydrates. Since an acid catalyst typically promotes the transformation mentioned above, it is possible to develop catalysts that work well for all the feedstocks.¹⁷⁸

Due to the adverse health effects of Bisphenol A (BPA), widely used as a monomer in producing polycarbonates and epoxy resins, there is research for its safer, more efficient, and more sustainable substitute.¹³ Diphenolic acid (DPA), produced by reacting LA with two phenol molecules, has been proposed as an economically viable and environmentally acceptable alternative to BPA (Scheme 5).¹⁷⁹

Scheme 5. Production of Diphenolic Acid As a Renewable Substitute for Bisphenol A



Even though phenol and acetone can be synthesized from biomass (or carbohydrates) for renewable BPA, the focus is explicitly given to DPA as a safer and more efficient product following the fourth principle of green chemistry.¹⁸⁰ The latest research in producing DPA focused on developing efficient and eco-friendly acid catalysts while aiming for higher selectivity and yield.¹⁸¹

7.4. Isosorbide. Selective reduction of the aldehyde group in glucose forms sorbitol. Sorbitol gets converted into 1,4:3,6-dianhydro-d-sorbitol or IS on double-dehydration under acid catalysis. Polymeric carbohydrates can be converted directly into IS by a cascade of catalytic steps, i.e., hydrolysis-hydrogenation-dehydration. Multifunctional catalysts have been developed for the one-pot synthesis of IS starting from inexpensive carbohydrates. As a C6 chemical building block, IS has huge derivative chemistry; many are commercially available or on the verge of commercialization.

Dimethyl isosorbide (DMI) is a promising ether-based bio-renewable solvent being examined for various organic

transformations, biomass pretreatment, and an electrolyte in battery applications.^{182–186} DMI has been used as a nontoxic solvent and emollient in formulating various cosmetics and personal care products (e.g., lotion, cream, etc.).¹⁸⁵ The initial attempts to synthesize DMI included using strong bases (e.g., NaH) and powerful electrophiles (e.g., methyl iodide, dimethyl sulfate). However, the special reaction conditions (e.g., inert atmosphere, moisture-free) and toxicity of the reagents limit the scalability and practicality of the processes. Recent synthetic attempts have used bases that are catalytic and greener reagents. For example, dimethyl carbonate (DMC) has been used as a greener methylating agent. DMC can be produced renewably from CO₂ and methanol, which may be sourced from biomass. The process works under acceptable reaction conditions and affords satisfactory yields of DMI. Table 2 lists the literature on

Table 2. Literature on the Methylation of Isosorbide into 2,5-Dimethylisosorbide Using Various Alkylating Agents

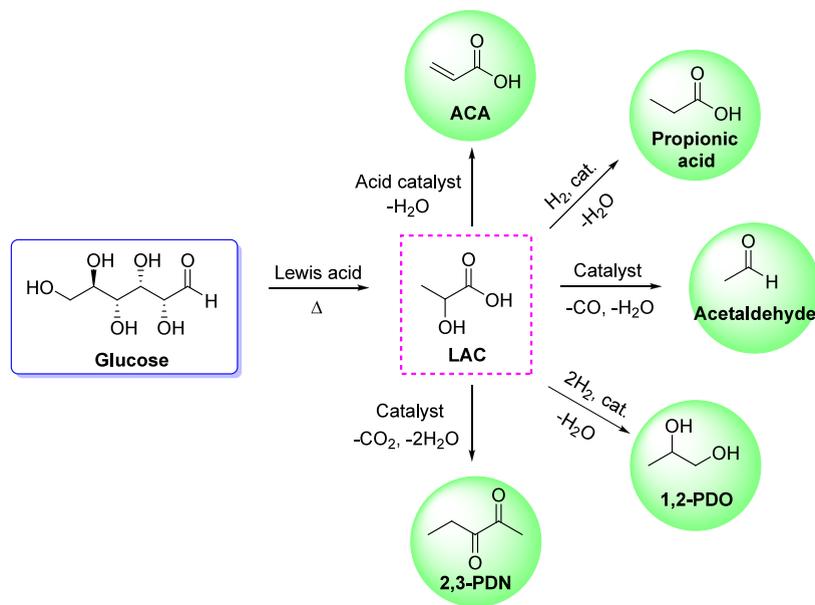
Entry	Alkylating agent	Catalyst	Reaction conditions	Yield (%)	Ref.
1		Amberlyst-36	DMC (excess), 100 wt.% acid catalyst, 200 °C, 6 h.	78	188
2		-	1,4-dioxane or triglyme, alkylating agent (2 equiv), KOH (7 equiv), 65 °C, 1.5 h	96	189
3		Fe(OTf) ₂ (4 mol%)	Pressure tube, alkylating agent (3 equiv), 100 °C, 15 h	54	190
4		H ₃ PO ₁₂ O ₄₀ (0.95 mol%)	Alkylating agent (21.5 equiv), 150 °C, 10 h	80 ^[a]	191

^aGC yield.

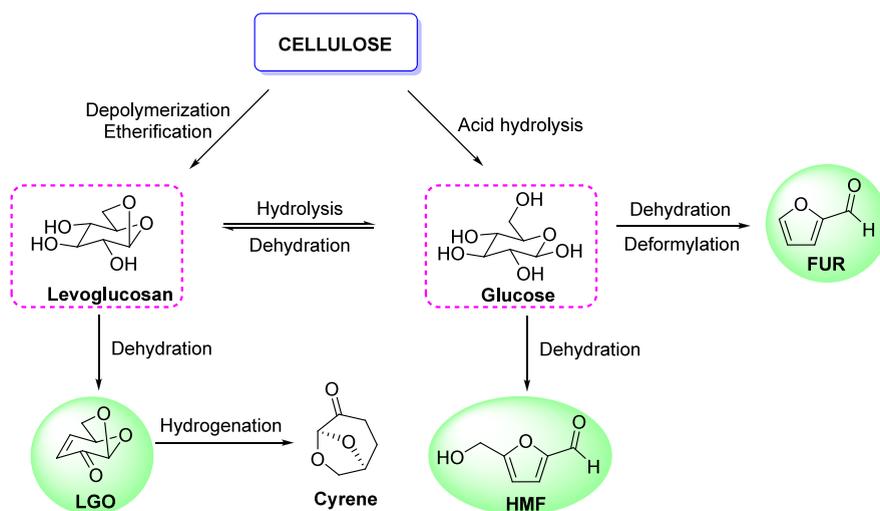
synthesizing DMI from IS using various methylating agents, such as dimethyl carbonate (DMC), dimethyl sulfate (DMS), 1,2-dimethoxyethane (DME), and trimethyl phosphate (TMP). In the case of DMS, a highly reactive methylating agent, no catalyst was required. However, moderately reactive methylating agents, such as DME and DMC, warranted a suitable catalyst candidate. A crucial criterion for the economic and environmental practicality of the process involves choosing the proper methylating agent. In this regard, DMC has attracted particular attention due to its low toxicity, inexpensiveness, and sustainable production from methanol and CO₂.¹⁸⁷ The byproducts produced during DMI synthesis using DMC are methanol and CO₂, which are relatively harmless and could be recycled to produce fresh DMC. In other methylating agents used for DMI synthesis, significant amounts of harmful wastes are formed as the byproduct. For example, DME will produce EG, and TMP produces diethylphosphoric acid as a byproduct during DMI production. The efficiency of various catalysts for producing DMI from IS using DMC has been explored. Using a catalyst not only ensured energy efficiency by faster kinetics but also improved the selectivity of the yield of DMI. Interestingly, DMC has been employed for the one-pot synthesis of DMI directly from sorbitol, thereby improving the step-efficiency of the synthetic process and avoiding the purification of the IS as an intermediate.

7.5. Diols and Polyols. Catalytic hydrogenation of the aldehyde group in glucose leads to sorbitol, a polyol compound.¹⁹² While sorbitol has established markets, it can be further converted into high-value products, including fuels, chemicals, polymers, and also vitamins.¹⁹³ For example, the acid-

Scheme 6. Biorenewable Production and Value Addition of Lactic Acid



Scheme 7. Production of Levoglucosone from Cellulose in the Presence of Other Competing Mechanistic Pathways



catalyzed double-dehydration with concomitant cyclization leads to IS (discussed separately). Glucose can be broken down to erythrose, a C4 sugar, in supercritical water in the presence of the right catalyst candidate by retro aldol reaction.¹⁹⁴ Under a reductive atmosphere (e.g., overpressure of hydrogen and a metal-based catalyst), glucose can be converted into three moles of EG through the intermediary of glycolaldehyde.^{195,196} The hydrogenolysis of the C3–C4 bond in sorbitol can lead to two moles of glycerol (GLY). However, the selectivity toward GLY remains an issue to date.¹⁹⁷

7.6. Lactic Acid. Glucose or cellulose-derived LAC can be a convenient starting material for biorenewable ACA to replace petroleum-derived ACA in acrylic polymers.^{198,199} Moreover, LAC can be used as a biorenewable monomer for synthesizing polylactic acid as a biodegradable polymer.^{200,201} According to the balanced chemical equation, a glucose molecule can be transformed into two LAC molecules without any byproduct formation in the presence of a suitable acid or base catalyst.²⁰² Cellulose can be converted to LAC in a single pot using a

multifunctional catalyst that promotes a series of tandem steps.²⁰³ The mechanism starts with the isomerization of glucose into fructose, the retro-aldol condensation of fructose into glyceraldehyde, and a series of isomerization steps involving a 1,2-hydride shift.^{204,205} The challenge is to product LAC in excellent selectivity at acceptable conversion of the carbohydrate feedstock. Separation and purification of LAC from unreacted sugar and other side products is cumbersome. For example, the dehydration of sugars into HMF often competes with the LAC formation.^{206,207} Several high-value chemicals can be prepared from LAC following catalytic pathways (Scheme 6). The acid-catalyzed dehydration of LAC leads to ACA and various heterogeneous catalysts (e.g., zeolite) have been studied systematically for the gas-phase transformation.^{208,209} Noble metal nanoparticles supported on various materials (e.g., SiO₂, TiO₂, AC, γ -Al₂O₃) have been used as heterogeneous catalysts for hydrogenating LAC into propionic acid.^{210,211}

The decarbonylation and dehydration of LAC can lead to acetaldehyde. Alternative reaction mechanism involves decar-

boxylation and dehydrogenation reactions.²¹² A recent publication used mesoporous aluminum phosphate catalyst for producing biorenewable acetaldehyde from LAC.²¹³ Heteropoly acids supported on silica-based materials have also shown high selectivity toward acetaldehyde.²¹² The challenge is to slow down the low-lying alternative reaction pathways, such as hydrogenation and dehydration steps.²¹⁴ Selective reduction of LAC under catalytic hydrogenation conditions forms 1,2-propanediol (1,2-PDO). Ruthenium NPs supported on titania has provided a 70% yield of 1,2-PDO at 79% conversion of LAC (i.e., 88.6% selectivity) under optimized parameters (130 °C, 20 h).²¹⁰ The decarboxylative ketonization with concomitant dehydration leads to 2,3-pentanedione (2,3-PDN).^{215–217} In all the process, the primary challenge is to develop a robust, selective, and eco-friendly catalysts for the transformation under economically feasible and environmentally acceptable conditions. Catalysts that can handle technical grade LAC (with minor amounts of water and other organic impurities) will be given preference. Except acetaldehyde and 2,3-PDN, all the derivatives of LAC discussed above do not involve losing carbon atoms during their synthesis and therefore enjoy 100% carbon efficiency starting from glucose or cellulose.

7.7. Levoglucosenone. Levoglucosenone (LGO), an unsaturated bicyclic ketone-diether formed from cellulose-derived levoglucosan by double dehydration, is a C6 chemical building block produced by the pyrolytic deconstruction of cellulose promoted by an acid catalyst (Scheme 7).²¹⁸ Mineral acids like H₂SO₄ and H₃PO₄ were used as catalyst in earlier studies, which is now being replaced with heterogeneous acid catalysts (e.g., zeolites).²¹⁹ LGO can be used as a chiral moiety to synthesize chiral bioactive molecules, biobased polymers, and develop chiral ligands for asymmetric synthesis.^{220–222} Hydrogenation of the olefinic group in LGO leads to cyrene, which is a promising biorenewable solvent.²²³ However, the production of LGO must be improved (e.g., yield, scalability) further to improve the availability and decrease the cost of cyrene.

8. CONCLUSION AND FUTURE PERSPECTIVES

As discussed in the earlier sections, the principles of green chemistry act as the toolkit that helps design sustainable synthetic strategies for converting biomass-derived carbohydrates into valuable organic products, including fuels, fine chemicals, and synthetic polymers. Even though biomass can be converted into heat, electricity, and transportation fuels, the same may be achieved from emission-free renewable energy technologies (e.g., solar). A more useful application of this renewable carbon-based feedstock is synthesizing organic chemicals and synthetic polymers for long-anticipated sustainability in the chemical industry. The knowledge database developed on sustainable organic synthesis will continue to shape the biorefineries by improving their societal outreach, economic feasibility, and environmental acceptability. The rationality in selecting the feedstock, reagents, reaction auxiliaries, and reaction conditions helps minimize the energy and materials requirement, resulting in economic and environmental benefits. The drop-in bioproducts structurally indistinguishable from petrochemicals can easily be assimilated into the pre-existing infrastructure. The major challenges are lowering the break-even price of carbohydrate-derived chemicals, ensuring continuous feedstock supply, and lowering the carbon footprint throughout the process. On the other hand, the functional substitutes of petroproducts typically face more resistance while entering the market. Supportive economic and

environmental policies at the national and international levels will continue to play a pivotal role in expanding the scope and applicability of bioproducts. In a short-term strategy, subsidies extended to sustainable chemicals can encourage startups working in this area. In the long term strategy, dedicated funding to research and development activities in this area and increasing public awareness about sustainability and biobased economy will help. As the technologies mature and demand for sustainable chemicals increases, the processes will likely fend for themselves. Catalysis remains at the heart of sustainable chemistry, allowing access to targeted products in desired selectivity, yield, and scalability. Catalysis allows the process to employ abundant, inexpensive, and innocuous starting materials and reagents under energy-efficient conditions. A new generation of robust, highly selective, and recyclable heterogeneous catalysts that allow the formation of the desired product in high TON and TOF has been developed. Tailor-made nanocatalysts and SAC, with precise control over their active sites, particle size distribution, surface area, and pore structures, are increasingly used for synthesizing biorenewable chemicals starting from carbohydrates for their economic and environmental advantages over conventional heterogeneous benefits. Such catalysts, especially those using expensive noble metals as active sites, minimize the moles of metal required per mole of product produced. High activity and selectivity of such catalysts have been observed in specific value-addition pathways of carbohydrates. However, more research (experimental and computational) must be devoted to a detailed understanding of the mechanistic pathway, deactivation mechanism, and recyclability. Reproducibility in the production and activity of such catalysts must also be examined before scaling up processes using such catalysts. The synthesis of dense-functionalized and elaborate molecular architecture from carbohydrate-derived platform chemicals can be attempted using multicomponent reactions involving organocatalysts. Multifunctional catalysts that allow more than one type of reaction to be performed sequentially in a single pot without isolating the intermediate(s) are being developed. It is preferred to develop catalytic strategies that allow the carbohydrates to be transformed into the targeted organic chemical(s) in a single pot without isolation or purification of the intermediates. This strategy decreases the number of synthetic steps, reducing the amount of waste accumulating over subsequent synthetic steps.

Serious deliberation should be given to choosing marine biomass feedstock for producing biofuels and biochemicals due to their high productivity, low land footprint, and minimal associated costs to their growth (e.g., irrigation, fertilizer). The largely manual cultivation process of marine biomass can be automated for improved productivity and cost reduction. Theoretical and experimental research on developing catalysts for carbohydrate value addition must be intensified. A thorough investigation of the mechanisms of transformation will help design catalysts, reactors, and reaction parameters for the best selectivity and yield of the targeted product. Electrocatalysis, photocatalysis, and electrophotocatalysis should be explored more in the biorefinery settings since the processes are inherently reagent-economic and produce less waste. However, efficient electrode materials, electrocatalysts, photocatalysts, and straightforward electrolytes must be developed for such processes. The scalability of such processes must also be evaluated. Moreover, the wastes generated from other biomass fractions must be managed appropriately for superior process economy and environmental acceptability. For example, lignin

will be a significant waste for a carbohydrate-centric biorefinery using terrestrial lignocellulosic biomass. Besides combusting lignin to generate process heat for the catalytic transformations of carbohydrates, more profitable applications, such as synthesizing phenolic chemicals and resins, may be explored. Detailed LCA and TEA will be crucial for successfully operating a carbohydrate-centric biorefinery at a local or regional level. Systemic collaboration between synthetic chemists, materials scientists, and chemical engineers will accelerate the transition of efficient and safe synthetic processes from the research laboratory to industry. Major commercial breakthroughs in the catalytic value addition of carbohydrates biorenewable products that are affordable, sustainable, and innocuous are envisioned in the near future.

AUTHOR INFORMATION

Corresponding Author

Saikat Dutta – Department of Chemistry, National Institute of Technology Karnataka (NITK), Mangalore 575025 Karnataka, India; orcid.org/0000-0003-3310-348X; Email: sdutta@nitk.edu.in

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.4c01960>

Notes

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ABBREVIATIONS

AAF: 3-Acetamido-5-acetylfuran
 ACA: Acrylic acid
 AcMF: 5-(Acetoxymethyl)furfural
 ADA: Adipic acid
 AE: Atom economy
 AGL: Angelica lactone
 BHMF: 2,5-Bis(hydroxymethyl)furan
 BPA: Bisphenol A
 ChCl: Choline chloride
 CMF: 5-(Chloromethyl)furfural
 CPN: Cyclopentanone
 CSTR: Continuous stirred tank reactor
 DES: Deep eutectic solvent
 DMC: Dimethyl carbonate
 DME: 1,2-Dimethoxyethane
 DMI: Dimethyl isosorbide
 DMS: Dimethyl sulfate
 DMTHF: 2,5-Dimethyltetrahydrofuran
 DPA: Diphenolic acid
 EG: Ethylene glycol
 EL: Ethyl levulinate
 FA: Formic acid
 ELA: Ethyl lactate
 FAL: Furfuryl alcohol
 FMF: 5-(Formyloxymethyl)furfural
 FDCA: 2,5-Furandicarboxylic acid
 FUR: Furfural
 GLY: Glycerol

GVL: γ -Valerolactone
 HDO: 1,6-Hexanediol
 HMF: 5-(Hydroxymethyl)furfural
 IL: Ionic liquid
 IS: Isosorbide
 LA: Levulinic acid
 LAC: Lactic acid
 LCA: Life cycle assessment
 LGO: Levoglucosone
 MTHF: 2-Methyltetrahydrofuran
 SMF: 5-Methylfurfural
 MFU: 2-Methylfuran
 MW: Microwave
 NAG: N-Acetylglucosamine
 NP: Nanoparticle
 2,3-PDN: 2,3-Pentanedione
 1,2-PDO: 1,2-Propanediol
 PFR: Plug-flow reactor
 SAC: Single-atom catalyst
 SCF: Supercritical fluid
 TEA: Techno-economic analysis
 TMP: Trimethyl phosphate
 THF: Tetrahydrofuran
 TON: Turnover number
 TOF: Turnover frequency

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