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Green Furanics after the 5-(Hydroxymethyl)furfural Bottleneck: Carbon-Efficient Transformations of Biomass into Molecular Complexity, Functional Materials and Circular Chemical Platforms

Valentine P. Ananikov[1,*], Konstantin I. Galkin[1,*]

[1]Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991, Russia

[*]Correspondence: glkn@ioc.ac.ru, val@ioc.ac.ru

Abstract

Furanic molecules obtained by dehydration and upgrading of carbohydrates have become a central chemical language for translating renewable biomass into fuels, polymers, solvents, ionic liquids, pharmaceuticals, adsorbents and aromatic building blocks. Yet the field has reached a stage at which the word 'platform' is no longer sufficient. The current frontier is not simply the preparation of 5-(hydroxymethyl)furfural (HMF), furfural (FF), 2,5-diformylfuran (DFF), 2,5-bis(hydroxymethyl)furan (BHMF) or 2,5-furandicarboxylic acid (FDCA), but the disciplined design of carbon-efficient sequences in which feedstock variability, product instability, separations, toxicity, catalytic durability and end-of-life chemistry are treated as one connected problem. This review develops this unified approach around green furanics after the HMF bottleneck. The literature selected herein is used as a core scaffold for discussion of carbohydrate-to-HMF chemistry, HMF aging and stability, electrochemical and catalytic oxidation, hydrogenation and hydrodeoxygenation, Diels-Alder furan-to-aromatics chemistry, C-H functionalization, materials, antimicrobial and adsorption applications, humins valorization and biodegradation. Placing these studies in a broader contemporary landscape – encompassing HMF electrooxidation, paired electrolysis, PEF scale-up, earth-abundant catalysis, furan-core editing, and circular materials – highlights the next decisive challenges. The review argues that the next decisive advances will come from treating HMF not as a molecule to be isolated at any cost, but as a node in adaptive reaction networks where the best intermediate is selected by stability, reactivity, separation and product function.

Keywords: biomass conversion, 5-(hydroxymethyl)furfural, furanics, FDCA, DFF, BHMF, Diels-Alder, furan-to-aromatics, green chemistry, sustainable polymers, circular materials

1. Introduction: from platform chemicals to platform decisions

The conversion of plant biomass into defined molecules is one of the few routes by which chemical manufacturing can acquire renewable carbon without first converting all carbon to syngas or burning it for heat. HMF occupies a privileged position in this conversation because the C_6 skeleton of hexoses can

be dehydrated into a furanic aldehyde-alcohol whose two substituents provide orthogonal handles for oxidation, reduction, substitution, condensation, cycloaddition and polymer chemistry. Classic and recent reviews have established the breadth of HMF synthesis and use,[1–4] while broader analyses of biomass catalysis, heterogeneous catalyst design and biorefinery product selection have framed the field as a systems problem rather than a single-reaction problem.[5–9]

The most important conceptual shift since the early platform-chemical literature is that furanics are now expected to perform beyond simple oxygenate substitution. FDCA should not merely replace terephthalic acid; it must enable high-barrier, recyclable and economically credible PEF products. DFF and BHMF should not only be symmetric derivatives of HMF; they should open material and medicinal domains that are less accessible from petroleum. Cycloaddition chemistry should not just prove that furan can behave as a diene; it should map credible furan-to-aromatics routes that preserve carbon and manage selectivity. This review therefore treats HMF chemistry as a network of decisions, not as a linear biomass-to-product funnel.[10] This network view is consistent with broader analyses in which HMF is not only a dehydration product, but a multifunctional node connecting fuels, monomers, solvents, fine chemicals and materials.[11,12] Cycloaddition chemistry provides one concrete route from C_6 furanics to aromatic building blocks,[13] but independent studies on furan/olefin and DMF/ethylene chemistry show that catalyst architecture, water management and side-reaction suppression determine whether renewable aromatics are synthetically credible.[14,15] Earlier discussion of sustainable furanic materials and fuels[16] should therefore be considered alongside process-oriented studies that evaluate separations, catalyst recycling and polymer-grade product quality rather than isolated yield alone.[17]

HMF formation in ionic liquids was examined at the molecular level,[18] while the broader field established complementary strategies based on metal chlorides in ionic liquids, biphasic extraction and direct cellulose or lignocellulose conversion.[19–21] Medium structuring and water-containing domains in ionic liquids further illustrate that solvent organization can influence HMF formation directly,[22] a point reinforced by later work on Lewis/Brønsted acid cooperation and biphasic glucose dehydration.[23] HMF quality, aging and decomposition,[24,25] must be considered together with mechanistic studies of HMF-derived humins, which show that carbon loss is controlled not only by primary dehydration selectivity but also by subsequent condensation and particle-growth processes.[26,27] Stability studies of furanic platform chemicals[28] therefore provide a bridge from synthesis to downstream reliability, because the same molecule can behave as a useful synthon or as a source of oligomeric waste depending on medium, storage and reaction history.

Selective upgrading is similarly diverse. Electrochemical DFF synthesis[29] is complemented by aerobic heterogeneous oxidation routes to DFF, showing that HMF oxidation can be tuned by catalyst, oxidant, electrolyte and reactor design.[30,31] HMF alkynylation[32] and self-clickable azido-alkynyl furan chemistry[33] show how side-chain editing can connect biomass to click chemistry, while DFF-based imine-linked porous frameworks demonstrate that the same dialdehyde platform can also be used to build functional porous materials.[34] Cascade cycloadditions of HMF derivatives[35] belong to a broader furan-to-aromatics landscape that includes renewable p-xylene formation from DMF and ethylene and zeolite-controlled Diels–Alder/dehydration networks.[14,36] C-H functionalization of furan aldehydes[37] fits into a growing body of work on direct furfural core editing, where protecting-group, directing-group and carbonyl-promoted strategies are used to overcome substrate fragility.[38,39] Finally, biodegradation of furanic aldehydes[40] should be placed beside earlier genetic, biochemical and microbial studies showing that furfural and HMF detoxification is an integral part of lignocellulosic biorefinery design.[41,42]

The articles selected for this review are particularly useful for this task, as they cover studies on HMF formation, quality, aging and stability; selective conversion to DFF, FDCA derivatives, ionic liquids,

surfactants and pharmaceutical motifs; furan-core C-H and cycloaddition chemistry; PEF and furanic polymers; and waste detoxification or valorization. Figure 1 condenses the central gap analysis that emerges from this literature.

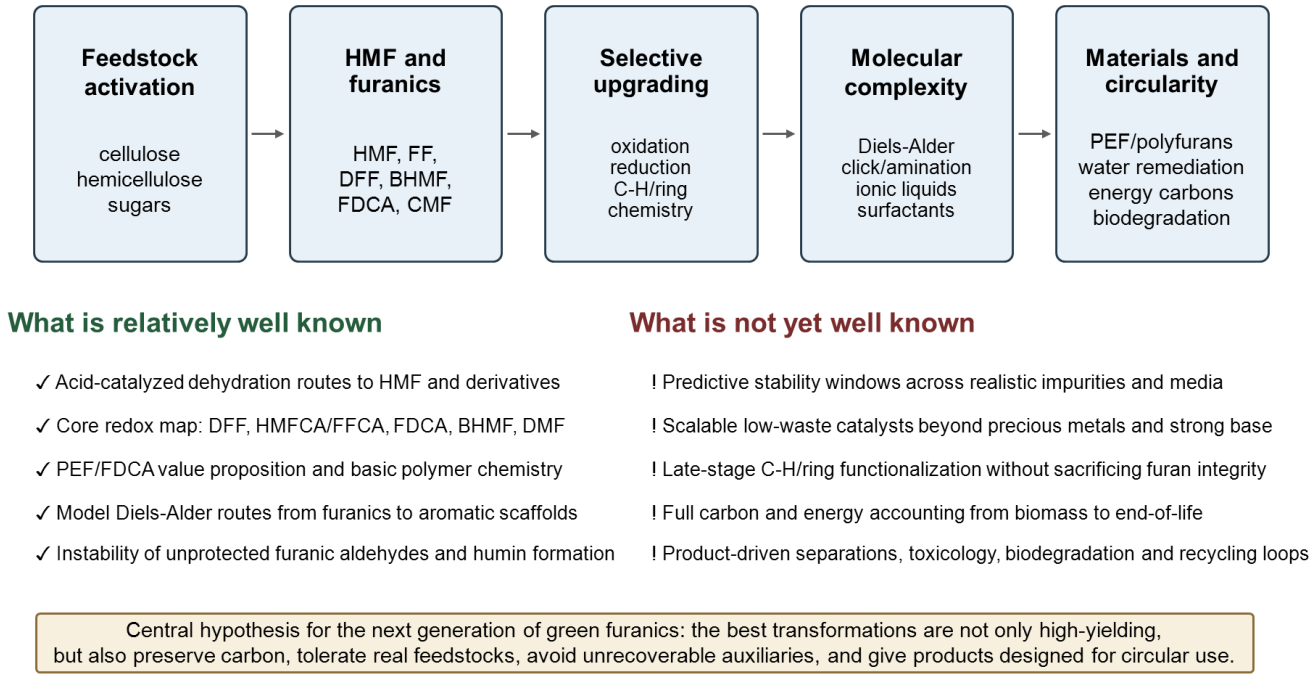

Figure 1. Gap analysis for green furanics after the HMF bottleneck. This figure separates areas with substantial accumulated knowledge from areas where predictive, scalable and circular design rules remain insufficiently established. CMF = 5-(chloromethyl)furfural.

It should be pointed out that the present review is based on a relatively small number of selected representative studies to perform the analysis. A comprehensive literature citation is out of scope for the present review, as we have a different goal. The concept described below is deliberately product-oriented: each transformation is evaluated by what it does to carbon retention, oxygen management, molecular complexity, separation burden and end-of-life options. In this sense, the term green furanics is narrower than all chemistry of furans, but broader than HMF alone. It encompasses a family of biomass-derived furanic molecules whose value depends on preserving renewable carbon while converting high oxygen content into useful function rather than waste.

2. Building HMF: dehydration chemistry, media and the quality problem

Carbohydrate dehydration to HMF remains the entry point for much of the C_6-furanic value chain. Fructose, glucose, sucrose, cellulose and lignocellulosic feedstocks impose different kinetic and mechanistic requirements: fructose dehydration can be rapid and selective under Brønsted acid catalysis, while glucose and cellulose require isomerization, depolymerization, disruption of hydrogen-bonded solids and suppression of rehydration or condensation. Biphasic fructose dehydration showed early that phase modifiers and extraction can protect HMF from the aqueous acidic phase and improve productive carbon flow.[20] Metal chlorides in ionic liquids then demonstrated that glucose can be converted to HMF through coupled isomerization/dehydration chemistry, making catalyst speciation and the ionic medium central design variables.[19] Molecular-level monitoring in ionic liquids further revealed that apparently

simple sugar dehydration is strongly influenced by the speciation of catalysts, water and intermediates, and that additives such as B_2O_3 can promote environmentally milder formation of HMF.[18] Later microscopic observations of water-containing domains in ionic liquids showed that the reaction medium itself can become a structured, dynamic actor in HMF formation, rather than a passive solvent.[22] Direct conversion of cellulose and lignocellulosic biomass in DMA/LiCl-based systems extended this logic from model sugars to recalcitrant feedstocks, emphasizing that solvent-assisted disruption of hydrogen bonding can be as important as acid catalysis.[21]

This insight matters because the major practical loss in HMF production is not only incomplete carbohydrate conversion. It is the conversion of desired HMF into levulinic acid, formic acid, humins and oligomeric degradation products during reaction, isolation and storage. Technological studies on high-purity crystalline HMF from fructose emphasized continuous water removal, biphasic extraction and recycling of catalytic systems as routes to product quality, but also noted that large-scale HMF production remains nontrivial.[43] The comparison between oil-like and crystalline HMF is especially important: aged oily HMF can be much less useful in downstream synthesis than crystalline material, and the difference can be decisive in pharmaceutical model reactions.[24]

The quality problem explains why stable derivatives such as 5-chloromethylfurfural, 5-acetoxymethylfurfural and 5-formyloxymethylfurfural have attracted attention as alternatives to isolated HMF. They may be easier to extract, purify and store, although the full sustainability balance depends on acid load, halogen handling, solvent use and downstream replacement chemistry.[16,44] At the same time, the chemistry of HMF cannot be optimized by yield alone. A process that gives a higher apparent HMF yield but produces a material prone to rapid oligomerization can be less useful than a lower-yielding process that gives a crystalline, stable and synthetically reliable intermediate.[24,43]

The current frontier in HMF formation is therefore a triad of reaction engineering, physical chemistry and downstream compatibility. Ionic liquids, deep eutectic solvents, biphasic solvent systems, solid acids and homogeneous acid-salt systems should be compared by integrated metrics: carbohydrate scope, water tolerance, product isolation, catalyst recycle, corrosion, impurities, humin formation and the performance of the isolated product in the next transformation. This is where classical platform-chemical chemistry becomes a platform-decision problem.[1,7,8,45]

3. The C6-furanic reaction network: not one product, but a switchboard

HMF contains a hydroxymethyl group, an aldehyde and an electron-rich heteroaromatic ring. This combination makes the molecule synthetically rich but chemically fragile. Oxidation of the alcohol gives DFF; oxidation of the aldehyde gives HMFCA; sequential oxidation leads through 5-formyl-2-furancarboxylic acid (FFCA) to FDCA; reduction of the aldehyde gives BHMF; deeper hydrogenation and hydrodeoxygenation give 2,5-dimethylfuran (DMF), 2,5-bis(hydroxymethyl)tetrahydrofuran and dimethyltetrahydrofuran. Side-chain functionalization gives amines, azides, alkynes, esters, surfactants, ionic liquids and monomers. Ring reactions give cycloadducts and aromatics. This switchboard view is captured in broad perspectives on C_6 furanics and their applications.[10,45]

The challenge is that every switch changes the stability and reactivity of the rest of the molecule. HMF can self-associate through hydrogen bonding and age through oligomerization; electron-withdrawing substituents can decrease furan diene reactivity; acidic or basic media can trigger ring opening, polymerization or Cannizzaro-like side reactions; and polar aprotic solvents can stabilize certain furanic aldehydes under conditions where other media accelerate decomposition.[24,28] This gives a practical rule: do not classify a transformation only by the bond formed. Classify it by the stability window it creates for all remaining functional groups.

This stability study is particularly important because it treats furans as synthetic intermediates under realistic acidic and basic conditions rather than treating them as idealized structures. It shows that solvent and additive choice can dominate outcomes, with polar aprotic media such as DMF providing stabilizing effects for several sensitive furanics.[28] Independent mechanistic studies of humin formation support this conclusion from the opposite side: HMF-derived residues develop through condensation, hydration, ring-opening and particle-growth processes whose importance depends strongly on acid strength, solvent and carbohydrate-derived co-reactants.[26,27] Such observations explain why successful high-yield transformations often rely on protection, extraction, rapid consumption of reactive intermediates, biphasic control or cascade designs. They also explain why HMF oligomeric products, traditionally treated as waste, are now being reconsidered as starting points for new carbon materials.[46]

4. Oxidation of HMF: DFF, FDCA, FDME and the electrochemical turn

Oxidation is the dominant branch of HMF upgrading because it converts biomass into monomers and functional handles. FDCA is the most prominent target because it enables PEF and related furanic polyesters, while DFF is a bifunctional aldehyde for imines, resins, porous frameworks, pharmaceuticals and conjugated materials. Earlier catalytic systems based on noble metals, base, oxygen, peroxides or stoichiometric oxidants demonstrated the feasibility of HMF-to-FDCA chemistry,[47–49] and subsequent studies refined support effects, MnO_2 polymorphs, coordination-polymer catalysts and base-free operation.[50–53]

Selective DFF synthesis via 4-acetamido-TEMPO/halogen-mediated electrooxidation is a representative example. The method is noteworthy because it converts an otherwise oxidant-intensive transformation into an electrochemically regenerated process and demonstrates electrolyte recycling on a gram scale.[29] This work should be discussed beside aerobic heterogeneous DFF synthesis, where Ru catalysts supported on covalent triazine frameworks (CTFs) enabled selective oxidation of HMF to DFF under mild conditions and highlighted the importance of avoiding overoxidation to acids.[30] The related one-pot synthesis of DFF from carbohydrate feedstock emphasizes the same strategic point: DFF is not only an oxidation product, but a more symmetric and often more stable synthon for organic materials.[10,29] DFF-based imine-linked porous organic frameworks provide an independent materials example, showing that biomass-derived DFF can be directly translated into microporous furan-containing networks.[34] Oxidative esterification offers another bypass of isolation problems by producing FDME directly, using a tunable precious-metal-free MnO_2/NaCN system and adjusting water content to change product selectivity.[54]

The most rapidly expanding oxidation subfield is HMF electrooxidation, especially the HMF oxidation reaction (HMFOR) coupled to hydrogen evolution or paired synthesis. This area is attractive because it can replace the kinetically demanding oxygen evolution reaction while simultaneously generating FDCA or related products. NiFe layered double hydroxides and related transition-metal catalysts have established the relevance of earth-abundant electrocatalysts,[55–60] while recent reviews and studies focus on mechanistic complexity, pH effects, aldehyde hydration, catalyst reconstruction, paired electrolysis and operation under less alkaline conditions.[56–61] Figure 2 illustrates the common pH-dependent HMFOR product network.

The oxidation branch also contains a biological sub-branch. Whole-cell and enzymatic oxidation can selectively stop at HMFCA or proceed toward FDCA depending on microorganisms, enzymes, oxygen supply and cofactor regeneration. Examples include Comamonas testosteroni, Deinococcus wulumuqiensis and Gluconobacter oxydans systems for selective HMFCA formation,[62–64] and broader biotransformation reviews emphasize the promise and limitations of living catalysts under substrate toxicity and product-inhibition constraints.[65]

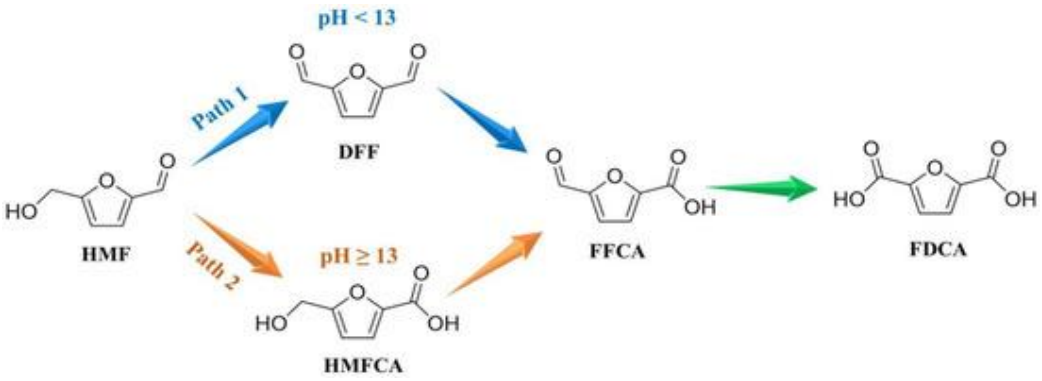

Figure 2. Representative HMF electrooxidation product pathways, highlighting pH-dependent routes through DFF or HMFCA to FFCA and FDCA. Reproduced from[59] under a CC BY 4.0 license.

The unresolved question for HMF oxidation is no longer whether FDCA or DFF can be made. It is how to make them under realistic feedstock, separation, and device conditions. Strong base can stabilize electrocatalyst performance but can degrade furanic intermediates and complicate product recovery. Precious metals can give high selectivity but may struggle with cost and durability. Electrochemistry can reduce chemical oxidant demand but introduces membrane, conductivity, product crossover and electricity-source constraints. The next generation of oxidation studies should therefore report not only yield and Faradaic efficiency, but carbon balance, humin formation, metal leaching, electrolyte recycling, product isolation and polymer-grade impurity profiles.

5. Reduction and hydrodeoxygenation: fuels, solvents and the oxygen-removal dilemma

Reduction of HMF addresses a different sustainability problem: carbohydrate-derived furanics are oxygen-rich, while liquid fuels and many solvent targets require lower oxygen content and higher energy density. Selective aldehyde hydrogenation gives BHMF, a monomer and synthetic building block. More extensive reduction gives bis(hydroxymethyl)tetrahydrofuran, DMF, 2,5-dimethyltetrahydrofuran and related fuels or fuel additives. The broad C_6-furanic perspective notes that oxidation and reduction together account for a large share of HMF transformations because they map directly onto two industrial targets: dicarboxylic acid monomers and deoxygenated fuel molecules.[10]

A particularly revealing “detour” is 5-methylfurfural (MF), a deoxygenated HMF analogue accessible from 6-deoxy sugars. MF is more stable and has a higher C/O ratio than HMF, and it can be converted selectively to DMF or used in condensation chemistry toward long-chain fuel precursors.[66] This strategy reframes the oxygen-removal problem: rather than making HMF first and then removing oxygen, feedstock selection can embed partial deoxygenation upstream. Related work on HMF hydrodeoxygenation to DMF shows that downstream oxygen removal can also be achieved by Co-, Cu-, Pd- and MOF-derived catalysts, but only when hydrogen supply, catalyst durability and ring preservation are treated as part of the sustainability calculation.[67–72] Such thinking is valuable when the target is fuel rather than oxygenated materials.

The dilemma is that reduction can easily destroy the features that make furanics valuable as renewable functional molecules. For example, retaining the furan ring can be crucial for polymer rigidity, Diels-Alder chemistry and bioactive scaffolds, whereas ring hydrogenation can improve fuel properties or polymer flexibility. Therefore, greener reduction should be product-specific: full hydrodeoxygenation is justified for fuels only when energy return, hydrogen origin and catalyst life are credible; partial hydrogenation is preferred when oxygenated functionality is the source of material value.

6. Side-chain diversification: from HMF and DFF to molecules with function

One way to move beyond commodity replacement is to use furanics as compact starting points for molecular complexity. HMF, DFF and BHMF contain differentiated or symmetrized side chains that can be converted into amines, alkynes, azides, esters, imines, salts, surfactants and pharmaceutical analogues. The work on alkynylation of HMF shows that acetylene-functionalized furans can connect biomass conversion with conjugated polymers and furanic pharmaceuticals in high yields.[32] In a broader materials context, DFF condensation with diamines gives furan-based imine-linked porous organic frameworks, indicating that aldehyde-rich furanics can function as renewable nodes for rigid porous architectures.[34] The synthesis of 2-azidomethyl-5-ethynylfuran then turns the furanic core into an ambivalent self-clickable monomer, placing renewable furanics directly inside click-polymer and triazole chemistry.[33]

DFF is a particularly useful node because two aldehyde groups enable reductive amination, imine formation, macrocycles, porous frameworks and drug-like scaffolds. The conversion of HMF-derived DFF into norcantharidin derivatives illustrates the idea that biomass-derived furanics can serve not merely as replacements for petrochemicals, but as concise entries into bioactive molecular space.[73] Figure 3 reproduces the key synthetic logic for this transformation. The same logic appears in the synthesis of CAP-1 analogues from biomass-derived furanic chemistry, where a demanded pharmaceutical motif becomes accessible through a biomass approach.[74] A broader lesson follows: the strongest argument for green furanics in fine chemicals is not always lower cost. It can be step economy, functional-group density, skeletal novelty or direct access to substitution patterns that are inconvenient from benzene.

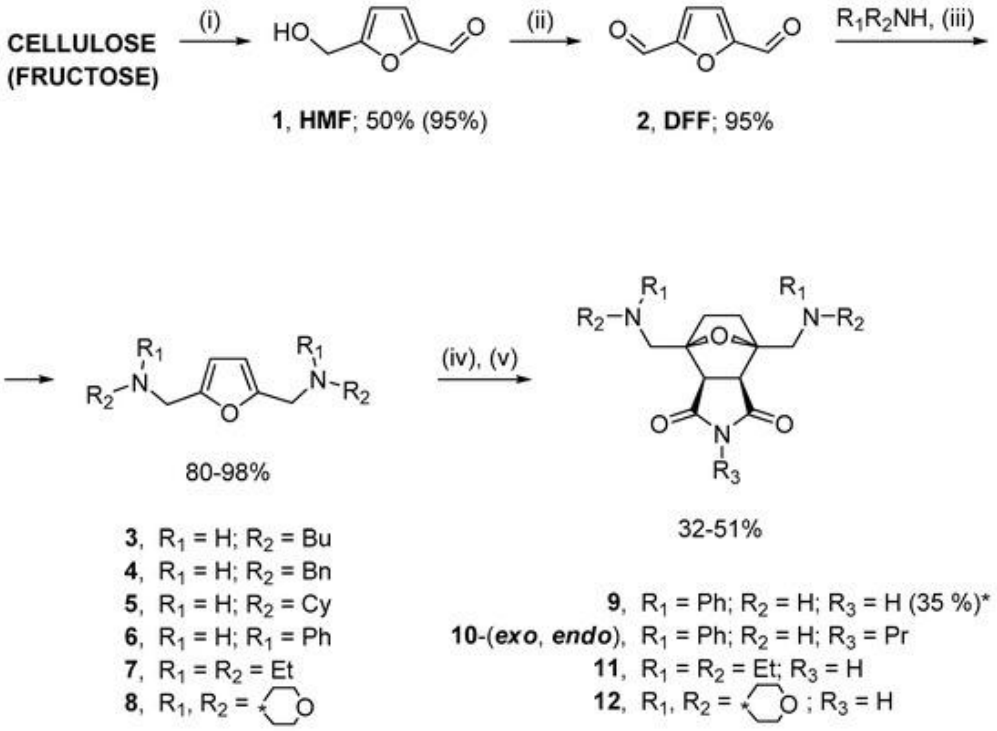

Figure 3. DFF as a biomass-derived synthon for norcantharidin derivatives.

(i) $CrCl_3 \cdot 6H_2O$, [BMIM]Cl, 120°C (H_2SO_4, [BMIM]Cl, 65°C); (ii) [Pip'(O)][BF4], [BMIM]Cl; (iii) $NaBH(OAc)_3$, $CHCl_3$; (iv) maleimide, THF; (v) H_2, 1 atm, 10% Pd/C, THF. *Yield using step-by-step procedure. Reproduced from[73] under a CC BY 4.0 license.

HMF-derived ionic liquids and surfactants extend side-chain diversification into soft materials and biological interfaces. Protic ammonium ionic liquids from HMF preserve the C_6 unit and show tunable cation-anion interactions, biological activity and cellulose-dissolution potential.[75] This direction belongs to a larger family of furanic amphiphiles and surfactants in which HMF, furfural and furan derivatives are used to introduce renewable hydrophobic, cationic, anionic or amphoteric fragments.[76] HMF-derived cationic surfactants incorporate fatty acid chains and bio-based amines to tune surface activity, antimicrobial activity, cytotoxicity and degradability.[77] Recent reviews of biobased surfactant design emphasize that renewable origin is not sufficient by itself; surface performance, biodegradability, toxicity and end-of-life fate must be optimized together.[78] These examples are significant because they ask an application-driven question: can the furanic core create performance profiles that justify the biomass-to-product sequence?

The unresolved issue is generality: side-chain chemistry is often demonstrated on clean HMF, DFF or BHMF, while industrial streams may contain water, salts, humins, levulinates, formates or related furans. Future studies should therefore report impurity tolerance and, where possible, one-pot or telescoped sequences from carbohydrate feedstock. The most valuable fine-chemical furanics will likely be those whose reactivity is orthogonal enough to tolerate upstream variability yet distinctive enough to give new chemical function.

7. Diels-Alder chemistry and the furan-to-aromatics challenge

Aromatic compounds are deeply embedded in the chemical industry, and replacing fossil aromatics is one of the most difficult tasks for renewable carbon. Furan-to-aromatics strategies exploit the diene character of furans in Diels-Alder reactions, followed by dehydration or aromatization. The concept has been developed for DMF plus ethylene to p-xylene, for furanics with maleimides or maleic anhydride, and for HMF/BHMF derivatives with alkynes or benzyne equivalents. The perspective on C_6 furans frames this as the furanics-to-benzene or furanics-to-aromatics problem and stresses that aromatics access is a key missing link in a renewable chemical industry.[13] Independent catalytic studies support this framing: ZSM-5-mediated conversion of furans and olefins showed that co-fed olefins can reshape aromatic selectivity, while zeolite-catalyzed DMF/ethylene cycloaddition demonstrated a direct renewable route to p-xylene.[14,15]

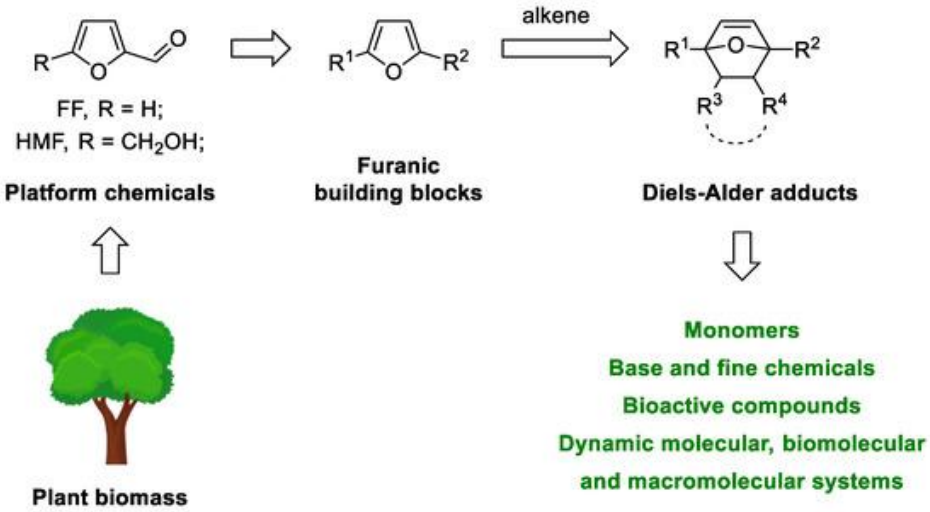

Figure 4. Diels-Alder chemistry as a route from renewable furanic platform molecules to fine chemicals, monomers and bioactive compounds. Reproduced from[79] under a CC BY 4.0 license.

The general Diels-Alder logic is shown in Figure 4. Furfural and HMF derivatives behave as renewable furanic dienes, while alkenes or alkynes generate oxanorbornene or oxanorbornadiene adducts that can be used directly or converted into aromatic molecules. The regio- and diastereoselectivity challenges are severe because substituents, electronics, solvent, Lewis acid activation, reversibility and aromatization all affect product distributions.[79] In polymer chemistry, the furan/maleimide Diels-Alder reaction has also become a major reversible "click/unclick" motif, showing that the same furan reactivity can be exploited either for aromatic production or for dynamic covalent materials.[80–82] The regio- and stereochemical problem is therefore more than academic. If furanics are to become scalable aromatic building blocks or reversible polymer units, selectivity must be predicted and controlled. Figure 5 summarizes the possible regio- and diastereomeric outcomes for substituted furans with substituted alkenes, emphasizing why high-throughput substrate maps and computational descriptors are important.[79]

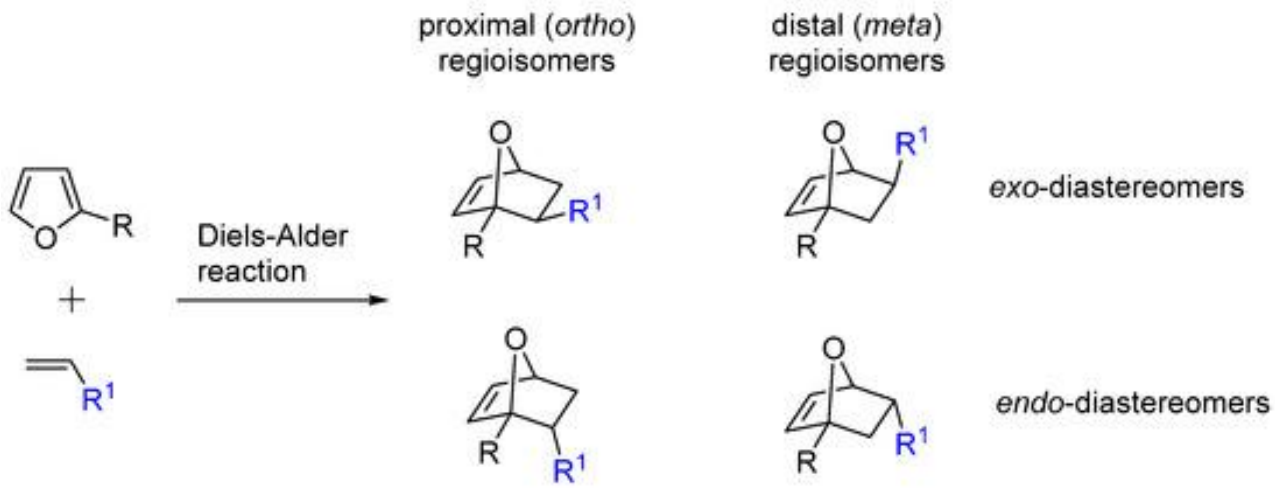

Figure 5. Regio- and diastereomeric possibilities in furan Diels-Alder chemistry. Reproduced from[79] under a CC BY 4.0 license.

The p-xylene route from DMF and ethylene is the most industrially developed furan-to-aromatics case. Diels-Alder cycloaddition gives an oxanorbornene intermediate, followed by acid-catalyzed dehydration to p-xylene, but side pathways include hydrolysis, alkylation, oligomerization and rearrangement. Early studies framed targeted aromatics production from furans and olefins,[15] catalytic production of renewable p-xylene,[14] and the reaction network over zeolites.[36] Later work refined phosphorus-containing zeolites, support effects, MWW catalysts and catalyst design for selectivity.[83–88] Figures 6 and 7 illustrate the reaction network and catalyst-dependent selectivity effects, respectively.

For HMF-derived substrates, ring electronics and side-chain instability make Diels-Alder chemistry harder than for DMF. The systematic study of HMF platform chemicals with alkynes shows that substrate electronics, protecting groups and side reactions control access to oxanorbornadienes, phenols and benzene derivatives.[89] HMF itself and some electron-poor derivatives can undergo side processes or fail to react, whereas protected or more electron-rich derivatives can be mapped by structure-reactivity relationships. This is precisely the kind of knowledge needed to convert furanics from attractive motifs into predictive building blocks.

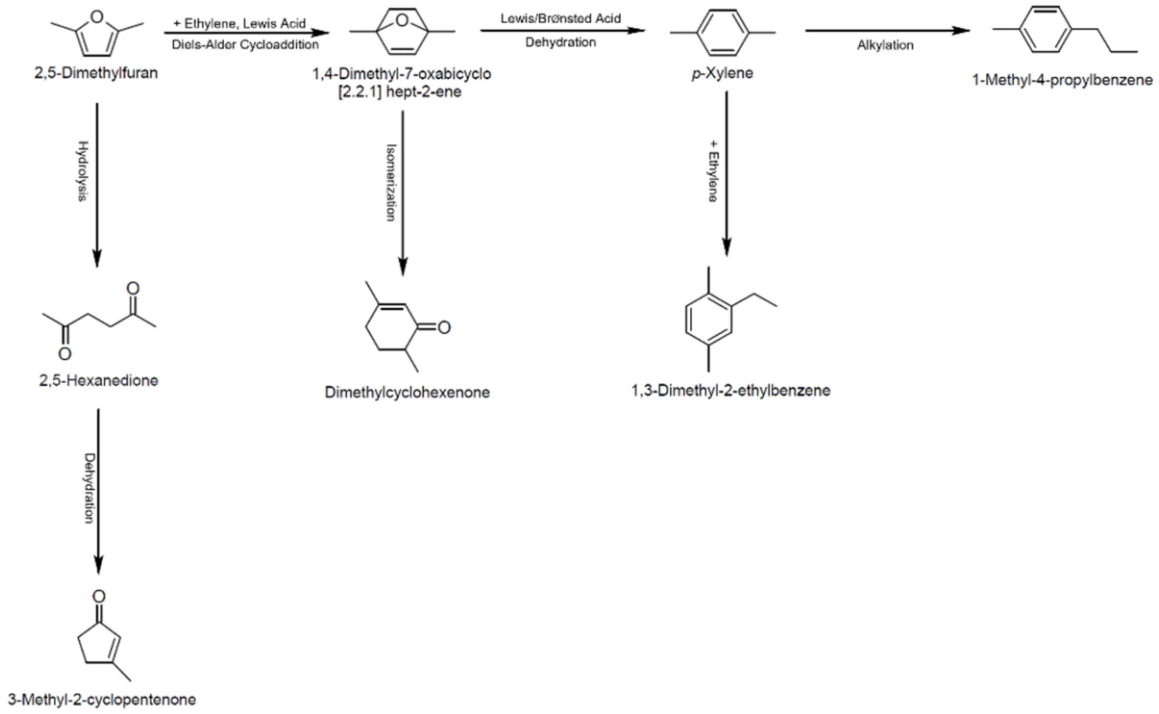

Figure 6. Reaction network for the conversion of 2,5-dimethylfuran and ethylene to p-xylene, including principal side reactions. Reproduced from[84] under a CC BY 4.0 license.

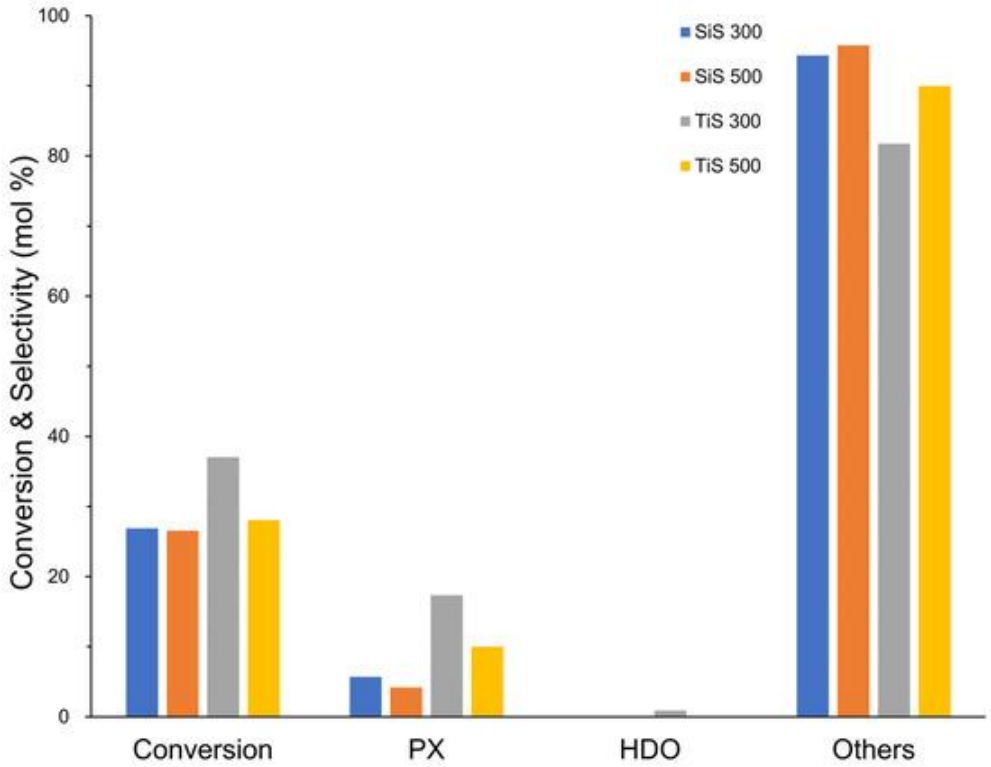

Figure 7. Catalyst-dependent conversion and selectivity in DMF-to-p-xylene chemistry over sulfated catalysts. Reproduced from[84] under a CC BY 4.0 license.

Cascade cycloadditions extend this logic by using dimeric HMF derivatives and alkynes to increase molecular complexity 3- to 5-fold in a single synthetic operation.[35] Such chemistry is important because biomass-derived feedstocks often contain oligomeric material that is treated as degradation waste. Turning those structures into complexity-generating substrates changes the sustainability narrative: not every oligomer must be avoided if its reactivity can be guided toward useful products.

8. C-H functionalization and furan-core editing

Side-chain chemistry and Diels-Alder chemistry are powerful, but they do not fully solve the problem of furan-core diversification. Direct C-H functionalization of furanic platform chemicals is attractive because it can install carbon-carbon bonds without prefunctionalization, but furfural, HMF and related aldehydes are reactive, acid-sensitive and prone to catalyst deactivation or side reactions. A review of catalytic C-H functionalization of unreactive furan cores emphasizes that the furan ring and the side-chain substituents must be considered together; harsh C-H activation conditions can destroy the very substrate one aims to valorize.[90] The same message is reinforced by recent reviews focused specifically on furfural derivatives, where imine formation, carbonyl assistance, borylation and transition-metal-catalyzed C-H arylation/alkenylation are presented as ways to valorize the furan core without changing the redox state of the aldehyde.[38]

Recent Ni/NHC-catalyzed C5-H alkylation and alkenylation of furan-2-carboxaldehydes and thiophene-2-carboxaldehydes provides a cutting-edge example. A recyclable N-PMP imine protecting group suppresses benzoin-type side chemistry, prevents NHC trapping, guides C5 functionalization and can be removed by acid hydrolysis with recovery of anisidine.[37] Other approaches demonstrate that furfural-derived carbonyl groups can also promote direct C-H functionalization under different catalytic regimes, including carbonyl-promoted C-H functionalization and Ru-catalyzed arylation or alkenylation of furfural imines with boronates.[39,91] This strategy shows how biomass-derived aldehydes can enter modern C-H functionalization if catalyst design, protecting-group economy and substrate stability are solved together.

The broader opportunity is to combine furan-core editing with downstream Diels-Alder, redox or polymer chemistry. C-H alkylation can tune solubility, biological activity or monomer properties; C-H alkenylation can introduce conjugation; and ring-functionalized aldehydes can enter imine, amination or cycloaddition networks. The key future challenge is to move from proof-of-concept substrate scope to reactions that tolerate HMF-derived complexity, avoid stoichiometric protecting-group waste where possible, and maintain a high carbon economy.

9. Furanic polymers, PEF and function-first materials

The most mature materials target in green furanics is FDCA-derived PEF. FDCA can replace terephthalic acid as a diacid monomer, but the furan ring is not a passive replacement for benzene. It changes chain rigidity, polarity, crystallization, gas-barrier properties, thermal behavior and degradation. Reviews on furanic polyesters and HMF-derived polymer precursors document progress in synthesis and property control.[92–94] The demonstration of fused deposition modeling with biomass-derived PEF is striking because it links cellulose-derived monomer chemistry to a manufactured object and then examines recycling through repeated 3D-printing cycles.[95]

The commercial story of FDCA and PEF is increasingly tied to process sustainability and techno-economics rather than polymer properties alone. Recent work on the road to FDCA/PEF markets and on PEF production processes, sustainability and techno-economics emphasizes that the decisive questions are feedstock, purification, polymer-grade FDCA, polymerization route, recyclability and market entry.[96–98] The quest for high-T_g bioplastics adds another design criterion: furanics should not only imitate PET, but

can also generate distinctive thermal and barrier profiles when monomer architecture is chosen rationally.[99]

Furanic materials also extend beyond linear polyesters. FDCA-derived diallyl esters have been used as crosslinkers for ion-exchange, metal-adsorbing and antimicrobial materials that outperform or complement commercial resins in certain water purification tasks.[100] HMF-derived ionic liquids and surfactants demonstrate another materials direction in which the furanic core becomes part of a tunable charged amphiphile or solvent system.[75,77,78] Furan-containing polymeric materials more broadly include thermoplastics, thermosets, blends, composites, dynamic covalent networks and crosslinked systems whose sustainability depends on both renewable content and end-of-life behavior.[93,101,102]

A function-first view is essential: biobased content alone cannot justify a new material if synthesis is wasteful, performance is ordinary and recycling is undefined. Conversely, a furanic material with superior oxygen barrier, adsorption, antimicrobial performance, dynamic reversibility or 3D-printing recyclability may justify more elaborate monomer preparation. The design question should be: which unique feature of the furan ring is being used? If the answer is none, the molecule may be a biobased label rather than a green material.

10. Waste, humins, toxicity and biological closure

HMF chemistry has a waste problem that is inseparable from its production chemistry. Acidic dehydration generates humins through polymerization, aldol-like condensation, ether formation and reactions of furans with sugars or degradation products. Traditionally, humins formation is treated as yield loss. Recent work reframes them as possible carbon resources. The liquid-to-solid conversion study shows that liquid humin waste can be polycondensed with melamine to create solid N-doped carbon precursors, which are then transformed into carbon materials for energy storage.[46] This is not a substitute for selectivity, but it is a practical circularity strategy: unavoidable carbonaceous residues should be engineered into useful materials rather than merely disposed.

The microbial literature shows that furfural and HMF are not merely unwanted analytical impurities: they are fermentation inhibitors that can be oxidized, reduced, assimilated or detoxified depending on the organism and pathway. Identification of bacterial HMF/furfural degradation pathways in Cupriavidus basilensis HMF14 provided a genetic and biochemical basis for treating furanic aldehydes as biodegradable but process-relevant compounds.[41] A broader review of microbial furan metabolism further emphasized that oxidation to acids and reduction to alcohols are common initial detoxification strategies, but that strain specificity and oxygen availability strongly affect product distribution.[42]

Toxicity and biodegradation are also important factors to consider. Furfural and HMF can inhibit microbial fermentation and impair wastewater treatment, creating bottlenecks in lignocellulosic biorefineries. A bacterial consortium study reports biodegradation and transformation of furfural and HMF, with pathways changing with aeration: reduction can produce furfuryl alcohol and BHMF, whereas oxidative routes can give furoic acid, DFF and FDCA-related products.[40] More generally, microbial detoxification studies emphasize that furanic aldehyde toxicity is both a process challenge and a sustainability metric.[65,103]

The implication is that the boundary of green furanics should extend beyond the reactor that makes the target molecule. This expanded boundary must include wastewater, residual solvent, unconverted sugars, salts, catalysts, humins, product toxicity and biodegradation products. A process that makes FDCA or DMF in high selectivity but leaves persistent, toxic or metal-contaminated streams has not solved the sustainability problem; it has shifted it. This is why stability studies, biological detoxification and humin valorization deserve to be discussed alongside catalyst optimization.

11. Cross-cutting design rules from the considered literature

Several design rules emerge from the considered literature. First, isolate or consume HMF in a form that preserves its downstream performance; crystalline HMF, protected derivatives, extracted intermediates or telescoped reactions may outperform oily stored HMF even when nominal yields are lower.[24,43] This conclusion is supported by independent HMF production studies in which phase separation, ionic-liquid media, solvent-assisted cellulose disruption and extraction were used to limit secondary degradation.[19–21] Second, match oxygen management to product function: oxidize to create polymer-grade diacids or aldehyde synthons, reduce only when lower oxygen content directly improves fuel or solvent properties.[12,55] Third, do not treat ring reactions as generic Diels-Alder chemistry; electronics, reversibility, aromatization and side-chain stability must be mapped together.[13,83–85] This point is reinforced by independent renewable p-xylene studies and by furan/maleimide dynamic covalent chemistry, which show that the same furan diene motif can lead either to aromatic hydrocarbons or to reversible polymer networks depending on catalyst, dienophile and thermal history.[14,36,80]

Fourth, earth-abundant and electrochemical catalysts are promising only when stability, product recovery and electrolyte or solvent reuse are demonstrated. Faradaic efficiency without isolated polymer-grade FDCA is not enough; high catalyst turnover without impurity tolerance is not enough.[56,58,60] Fifth, furanic materials should exploit a property that the furan ring provides, such as barrier performance, polarity, dynamic cycloaddition behavior, antimicrobial activity, adsorption, rigidity or recyclability.[93,95,100] Sixth, waste and toxicity must be integrated at the concept stage; humins and furanic aldehydes are not peripheral impurities but central features of real biorefineries.[40,46]

Table 1 summarizes the factual transformation classes discussed above and extracts design conclusions for the field. The purpose is not to rank reactions by yield, but to connect products, catalytic logic, sustainability leverage and unresolved gaps. The table is presented to show the analysis via the i) transformation node; ii) representative products; iii) chemistry and catalysts; iv) sustainability leverage; v) main gap/design rule categories. The table is built on a selective set of representative reactions, and more examples can be found in the literature.

Table 1. Analytical summary of green furanic transformation space. Abbreviations: AMF = 5-acetoxymethylfurfural; ILs = ionic liquids; SAILs = surface-active ionic liquids; TEA = techno-economic analysis; LCA = life-cycle assessment.

Transformation node	Representative products	Chemistry and catalysts	Sustainability leverage	Main gap/design rule
Carbohydrate dehydration	HMF, CMF, AMF	Brønsted/Lewis acids, ionic liquids, biphasic extraction, water control[18,20–22,44]	Direct entry from sugars/cellulose; high carbon retention if humins minimized	Product quality and isolation can dominate yield; prefer stable or immediately consumed intermediates
HMF quality and stability	Crystalline HMF; protected derivatives	Hydrogen-bond network control, crystallization, polar aprotic stabilization and humin-suppression logic[24,26–28]	Higher downstream synthetic reliability	Report product age, purity, storage form and impurity profile
Selective oxidation to DFF	DFF	TEMPO/halogen electrooxidation, aerobic Ru/CTF oxidation, one-pot oxidation[29,30]	Access to bifunctional aldehyde monomers and bioactive scaffolds	Avoid stoichiometric oxidants; demonstrate electrolyte and mediator recycling

Transformation node	Representative products	Chemistry and catalysts	Sustainability leverage	Main gap/design rule
Oxidation to FDCA/FDME	FDCA, FDME, FFCA, HMFCA	Au, Au-Cu, MnO_2, Pt/CeCP, electrochemical NiFe catalysts[47,48,54,55]	PEF and polyester monomers; potential paired electrolysis	Need polymer-grade product, base management, impurity tolerance and carbon balance
Biocatalytic oxidation	HMFCA, FDCA-related products	Whole cells, enzymes, aldehyde oxidation[62,63,65]	Mild aqueous chemistry and detoxification links	Substrate toxicity, cofactor needs and product isolation limit scale
Reduction/hydrodeoxygenation	BHMF, DMF, DMTHF	H_2, transfer hydrogenation, Co/Cu/Pd catalysts[67,68,70]	Fuel-range molecules and monomers	Use renewable H_2 and avoid unnecessary destruction of useful oxygen functionality
Alternative C_6 aldehyde platform	5-Methylfurfural	Lewis acid conversion of deoxy sugars; hydrogenation to DMF[66]	Improved stability and higher C/O ratio	Feedstock availability and integration with carbohydrate streams remain key
Side-chain diversification	Amines, alkynes, azides, triazoles	Alkynylation, click chemistry, reductive amination and imine-linked porous-network formation[32–34]	Rapid access to functional molecules	Need impurity-tolerant, telescoped routes from HMF or DFF
Bioactive scaffolds	CAP-1 analogues, norcantharidins	DFF amination/cyclization, biomass-derived drug cores[73,74]	Step economy and renewable skeletal diversity	Performance must justify fine-chemical processing cost
Furan-to-aromatics	p-Xylene, phenols, benzene derivatives	Diels-Alder plus dehydration/ aromatization; zeolite-controlled p-xylene routes[13–15,36]	Renewable entry to aromatic value chains	Control side reactions and catalyst deactivation; quantify carbon losses
Cascade cycloadditions	Complex oxanorbornadienes and aromatics	HMF dimers plus alkynes; kinetic/ thermodynamic control[35]	Transforms oligomeric material into complexity	Generalize beyond model dienophiles and isolated substrates
C-H functionalization	C5-alkylated/alkenylated furfurals	Ni/NHC catalysis, recyclable imine protection, carbonyl-promoted and imine-directed C-H functionalization[37–39,90,91]	Atom economy and late-stage furan-core editing	Reduce protecting-group burden and test HMF-derived substrates
Polyesters and printing	PEF, furanic polyesters	FDCA polymerization, FDM 3D printing[95–97]	Biobased materials, barrier properties and recycling opportunities	Commercial viability requires integrated TEA, LCA and recycling data
Functional furanic materials	Adsorbents, ILs, surfactants	FDCA crosslinkers, HMF-derived ILs, furanic amphiphiles and SAILs[75–78,100]	Performance-driven sustainability in water and antimicrobial applications	Balance biological activity, cytotoxicity and degradability

Transformation node	Representative products	Chemistry and catalysts	Sustainability leverage	Main gap/design rule
Waste and detoxification	Humins-derived carbons; degraded furanics	Melamine solidification, microbial consortia and genetically defined furan-degradation pathways[40–42,46]	Converts process liabilities into value or detoxified streams	Include waste valorization and toxicity in primary process design

12. Conclusions and outlook: what should be revealed next

Green furanics have advanced from proof that biomass can supply interesting molecules to proof that those molecules can deliver materials, fuels, fine chemicals and catalytic platforms. The next stage is more demanding. The field must reveal when a furanic intermediate should be isolated, protected, oxidized, reduced, subjected to cycloaddition, functionalized, polymerized or deliberately avoided. It must also reveal which impurities are tolerable, which catalysts survive real streams, which products are truly circular and which waste streams can be converted into value. Considerations for constructing a roadmap for the development of the next generation of green furanics are presented in Figure 8.

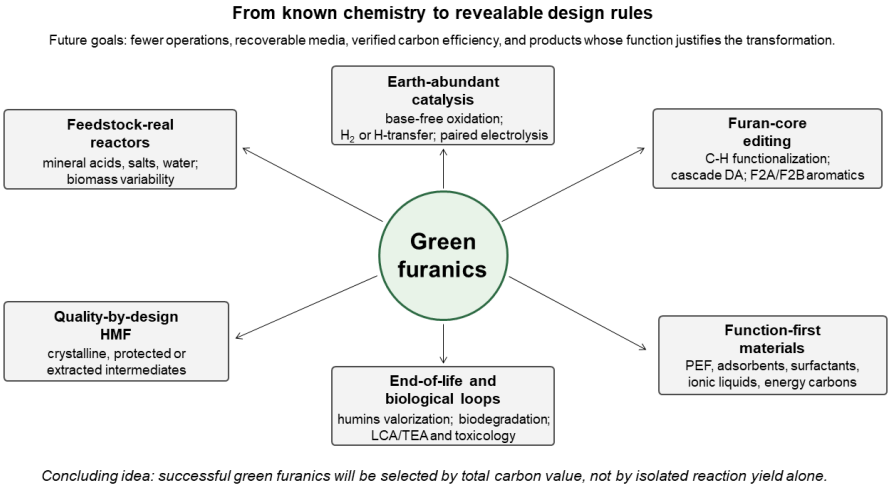

Figure 8. Concluding roadmap for the next generation of green furanics. Abbreviations: DA = Diels–Alder; F2A = furanics-to-aromatics; F2B = furanics-to-benzene.

The most persuasive future studies will combine reaction discovery with process realism. A high-yield HMF oxidation should be accompanied by product isolation, electrolyte or solvent recycling, catalyst stability and polymer-grade impurity analysis. A new furan-to-aromatics route should report carbon balance and side-product fate, not only aromatic selectivity. A new HMF-derived material should show why the furan ring matters to performance and how the material can be recovered, recycled, biodegraded or safely disposed. A new C-H functionalization should demonstrate that protecting-group and catalyst choices are not only elegant but recoverable and scalable.

The final message is that HMF is no longer merely a “sleeping giant” waiting for one decisive industrial process. It is a reactive node in a family of green furanics whose value will be unlocked by matching molecular reactivity to application, process integration and circularity. The chemistry is now

rich enough that selectivity alone is not the frontier; the frontier is designing transformations that remain practical when the full life of carbon is considered.

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