Green Chemistry

ROYAL SOCIETY OF CHEMISTRY

CRITICAL REVIEW

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Cite this: *Green Chem.*, 2025, **27**, 14436

How to make furfural and HMF production greener? Lessons from life cycle assessments

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Received 20th July 2025,
Accepted 7th October 2025

DOI: 10.1039/d5gc03729h

rsc.li/greenchem

As part of the increasing demand for sustainable methodologies, there is an ongoing need for green and sustainable industrialization of platform chemical production, including furfural and 5-hydroxymethylfurfural (HMF). While the existing literature contains a wide range of reviews on furanic compounds, there is a notable lack of coverage of the sustainability, environmental and economic perspectives. Thus, this review presents a comprehensive survey and critical analysis regarding the production of furanic compounds based on existing life cycle assessments (LCAs), elucidating the effects of feedstock, solvent, catalyst, energy resource, mass efficiency, and energy efficiency on environmental impact. Several green solvents with the greatest potential for future biorefinery scenarios were carefully chosen, guided by LCA results, cost-effectiveness, safety and health. In addition, this review thoroughly examines the benefits and drawbacks of selected solvents, investigates several application scenarios, and outlines future research directions. Meanwhile, the potential choice, research and development of feedstocks and catalysts are discussed, incorporating the LCA investigations to provide potential directions for enhancing the sustainability and viability of furanic compounds through the improvement of synthetic routes. Moving forward, we recommend macroalgae as a new feedstock that has the potential to produce furanic compounds because of its high carbohydrate content, significant carbon sink capacity, and simultaneous capacity for domestic sewage treatment. To accelerate the green and cost-effective development of biomass pretreatment, HMF and furfural in biorefineries from lab scale to commercial scale needs a greater use of *ex-ante* LCA and TEA methodologies integrating chemical process simulations, artificial intelligence, and other computational techniques.

Green foundation

1. This review describes the findings of life cycle assessments (LCAs) of the published methods of converting biomass into furfural and hydroxymethylfurfural, including identification of the factors, steps, and choices that can lead to minimized environmental harm.
2. Furans are among the most widely studied bioderived platform chemicals. Lessons learned from the LCA literature of furans production can guide green decision making not only for furans but for all other bioderived platform chemicals and final products.
3. As LCAs become progressively more readily available, they should increasingly be used in guiding the design and development of green chemical syntheses.

1 Introduction

Global greenhouse gas emissions (GHGs) must be cut by 25–50% so that the global carbon emission control program will be on track to meet the 2015 Paris Agreement goal of containing global warming to 1.5–2 °C by 2050. As is well known, the world primarily uses fossil fuel-derived forms of energy that have significantly contributed to global GHGs.[1] It is predicted that between 2000 and 2050, the world's energy demands in the heat, power, transportation, and chemical sectors will double. Meanwhile, the availability of non-renewable fossil resources is uncertain, and there could be future energy shortages. Along with this, there has been a significant increase in concern for the ecosystem and human health. We must therefore strike a balance in the ensuing decades to meet the rising demand for energy and value goods like fuel, fine

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chemicals, and plastics, as well as to attain net zero goals and safeguard the environment. The most practical and necessary way to achieve this balance is to switch existing energy and feedstock resources from those with high carbon emissions and non-sustainability to those with low carbon emissions and sustainability.

Biomass, which sequesters carbon dioxide during its growth process, represents the sole naturally occurring source of renewable organic carbon. Using biomass through various conversion methods is crucial in replacing fossil energy and facilitating the transition to a sustainable, zero-carbon society. Biomass has been employed since prehistory to generate ethanol through biological fermentation. Then, thermochemical methods such as pyrolysis, gasification, and liquefaction were developed to realize biomass conversion to syngas and bio-oil. Although the technologies mentioned above have enabled biomass use, biological conversion is often inefficient especially if a biopolymer such as cellulose is used as feedstock. Thermochemical methods require harsh conditions (such as high temperature and pressure) and often produce low-value products and poor selectivity. Therefore, such complex processes make it difficult to fully and efficiently use biomass. As a result, studies on improved syntheses of bio-derived chemicals and fuels have been actively promoted. Biomass resources must be converted into high-value chemicals through green, sustainable and efficient approaches because such processes maximize the value of the resources while achieving low-carbon or even negative-carbon effects. By using biomass resources, it is possible to alleviate the global fossil fuel shortage and reduce the impact of global warming. Furthermore, global markets demand the green technologies of biomass-based products to help the future transition to a circular and sustainable economy.

The primary objective of producing platform compounds extends beyond resolving the energy shortage to encompass a wider array of chemical products essential for a circular society. This pursuit entails ensuring that both the products and their production processes minimize environmental impact, aligning with the goals of green, low-footprint development, and carbon neutrality. Several chemical companies have successfully implemented more sustainable practices. For instance, BASF, a German chemical company, has pledged a 25% reduction in greenhouse gas emissions by 2030 and has invested in renewable energy sources and emission-reducing technologies. Similarly, Dow Chemical aims to decrease net annual carbon emissions by 5 million metric tons by 2030 while also investing in renewable energy and developing more sustainable products.

In the past decade, considerable attention has been devoted to the conversion of carbohydrates into fine chemicals, including furfural, 5-hydroxymethylfurfural (HMF), formic acid, acetic acid, lactic acid, and fuel hydrogen.[2] This interest stems from the US Department of Energy's (DOE) identification of the "Top 10" platform molecules in 2004, which included HMF and furfural, as well as the subsequent revision of the list to include four additional molecules, known as the "Top 10 + 4"(Fig. 1). Notably, the DOE's list reflects the potential for large-scale production and commercial viability, as well as derivatization ability.[3] As shown in Fig. 2, research on the conversion of biomass into HMF and furfural has been increasing steadily since 2009.

HMF was first detected in 1875 and first synthesized in 1895, with the method involving heating inulin in an acidic

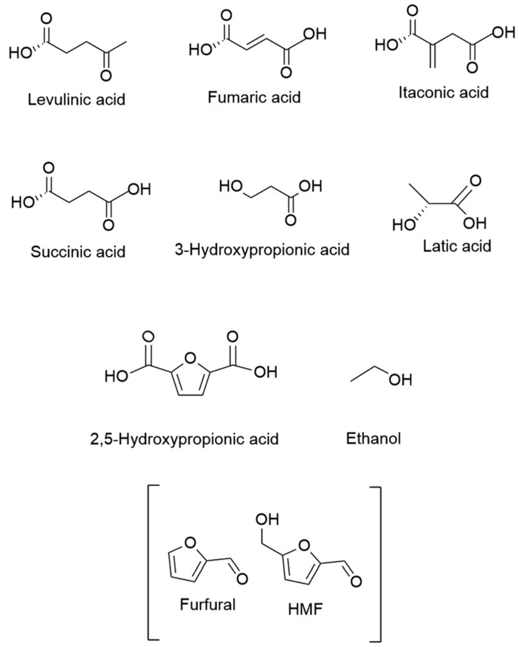

Fig. 1 Selected molecules from the "Top 10 + 4" list of most promising candidates from carbohydrates.

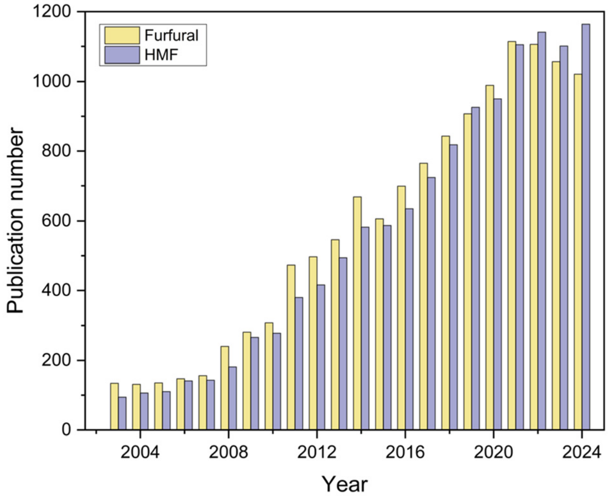

Fig. 2 The number of publications on furfural and HMF per year (2003–2024). Source: Web of Science (keywords: "furfural", "HMF or 5-hydroxymethylfurfural").

aqueous solution.[4] The history of HMF has been divided into three stages: the early stage, from 1895 to 1980; the development stage, from 1980 to 2000; and the active stage, after 2000 (Fig. 3).[5] Beginning in 2008, there was an enormous increase in HMF-related publications, from 181 publications in 2008 to 1164 publications in 2024 (Fig. 2). The growing interest in HMF production is a result of the overwhelming need for successful implementation of bio-renewable products to replace fossil fuel-based products. HMF and its derivatives could be widely used as platforms or starting materials in bulk chemical and fuel production; its active functional groups, aldehyde and hydroxyl, allow for upgrading HMF into more valuable products. For instance, 2,5-furandicarboxylic acid (FDCA), an HMF derivative, could be used in the poly(ethylene terephthalate) (PET) industry to produce biodegradable plastic materials as a bio-derived substitute for PET.[5]

HMF and furfural were discovered in the nineteenth century; however, HMF industrial applications are still lagging, whereas furfural production was commercialized in 1921 and has been used for nearly a century. Avalon Industries AG (AVA) produced the first commercial small-scale HMF (300 t per year) in 2014. AVA announced they would focus on the global implementation of hydrothermal carbonization (HTC) technology for industrial-scale HMF production. Although AVA claimed to have reached technology readiness level 9, it has not yet succeeded in large-scale industrial production, with only an HMF plant with an annual operating capacity of 300 tons in Mütenz, Switzerland. AVA announced in 2019 that a new HMF production plant with a capacity of 5000–10 000 tons per year was in the works, but so far, the plan hasn't come to fruition. In October 2018, on-farm biorefinery technology in Stuttgart-Hohenheim (Germany) was officially put into operation. The core module of this small biomass-based plant was an HMF production module. The EU "Grace" project (2017–2022) also planned to develop a new HMF production process using *Miscanthus* as a raw material. To sum up, there has been no large-scale HMF production so far, which is also reflected in the exorbitant price of HMF (Millipore-Sigma, €3500 per kg in 2022).[6] Presently, investigations about HMF are centered around the advancement of eco-friendly and productive methodologies for its synthesis, while simultaneously striving for its industrial implementation. For the successful industrialization of HMF, careful consideration for the choice of appropriate feedstock, solvents, catalysts, purification techniques, and reaction pathways ensures optimal selectivity, recovery, sustainable development, and cost-effectiveness in the preparation method.

Furfural was first reported by Johann Wolfgang Döbereiner in 1832 and has since become a molecule of great interest.[7] It can be produced from pentose sugars such as xylose, which is obtained from hemicellulose in lignocellulosic biomass. Its furan ring and aldehyde group make it a versatile platform molecule that give it utility in various applications, for example, as an extractant in the refining of lubricants and vegetable and diesel oil.[8] There has also been a growing interest in the use of furfural as a platform feedstock for the generation of biofuels, bio-derived plastics, and bio-based chemicals.[8] In 2022, the estimated global market value of furfural stood at 556 million USD, with projections indicating an increase to 954 million USD by 2030.[9]

The history of furfural syntheses has also been divided into three stages: the early stage: 1832–1923; the furfural industrial use stage: 1923–2000; and the development stage: 2009 and onwards (Fig. 4). The first two stages are focused on the best production methods for furfural and its derivatives based on yields, while the development stage is focused on green and sustainable furfural synthesis.

In 1921, the first commercial process for the production of furfural was established by Quaker Oats, in which oat husk was used as the raw feedstock material.[10] Quaker Oats used diluted sulfuric acid as the catalyst and steam as the heat source in the aqueous phase, facilitating the conversion of oat husk-derived pentose sugars into furfural. This process obtained a furfural yield of less than 50% at 153 °C.[11,12] To this day, more than 70% of furfural production companies still use the Quaker Oats method to produce furfural on a large

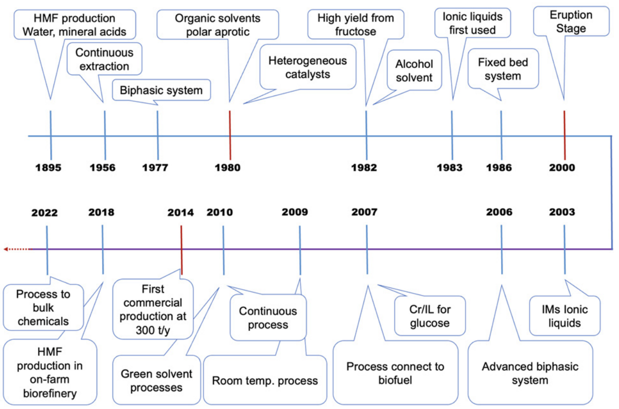

Fig. 3 The significant milestones of HMF synthesis since its discovery in 1895. Reproduced from ref. 5 with permission from the RSC,[5] copyright 2014.

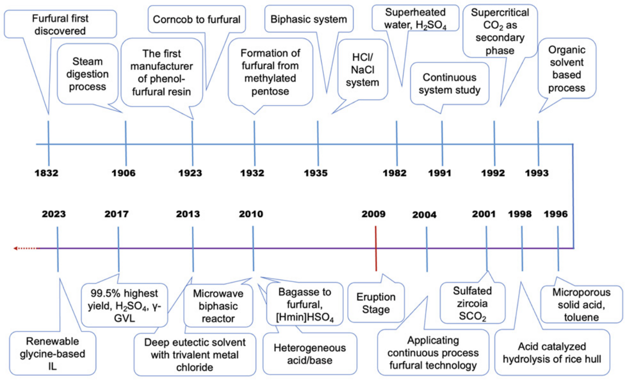

Fig. 4 The significant milestones of furfural synthesis methods since its discovery in 1832.

scale. Prior to 2004, these companies obtained a final furfural yield of 40 to 50% and produced approximately 280 000 metric tons of furfural per year.[11,13,14] Up to now, Chinese companies are the main producers of furfural.

There are, however, limitations associated with the traditional furfural production process, which include: (1) The amount of superheated steam consumed is 50 times greater than the amount of furfural produced, and a long reaction time (5 h) is required, resulting in a large energy consumption of about 400 kWh per ton;[15,16] (2) Extensive equipment corrosion is common; (3) diluted sulfuric acid can be neither separated nor reused; (4) a large amount of acidic wastewater is generated (chemical oxygen demand (COD) of 10 000 to 50 000 mg L^{-1}, biochemical oxygen demand (BOD) of 3000 to 8000 mg L^{-1}, and 200 to 600 mg L^{-1} of oil and grease), which is difficult to treat; and (5) large volumes of side products are formed in the aqueous solution.[17] Given that the demand for furfural in various fields is expanding, there is an urgent need for green, sustainable, and low-carbon furfural production processes. Therefore, more recent studies in furfural production have mainly focused on developing more sustainable and efficient production processes.

Mass production of furanic compounds currently faces economic and environmental challenges, solving these challenges can be likened to solving a complex "multivariate equation." This involves the careful selection of starting materials, solvents, catalysts, and process routes, all of which are interdependent and can simultaneously impact the economic and environmental performance of the synthesis. Leveraging economic and environmental factors is a critical consideration for future green technology development and industrialization of furfural compounds. Several reviews on the synthesis of furanic compounds, including HMF and furfural, have been published, emphasizing solvents,[18–21] catalysts,[22–25] raw materials,[26,27] and applications.[28–31] While existing reviews have addressed various aspects of furanic compounds, none have simultaneously covered their synthesis alongside life cycle assessment (LCA) studies. Therefore, this review aims to bridge that gap by exploring LCA studies related to furanic compound production. We highlight the selection of environmentally friendly solvents, assess potential feedstocks, and evaluate catalysts involved in the process. Additionally, we provide a comprehensive review of crucial yet often overlooked aspects, such as the separation and purification of furanic components, transportation logistics, and biomass pretreatment. By examining these multiple dimensions, this review seeks to promote greener, more sustainable and cost-effective industrial production of furanic compounds within the context of biorefineries.

2 LCA studies

LCA is the process of analysing the environmental impacts associated with all stages of a product's life, from the cradle to the grave, by quantitatively assessing its use of energy and natural resources and monitoring the generation of waste and products, all of which have associated impacts on the environment.[32,33] LCA has been identified as a critical part of the strategy to decarbonize the chemical industry, not only as a means of quantifying environmental impacts but also as a way of justifying investment into new sustainable technologies (Fig. 5).[33–35] Therefore, a reliable justification for further investment and development in emerging green chemical technologies from LCA is essential.[36,37] LCA studies that have already been done on the production of HMF and furfural are reviewed in this section, illuminating the path taken by researchers to find greener methods to produce HMF and furfural. Tables 1 and 2 provide additional relevant information that further explains the details of the reviewed LCA studies.

LCAs are categorized into four types based on varying scopes: cradle-to-grave, cradle-to-gate, gate-to-gate, and cradle-to-cradle (Fig. 6).[38] The selection of scope in LCA is critical since it has a direct impact on the results.[39] Product life cycles typically involve five key stages: raw material extraction (known as the "cradle"), manufacturing and processing, transportation, usage and retail, and waste disposal (known as the "grave"). A cradle-to-grave LCA includes all of these stages. In contrast, a cradle-to-gate LCA focuses on the first three stages while ignoring the environmental impacts of the product's use and end-of-life phases. Similarly, the gate-to-gate LCA concentrates on the environmental implications of a specific process or activity within a product's life cycle, while neglecting the effects of upstream and downstream stages. Finally, cradle-to-cradle LCA highlights the construction of closed-loop systems that reduce waste and allow for continuous reuse or recycling of materials.[40]

Within the life cycle of a product, the step which causes the most harm is called a hotspot. For example, the agricultural production of corn may be the step that causes the most eutrophication in the life cycle of corn-derived ethanol. If so, then it is the eutrophication hotspot. The hotspot for other impacts like global warming or smog formation might be different steps. An indirect hotspot is a step that doesn't cause the most harm itself but indirectly influences the harm of a hotspot. For example, if the fermentation step for converting corn-derived

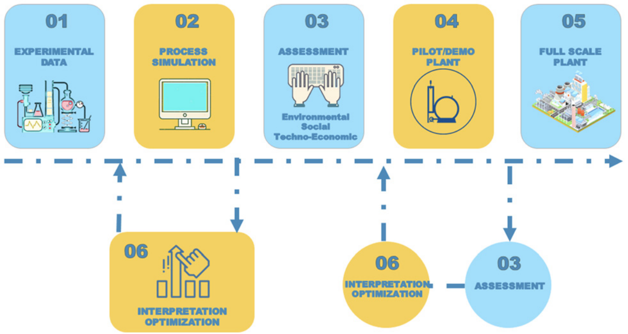

Fig. 5 Framework for the design of new green production routes. Reproduced from ref. 35 with permission from RSC.[35] copyright 2021.

Table 1 A table summarizing the key features of the reviewed HMF LCA studies

Paper	Key features	Catalytic system	Feedstocks	Products	Data sources	Climate change/GHGs
Eerhart *et al.* (2012)[44]	Function unit: 1 ton PEF; allocation method: mass and economic allocation; system boundary: cradle-to-gate	HMF was produced using sulfuric acid as the catalyst in a solvent of water and methanol	Fructose and HFCS (high fructose corn syrup)	HMF derived PEF, fossil PET	PlasticsEurope eco-profile, EcoInvent database, Aspen Plus simulation, literature reports, patents	2.0–2.4 kg CO_2 eq. per kg PEF
Dros *et al.* (2015)[45]	Function unit: 1 kg HMDA; allocation method: n/a; system boundary: cradle-to-gate	HMF was produced from HFS in DMSO using Cu $(NTF_2)_2$ as the catalyst	HFCS	Fossil and bio-based HMDA	EcoInvent database, literature reports, patents	~4.7–9.9 kg CO_2 eq. per kg HMDA
Lin *et al.* (2015)[46]	Function unit: 1 ton *p*-xylene; allocation method: economic and mass allocation; system boundary: cradle-to-gate	HMF was produced using HCl and NaCl as the catalysts in THF	Fructose (from corn starch and oak)	HMF derived *p*-xylene	EcoInvent database, literature reports and US LCI database	~1.1–10.8 kg CO_2 eq. per kg *p*-xylene
Isola *et al.* (2017)[47]	Function unit: 1 g polymer; allocation method: mass allocation; system boundary: cradle-to-grave	HMF (45%) was produced from fructose in DMA/water using sulfuric acid and LiBr as catalyst at 100 °C for 6 h	Fructose (from corn)	HMF derived 2,5-furandicarboxylic acid FDCA	EcoInvent database, experimental lab-scale data., energy information, administration, literature reports	53.0 kg CO_2 eq. per g FDCA
Lam *et al.* (2018)[42]	Function unit: 1 g converted food substrate; allocation method: n/a; system boundary: cradle-to-gate	Scenario 1 used bread waste as the substrate, $SnCl_4$ catalyst, and DMSO–water medium at 160 °C for 20 min; Scenario 2 used the same substrate, medium, catalyst and reaction time but at 140 °C; Scenario 3 used bread waste, $SnCl_4$ catalyst, and DMSO–water medium at 140 °C for 60 min; Scenario 4 used bread waste, $SnCl_4$ catalyst, and THF/water medium at 140 °C for 120 min; Scenario 5 used bread waste, $SnCl_4$ catalyst, and acetone/water medium at 140 °C for 10 min; Scenario 6 used bread waste, $AlCl_3$ catalyst, and acetone/water medium at 140 °C for 30 min; Scenario 7 used rice as substrate, $SnCl_4$ catalyst, and DMSO/water medium at 140 °C for 40 min; Scenario 8 used kiwi fruit substrate, $SnCl_4$ catalyst and DMSO/water medium at 140 °C for 20 min	HMF	Food substrate	EcoInvent database, literature reports, agri-footprint, US LCI database	n/a
Bello *et al.* (2019)[43]	Function unit: 1 kg h^{-1} FDCA; allocation method: economic allocation; system boundary: cradle-to-gate	HMF synthesized from glucose mixture (7.8 wt%) using Sn_2O-γ-Al_2O_3 in DMSO/water (8/2)	Glucose	HMF derived FDCA	Aspen Plus simulation, literature reports	n/a
Kim *et al.* (2020)[55]	Function unit: 1 kg FDCA; allocation method: mass allocation; system boundary: cradle-to-gate	HMF was produced from cellulose using a THF/H_2O solvent (90 : 10 mass ratio) containing dilute H_2SO_4 (20 mM) as catalysts	Cellulose (from wood chips)	HMF derived FDCA	EcoInvent database, Aspen Plus simulation, literature reports	2.5 kg CO_2 eq. per kg FDCA
Kim *et al.* (2020)[56]	Function unit: 1 kg FDCA; allocation method: n/a; system boundary: cradle-to-gate	HMF was produced from cellulose using a THF/H_2O solvent (90 : 10 mass ratio) containing dilute H_2SO_4 (20 mM) as catalysts	Cellulose (from wood chips)	HMF as an intermediate for FDCA	EcoInvent database, Aspen Plus simulation, literature reports	2.4 kg CO_2 eq. per kg FDCA.
Kim *et al.* (2020)[57]	Function unit: 1 kg of FDCA; allocation method: n/a; system boundary: cradle-to-gate	HMF was obtained from cellulose (3% loading) using THF/H_2O over H_2SO_4	Cellulose	HMF as an intermediate, FDCA	Experimental data and simulation results, NREL report, literature reports, the chemical engineering plant cost index	1.6 kg CO_2 eq. per kg FDCA

Table 1 *(Contd.)*

Paper	Key features	Catalytic system	Feedstocks	Products	Data sources	Climate change/GHGs
Barman *et al.* (2021)[53]	Function unit: 1 kg HMF; allocation method: mass allocation; system boundary: cradle-to-gate	HMF was produced using FA-NPC* photo catalyst in cooked rice wastewater	Waste cooked rice water	HMF as final product	Ecoinvent database, experimental data	n/a
Zuiderveen *et al.* (2021)[49]	Function unit: 1 kg PEF; allocation method: economic allocation; system boundary: cradle-to-gate	HMF was synthesized in MIBK, 2-butanol, and DMSO, using HCl as a catalyst at 170 °C	Glucose, fructose/high-fructose corn syrup	PEF as final product	Ecoinvent database, agri-footprint, literature data, simulation data experimental data	n/a
Götz *et al.* (2023)[58]	Function unit: 1 kg HMF; allocation method: economic and physical allocation; system boundary: cradle-to-gate	HMF was produced using sulfuric acid in water	Maize based HFCS and miscanthus	HMF as final product	Ecoinvent database, experimental data	0.46–2.24 kg CO_2 eq. per kg HMF
Derosya *et al.* (2024)[39,52]	Function unit: 1 kg SPW; allocation method: n/a; system boundary: gate-to-gate	In the THF–water system, a 33% yield of HMF was achieved at 160 °C after 45 min using aluminum sulfate as the catalyst and sodium chloride as an additive. The DMSO–water system produced a higher yield of 58% HMF at 160 °C for 8 min	SPW	Crude HMF as final product	Ecoinvent database, experimental data, EU & DK Input–Output database, agri-footprint database	2.1–9.7 kg CO_2 eq. per kg HMF
Nakason *et al.* (2024)[54]	Function unit: 1 kg HMF; allocation method: n/a; system boundary: cradle-to-gate	HMF was obtained from fructose using H_2SO_4, TsOH, and $FeCl_3$ grafted biochar catalyst in i-PrOH/water at 175 °C for 30 minutes	Fructose	HMF as final product	Ecoinvent database, experimental data	477 kg CO_2 eq. per kg HMF

sugars into ethanol has a low yield, then the agricultural production of corn will have to increase, making that agricultural step cause even more eutrophication. Thus, the fermentation step is an indirect hotspot because it indirectly influences the true hotspot. Identifying hotspots is crucial to green chemistry because efforts to reduce the harm of processes are most effective if they focus on hotspots.[41]

2.1 HMF LCA studies

Due to the pressing need for environmentally friendly and sustainable bio-based bulk chemicals, the industrialization of HMF is gaining momentum. LCA has been proposed to quantitatively evaluate the greenness, sustainability, and feasibility of HMF commercial-scale synthesis and process routes. These studies could be divided into groups.

(1) Studies focusing on the environmental impact of lab-scale HMF synthesis technologies.

(2) Studies focusing on HMF-derived high-valued compounds.

(3) Studies focusing on the evaluation of various separation procedures used to isolate HMF.

(4) Studies comparing several HMF production catalysts.

(5) Comparative assessments of HMF production in biorefineries (Fig. 7).

Lab-scale HMF synthesis. In 2018, Lam *et al.*[42] conducted a comparative LCA study on six HMF synthesis methods that used food waste as feedstock. The results showed that the highest metal depletion impacts resulted from the production of metal chloride catalysts, while marine ecotoxicity, freshwater toxicity, and human toxicity mostly came from the production of solvents. LCA was used in this study to identify the best option for valorising food waste by balancing the damages and benefits. However, the data for HMF production was based on laboratory-scale synthesis.[42]

LCAs based on laboratory-scale data are valuable early indicators of strengths and weaknesses but are obviously not as accurate as late-stage LCAs in predicting the environmental harm of industrial processes. Davidson's discussed the key factors that affected the environmental impact of the HMF production process based on previous LCA studies that used large-scale data.[35] The comparison between laboratory, pilot, and industrial-scale LCA studies revealed that energy consumption is the primary contributor to the environmental impact. This study also showed that expanding the process scale from laboratory to pilot and industrial scale could significantly reduce environmental impact through general optimization and process efficiency improvements of over 60% and 90%, respectively. However, LCA research at the laboratory scale can help identify environmental hotspots and guide technology development through step optimization. Therefore, in the pre-evaluation period, testing the sensitivity of a laboratory-scale process to some step optimization is recommended to guide technology development. These findings highlight the importance of conducting LCA studies across different scales to ensure a comprehensive understanding of the environmental impact of the HMF production process.[33]

Table 2 A table summarizing the key features of the reviewed furfural LCA studies

Paper	Key features	Catalytic system	Feedstocks	Products	Data sources	Climate change/GHGs
Hong *et al.* (2015)[64]	Function unit: 1 t of furfuralcohol; allocation method: economic allocation; system boundary: n/a	Furfural was produced using water and sulfuric acid; methyl furan and furfuralcolhol were produced using Cu–Si catalyst and water	Corncob	Furfural, furfuralcohol, and methyl furan	Real industry-scale data, a furfuralcohol production site in Henan. Ecoinvent database, literature reports	1×10^3 kg CO_2 eq. (53% electricity, 25% transport.)
Raman *et al.* (2015)[80]	Function unit: a service based WtW (Well to Wheel) functional unit (1 km); allocation method: revenue; system boundary: cradle-to-gate	Furfural was produced sulfuric acid, water, Na_2CO_3, and lime	Vetiver	Ethanol, furfural, lignin for energy production	Literature reports, and ecoinvent, experimental data	0.003 kg CO_2 eq. for ethanol and furfural (reference case: 0.21 kg CO_2 eq.)
Farzad *et al.* (2017)[81]	Function unit: 5 (tDM per hour) tons of bagasse and trash per hour; allocation method: energy; system boundary: cradle-to-gate	Furfural was prepared using NaCl, HCl, and THF	Bagasse from a sugar mill	Scenario 1: EtOH; Scenario 2: EtOH-LA; Scenario 3: EtOH-furfural; Scenario 4: butanol; Scenario 5: methanol, FT syncrude	Industry-scale, Aspen plus simulation, ecoinvent, literature reports	n.a.
Pachón *et al.* (2020)[72]	Function unit: 1 kg lactic acid for Scenario 1, 1 kg lactic acid, and 0.33 kg furfural; allocation method: multiproduct allocated to bagasse; system boundary: cradle-to-gate	NaCl, THF, and water were used for furfural production; sulfuric acid, lime, methanol, and water were used for lactic acid	Vine shoots and bagasse	Scenario 1: lactic acid; Scenario 2: lactic acid and furfural	Industry-scale, process simulation, ecoinvent, literature reports	Conventional lactic acid production: 4.7 kg CO_2 eq.; Vine-derived lactic acid: 3.3 kg CO_2 eq.; (2) conventional furfural and LA production: 4.8 kg CO_2 eq.; vine-derived furfural and LA: 3.0 kg CO_2 eq.; 0.4 kg of CO_2 of climate change impact for 1 kg of LA from sugarcane bagasse and leaves
Wang *et al.* (2016)[82]	Function unit: 1 ton ethyl levulinate; allocation method: ethyl levulinate; system boundary: cradle-to-gate	Furfural and EL were prepared using sulfuric acid, Na_2SO_4, ethanol, and water	Cornstalk	Ethyl levulinate, furfural	Real industry data (a demonstration project in China.); literature reports (hypotheses), ecoinvent	2.3 net GHGs (CO_2 eq.) (t/t) 7.5 EL production (1 ton EL with 1.0 ton furfural)
Pachón *et al.* (2018)[70]	Function unit: 1 t of sugarcane; allocation method: economy; system boundary: cradle-to-gate	Furfural was prepared using sulfuric acid and NaCl in THF/H_2O	Sugarcane	Scenario 1: (base scenario) a typical sugar mill; Scenario 2: sugar mill integrated into a biorefinery producing sugar, lactic acid, and electricity; Scenario 3: sugar mill integrated into a biorefinery producing sugar, lactic acid, furfural, and electricity	Ecoinvent, experimental data, simulation, assumption	~90 kg CO_2 eq. 1 t sugarcane.
Bello *et al.* (2018)[76]	Function unit: 1 t h^{-1} of hardwood chips; allocation method: economy; system boundary: cradle-to-gate	Furfural was prepared using 1.25% sulfuric acid in 50% ethanol	Bench woodchips	Scenario 2: ethanol, furfural, and lignin; Scenario 3: ethanol, acetic acid, furfural, and lignin	Literature reports, ecoinvent, simulation using Aspen plus	Biorefinery 2 (4.2 kg CO_2 eq. per euro) and 2.5 (4.5 kg CO_2 eq. per euro)
Putra *et al.* (2021)[74]	Function unit: 1 kg of dissolving pulp product; allocation method: n.a; system boundary: cradle-to-gate	Furfural was produced using 6 wt% sulfuric acid in aqueous solution at 98 °C for 1 h	EFB from oil palms and wood	Dissolving pulp and furfural	Ecoinvent; agri-footprint, USLCI; field survey (conducted in dissolving pulp mill); literature reports; laboratory-scale data	Scenario 1: 1.8×10^8 kg CO_2 eq.; Scenario 2: 3.5×10^8 kg CO_2 eq.; Scenario 3: 4.3×10^8 kg CO_2 eq. for annually environmental impact assessment
Liu *et al.* (2021)[68]	Function unit:1 t ethanol; allocation method: economic-based allocation, as an alternative: mass and energy-based allocation; system boundary: cradle-to-gate	Formiline process: furfural was prepared in acetic acid in an aqueous phase with chloroform as extracting phase	Wheat straw	Furfural, lignin product, and ethanol	Literature report, simulation using Aspen plus, experimental data, ecoinvent	0.4 kg CO_2 eq. per kg furfural

Table 2 *(Contd.)*

Paper	Key features	Catalytic system	Feedstocks	Products	Data sources	Climate change/GHGs
Pachón *et al.* (2020)[71]	Function unit: 1 kg sugar/furfural/lactic acid, 1 kWh electricity; allocation method: economy; system boundary: cradle-to-gate	Scenario SM-FF: furfural was prepared using sulfuric acid in the aqueous phase and ethanol production using bacteria	Bagasse from a sugar mill	Scenario SM-FF: furfural and ethanol	Literature reports, simulation using Aspen plus, ecoinvent	0.6 kg CO_2 eq. per kg furfural in SM-FF scenario
Thompson *et al.* (2021)[66]	Function unit: 1 t of furfural; allocation method: economic allocation; system boundary: cradle-to-gate	(1) Furfural was prepared using sulfuric acid in the aqueous phase (hydrolysis); (2) furfural was prepared using sulfuric acid (pyrolysis)	Sugar beet pulp	Furfural	Experimental data, literature reports, ecoinvent	267 and 1095 kg CO_2 eq. per 1 t furfural using pyrolysis and hydrolysis
Hao *et al.* (2021)[67]	Function unit: 1 t of bio-jet fuel; allocation method: economic allocation; system boundary: cradle-to-gate	(1) Furfural was prepared using 8 wt% sulfuric acids in water. (2) 0.24 M sulfuric acid for levulinic acid production from cellulose	Cornstalk	Furfural, levulinic acid	Ecoinvent, literature reports	n.a.
Ng *et al.* (2022)[73]	Function unit: 100 kg of dried EFB feedstock; allocation method: n/a; system boundary: gate-to-gate	Furfural was prepared at 8.8 atm and 70 °C for 20 min using sulfuric acid in water	Empty fruit bunch biomass	Furfural and glucose	Europe life cycle database, simulation data	126 kg CO_2 eq. per kg furfural
Khounani *et al.* (2023)[9]	Function unit: 1 kg furfural; allocation method: mass; system boundary: cradle-to-gate	Furfural was prepared at 180 °C for 45 min using various metal catalysts ($FeCl_3$, $FeCl_2$, $CuCl_2$, $AlCl_3$, and $MgCl_2$)	Poplar wood	Furfural, lignin, glucose	Ecoinvent, literature reports	370–1790 kg CO_2 eq. per kg furfural

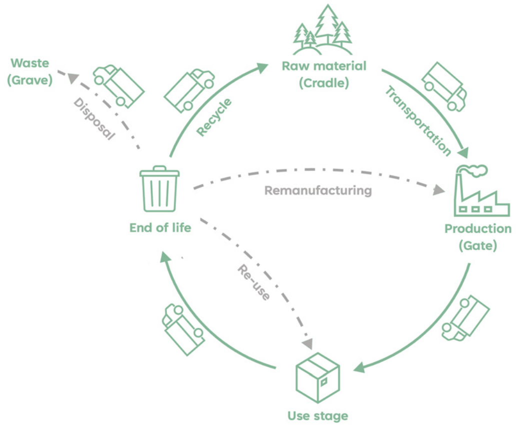

Fig. 6 Varying LCA scopes.

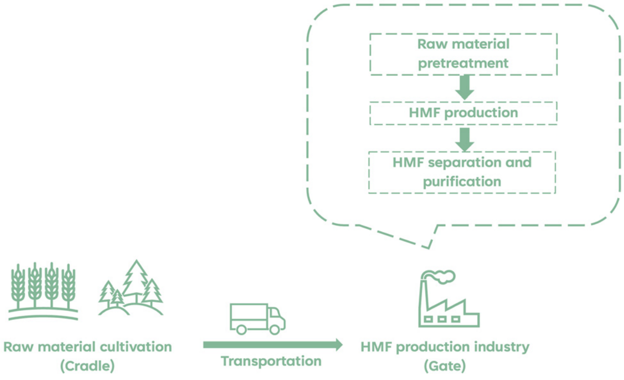

Fig. 7 The cradle-to-gate LCA for HMF production.

HMF-derived high-valued chemicals. An additional form of HMF-related LCA investigation has been conducted, with a specific focus on HMF as an intermediate product rather than a final output. The objective of this work is to explore the viability of converting HMF into high-value chemicals, thereby encompassing a diverse range of applications such as plastics, pharmaceuticals, food additives, and fuels. Notable examples of these chemicals include 2,5-furandicarboxylic acid (FDCA),[43] polyethylene furandicarboxylate (PEF),[44] hexamethylenediamine (HMDA),[45] and *p*-xylene.[46] For example, Eerhart *et al.*[44] performed a cradle-to-gate LCA study on the production of biobased PEF from corn-based fructose to evaluate its potential as a replacement for fossil-based PET. In this study, HMF and ethoxymethylfurfural were synthesized in a water-methanol mixture using sulfuric acid as the catalyst under milder reaction conditions, then HMF and ethoxymethylfurfural were oxidized into FDCA, after which PEF was synthesized by subsequent polymerization of FDCA and ethylene glycol (EG). The production of biobased PEF has been shown to have significant environmental benefits compared to petrochemical PET in terms of non-renewable energy use and GHG emissions. Compared to other biobased plastics (polylactic acid (PLA), polyhydroxyalkanoates (PHA), and polyethylene (PE)), PEF production is also superior in terms of GHG emissions.[44]

Isola *et al.*[47] conducted a cradle-to-grave LCA aimed at evaluating the sustainability of the production of FDCA from HMF, employing data obtained at the laboratory scale. The synthesis of HMF from fructose was accomplished with a yield of 45% in a mixed solvent system comprising water and dimethylacetamide, employing lithium bromide and H_2SO_4 as catalysts. Subsequently, a conversion of HMF to FDCA was achieved with a yield of 65%. Electricity consumption and the use of potassium permanganate made substantial contributions to climate change and human toxicity impacts during HMF production. Sensitivity analysis identified electricity and solvent as the main contributors to climate change. Encouragingly, the investigators have found that environmental impact can be lessened through FDCA recycling, potentially reducing the environmental impact by 11% to 23% by assuming a 40% recovery of FDCA weight during the recycling process.

Dros *et al.* investigated three bio-based pathways aimed at the production of 1,6-hexanediol, using maize-derived fructose syrup and potato-derived starch as the starting materials, with HMF serving as an intermediate. The objective of this study was to observe the most efficient and environmentally friendly route for 1,6-hexanediol production, with a focus on achieving optimal outcomes. The best case with the highest HMF yield (88%) was the preparation from fructose syrup in DMSO and water, while the worst case with the lowest HMF yield (49%) was prepared just in water using $Cu(NTF_2)_2$ as the catalyst. Sensitivity analysis revealed that HMF yield was a sensitive variable for the environmental impacts studied. An HMF yield variation from 49% (worst case) to 88% (best case) resulted in 8.6 and 5.7 kg CO_2 eq. per kg 1,6-hexanediol, respectively. The difference was mainly attributed to the higher steam consumption required for fructose syrup drying in the best case. Furthermore, HMF yield fluctuation of worst case and best case translated to 0.052 and 0.028 kg N eq. per kg 1,6-hexanediol for marine eutrophication which was primarily attributed to increased feedstock consumption and fertilizer use. These findings for the sustainable production of 1,6-hexanediol underscore the importance of optimizing HMF yield in the production process to mitigate environmental impacts.[48]

In a comprehensive study, Lin *et al.* undertook a comparative cradle-to-gate LCA analysis of two distinct routes to produce *p*-xylene: one derived from biomass sources such as red oak and maize starch with HMF serving as an intermediate, and the other sourced from petroleum. The investigation encompassed the hydrolysis of starch into glucose using an aqueous hydrochloric acid (HCl) solution. Subsequently, the resulting product mixture was combined with tetrahydrofuran (THF) and sodium chloride (NaCl) to yield a 10 wt% HMF solution. Sensitivity analysis was performed to evaluate the impact of feedstock variation on LCA results, revealing that cultivation and processing of maize starch were hotspots for most impacts, followed by the heating steam requirements. However, it was observed that as the concentration of HMF increased with sugar concentration, the environmental impact of THF had the potential to decrease. This was attributed to the reduced demand for THF, HCl, and NaCl by 44%, 52%, and 39%, respectively, as a result of higher sugar concentration.[46] This paper highlighted the importance of feedstock selection and optimization of the production process for the sustainable production of *p*-xylene.

Zuiderveen *et al.* conducted an *ex-ante* LCA to evaluate the cradle-to-gate environmental impacts of producing PEF *via* HMF and xylitol using a novel electrochemical process. The study encompasses TRL 2 to 4, spanning conceptual design. Specifically, HMF was produced through selective dehydration of fructose in an MIBK/2-butanol/DMSO solvent system, with HCl as a catalyst at 443 K. HMF production including upstream processes of corn glucose production, glucose-to-fructose conversion, and fructose dehydration to HMF accounts for 17% of total non-renewable energy use (NREU) impact, 18% of acidification impact, and 27% of GHG emissions. However, HMF production shows limited contributions to land use (7%) and eutrophication (2%). Notably, land use attributed to corn production for HMF and wood production for xylitol represents 65% and 30% of the total land use impact, respectively.[49]

Bello *et al.* performed cradle-to-gate LCA to compare two purification methods for FDCA production (Scenario 1: crystallization and Scenario 2: distillation). The study used lignocellulosic feedstocks, specifically hardwood chips, as the starting material for the production of FDCA *via* lignocellulosic biomass-derived HMF as an intermediate. The study aimed to identify key environmental hotspots in the early stage of process design. HMF was produced using $Sn_2O–Al_2O_3$ as the catalyst at 150 °C and 8.2 bar in DMSO. HMF (96.5% concentration) was extracted using a liquid–liquid extraction column with DCM/water (9/1). Results revealed that, in both scenarios, HMF production was the largest or second-largest hotspot in FDCA production across all environmental impacts, including global warming, ozone depletion, ozone formation, terrestrial acidification, freshwater eutrophication, marine eutrophication, freshwater ecotoxicity, marine ecotoxicity, human toxicity and fossil scarcity. Notably, DCM, employed during the recovery process of HMF, emerged as the primary contributor to climate change and ozone depletion, responsible for approximately 50% and 98% of the respective impacts. This can be attributed to its chlorinated nature, which possesses the potential to influence chemical reactions within the atmosphere. The use of the metal catalyst exhibited the most prominent influence on terrestrial acidification, freshwater eutrophication, freshwater ecotoxicity, and marine ecotoxicity, contributing impacts of 21%, 14%, 29%, and 28%, respectively.[50] It is worth noting that the lack of data on the catalyst in the database was addressed by using literature data and taking into account the use of platinum and zirconium oxide.[51]

Separation techniques for HMF isolation. Derosya *et al.* performed a gate-to-gate laboratory-scale LCA comparing THF–water and DMSO–water systems to produce HMF from sago pith waste (SPW). Under the THF–water system, 33% HMF yield was achieved at 160 °C for 45 min using aluminum sulfate as a catalyst and sodium chloride as an additive. In contrast, the DMSO–water system yielded 58% HMF under the same temperature conditions in 8 min. The LCA analysis revealed that, without considering HMF separation, the production process emitted 0.4 kg CO_2 eq. for the DMSO–water system and 0.8 kg CO_2 eq. for the THF–water system. However, when HMF separation was included, the environmental impact increased significantly. The DMSO–water system emitted 9.7 kg CO_2 eq., whereas the THF–water system emitted only 2.1 kg CO_2 eq. The lower environmental impact of the THF–water system can be attributed to its higher HMF concentration in the crude extract, and the low boiling point of THF reduces the energy required for separation. Experimental evidence further demonstrated the difficulty of separating HMF from DMSO, highlighting a key drawback of this solvent system.[39,52]

Different catalyst for HMF production. Barman *et al.* conducted a gate-to-gate LCA to compare two nano-photocatalysts (FA_NPC^{*O} and FA_NPC^{CO}) for the conversion of cooking rice water to HMF using lab-scale experimental data. FA_NPC^{*O} and FA_NPC^{CO} gave HMF yields of 38 mol% and 22 mol% under tungsten-halogen radiation and ultrasound at 70 °C in 60 min. Results showed that catalyst preparation, HMF production, and HMF purification were the three largest contributors to the total environmental impacts.[53] The findings of this study suggested that the selection of appropriate catalysts, optimization of HMF production and purification processes could significantly improve the environmental performance of the process.

Nakason *et al.* conducted a cradle-to-gate LCA of HMF production, comparing the performance of three catalysts: H_2SO_4, *p*-toluenesulfonic acid (TsOH), and $FeCl_3$ grafted onto biochar derived from cassava rhizomes, using laboratory-scale data. The highest HMF yield (53%) from fructose was achieved with the H_2SO_4 grafted biochar catalyst in an i-PrOH/water solvent system (v/v, 80/20) at 175 °C over 30 min. The other two catalysts demonstrated slightly lower yields, with reductions of 5–8% compared to the H_2SO_4 grafted biochar catalyst. Notably, the biochar-based catalysts exhibited excellent recyclability, maintaining consistent HMF yields over five reuse cycles. In HMF production, 7 processes including feedstock, transportation, pulverization, carbonization, acid grafting, HMF synthesis, and HMF extraction and purification were assessed. The LCA results revealed that the synthesis, extraction, and purification of HMF accounted for 80–99% of the impacts across all assessed categories. Specifically, electricity and solvent consumption during the synthesis step were identified as the primary contributors to environmental impact. Among the catalysts, the TsOH-grafted biochar-based catalyst demonstrated the lowest global warming potential (GWP), suggesting a more favourable environmental profile compared to the other catalysts. However, it is worth noting that the LCA study did not account for the potential environmental benefits of catalyst recycling, which could further influence the comparative sustainability of these systems.[54]

HMF production in biorefinery. Kim *et al.* conducted a series of enlightening cradle-to-gate LCA studies encompassing the synthesis of FDCA from HMF, derived from cellulose obtained from wood chips.[55–57] In their first publication, they compared the environmental impacts of biomass-derived FDCA and petroleum-derived terephthalic acid production. The study highlighted THF and electricity as the primary contributors to the environmental burdens associated with the process of HMF production.[55] Different from the first paper, their second and third papers, for example, include biomass pretreatment and the synthesis of furfural or furfural-derived products. The second work from Kim *et al.* assessed a method for the co-production of FDCA (converted from C_6 sugars *via* HMF), THFA (converted from C_5 sugars *via* furfural), and activated carbon (lignin) from wet wood chips, using γ-valerolactone (GVL)/H_2O as a pre-treatment solvent. Notably, the main takeaway from this work is that the use of THF, lime, and electricity in HMF production contributed to 50 to 80% of the overall impacts, including climate change, ozone depletion, terrestrial acidification, freshwater eutrophication, human toxicity, *etc.*, in FDCA production process. The study also suggested the potential for enhancing sustainability by substituting electricity-generating resources with renewable alternatives (*e.g.*, biogas, wood chips, hydropower, wind power, and nuclear power) rather than natural gas.[56] Their third cradle-to-gate LCA evaluated a new catalytic process for producing FDCA from cellulose. HMF production accounted for 7% of climate change, while electricity consumption, particularly in the heat pump, accounted for 36% (0.58 kg CO_2 eq.) of the climate change impact (Fig. 8). Remarkably, the HMF production subsystem emerged as the largest contributor to the capital costs associated with the process.[57] It should be mentioned that HMF (with a 42% yield) was generated entirely from the dehydration of cellulose (3% loading in solvent) using THF and H_2O as solvents (THF : H_2O = 9 : 1 mass ratio) over dilute H_2SO_4 (20 mM) in three publications. However, the disparities in results are related to differences in process procedures and feedstock.

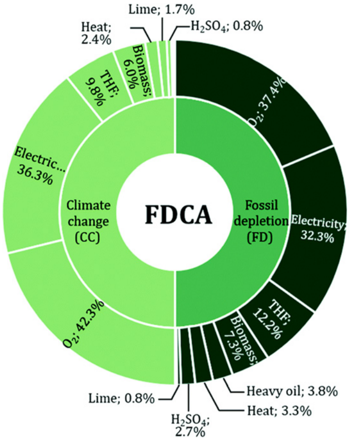

Fig. 8 Sunburst chart for the environmental impact of biomass-derived FDCA. Adapted from ref. 57 with permission from the RSC,[57] copyright 2020.

Götz *et al.* presented a comparative cradle-to-gate LCA of four simulated HMF biorefineries using maize-based high-fructose corn syrup (HFCS) and miscanthus as feedstocks. The scenarios investigated were as follows:

Scenario A: maize cultivated in Germany produces HMF and char as the main products.

Scenario B: maize cultivated in Hungary produces HMF and char as the main products.

Scenario C: miscanthus cultivated in Germany produces HMF, furfural, monomeric and oligomeric aromatic compounds, and char.

Scenario D: miscanthus cultivated in Germany produces HMF, furfural, lignin, and char.

LCA outcomes indicated that the miscanthus-based biorefineries exhibited lower emissions across all assessed impact categories compared to the HFCS biorefineries, with the sole exception of land occupation. Contribution analyses revealed that the primary environmental impact within HMF production arises from the auxiliary materials used in separation units and the heat required for processing.[58]

Through a comprehensive review of LCA studies of HMF production, significant insights were garnered concerning critical factors in the production process encompassing energy consumption, feedstock use, solvent selection, and catalyst efficacy. Notably, one of the major sources of environmental impact identified was the high energy demand associated with HMF production.[33] In light of these findings, it is imperative to focus on saving energy and improving energy efficiency in the pursuit of developing economically and environmentally sustainable processes for HMF production.

Identifying a suitable feedstock is a crucial factor in promoting environmentally friendly HMF production, given the significant environmental impact associated with feedstock cultivation which requires inputs such as energy, fertilizer, and land use, all of which are associated with environmental consequences.[47] Agricultural and forestry biomass are frequently used in HMF production. A cradle-to-gate LCA by Isola *et al.* contrasted the environmental impact of two feedstocks (maize and potato) for HMF production. They had radically different impacts in environmental categories like climate change, aquatic eutrophication, land use, and human toxicity (Fig. 9).[47] Specifically, aquatic eutrophication is driven by nitrogen and phosphorus, which are present in the fertilizers used for agricultural biomass cultivation.[48] In the case of forestry derived biomass, land occupation, terrestrial acidification, marine ecotoxicity, particulate matter formation, and freshwater ecotoxicity are primarily from the biomass production step.[47,59]

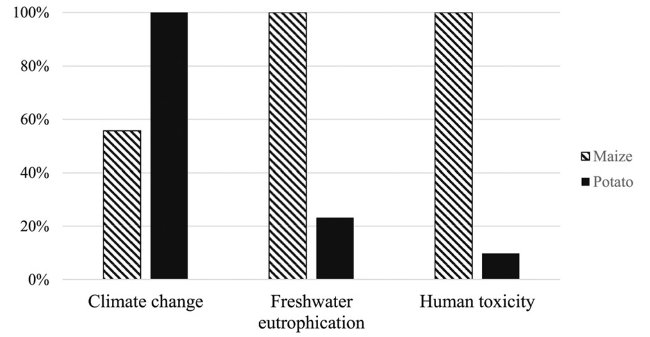

Fig. 9 Comparing maize and potato for HMF production. Adapted from ref. 47 with permission from Elsevier,[47] copyright 2017.

The key role of solvents in the development of environmentally conscious and sustainable technologies cannot be understated, as they often contribute significantly to the overall environmental impact of HMF production. The environmental impacts associated with solvent were attributed to two major factors: the toxicity of the organic solvents and the energy requirement in solvent production. Energy-associated impacts include climate change, photochemical oxidant formation, acidification, and fossil fuel depletion.[42,60] Among solvents used for HMF production, THF, commonly used, should be avoided because the highest energy consumption required for THF production and the large amount of THF used.[46] The production of THF incurred the highest environmental impacts because the petrochemical production process involves numerous conversion steps with high energy and resource requirements.[42,60] MeTHF, water and acetone have been proposed as more environmentally friendly alternatives.[42,61] To reduce the environmental impact of solvents in HMF production, the adoption of green solvent substitution and recycling practices has been suggested.[47] Moreover, future research should prioritize the investigation of green biomass-derived solvents for HMF and furfural production, illuminating the path toward sustainable solvent choices.

Despite extensive research on HMF production, there is a significant gap in LCA and technical studies specifically addressing the separation processes of HMF. This lack of research has led to a limited understanding of HMF and hampers the ability to perform a comprehensive comparative evaluation of different HMF isolation methods.[62,63] Most LCA studies involving the separation and purification of HMF are conducted in conjunction with LCA studies of high-value products derived from HMF, such as FDCA. These studies indicate that the separation and purification processes of HMF constitute a significant portion of the production cost and environmental impact.[50] Specifically, the challenges associated with HMF separation and purification stem from the substantial energy consumption and the extensive use of extracting agents, irrespective of the distillation method employed. This high energy usage results in poor environmental performance, particularly regarding GWP, acidification potential, ozone depletion, eutrophication potential, photochemical ozone formation potential, cumulative energy demand (CED), toxicity potential, and non-renewable energy use. To mitigate the energy consumption associated with distillation, one strategic approach involves the back-extraction of HMF into an organic phase characterized by a lower boiling point. Additionally, adsorption and membrane methods offer a greener alternative for the selective separation of HMF. This technique not only reduces energy use but also enhances the sustainability of the overall process.

Even a minimal quantity of a catalyst yields a noteworthy increase in the production of HMF while simultaneously influencing the results of LCAs. The use of different catalysts in HMF production raises significant concerns about their environmental impacts. For example, the widely used acidic catalyst, H_2SO_4, primarily contributes to the formation of particulate matter, terrestrial acidification, and depletion of water and metal resources.[64] Furthermore, the use of metal catalysts in chemical processes is highly relevant to several key environmental impact categories, including GWP, CED, terrestrial acidification, human toxicity, and aquatic ecotoxicity (both freshwater and marine). While these catalysts are often crucial for improving reaction efficiency and selectivity, they can contribute to environmental burdens throughout their life cycle starting from extraction and refining, continuing through their use, and extending to disposal. For example, the extraction and refining of metals typically require energy-intensive processes, which elevate CED and GWP. Additionally, the leaching of metal ions into aquatic environments can significantly increase freshwater and marine ecotoxicity.[50,65]

2.2 Furfural LCA studies

Within this section, a collection of LCA investigations relating to furfural production is presented. These studies naturally fall into five distinct categories.

(1) Studies based on actual industrial implementations and demonstration projects.

(2) Studies evaluating novel furfural synthesis methodologies.

(3) Comparative analyses of furfural production in a biorefinery context with different configurations.

(4) Comparative studies of different feedstock options for furfural production.

(5) Studies evaluating various separation techniques employed to isolate furfural.

Industrial and demonstration projects. Two noteworthy studies by Hong *et al.* and Wang *et al.* offer valuable insights into furfural production using actual industrial and demonstration project data. These comprehensive investigations have greatly contributed to refining and optimizing furfural large-scale production process. Hong *et al.* presented the first LCA analysis based on furfural industry data where 12.24 tons of corncob could yield 1.12 tons of furfural, 1 ton of furfuryl alcohol, and 0.11 tons of methyl furan. The furfural production process applied a traditional method using sulfuric acid as a catalyst in an aqueous phase, subsequently neutralized by sodium hydroxide. The sensitivity analysis highlighted that the environmental and economic performance of furfural production is predominantly affected by total electricity consumption, transportation logistics, and corncob feedstock, with lesser influence from other factors such as sulfuric acid usage and wastewater management.[64] To improve the environmental footprint of furfural production, it is recommended to increase furfural yield and optimize the efficiency of electricity use.[64] Wang *et al.* reported a cradle-to-grave LCA of ethyl levulinate and furfural production from cornstalk based on demonstration project data where 35.3 tons of cornstalk produced 3.7 tons of ethyl levulinate and 3.6 tons of furfural. The same synthesis method for furfural as in Hong *et al.* was used. Through sensitivity analysis, it was determined that a decrease in cornstalk revenue (the selling price of cornstalk) correspondingly reduced the amount of energy consumption and environmental emissions allocated to furfural, as the allocation percentages of energy consumption and environmental emissions were influenced by cornstalk revenue fluctuations.[82]

Lab-scale furfural synthesis. Thompson *et al.* compared the hydrolysis and pyrolysis pathways for furfural production from sugar beet pulp. The hydrolysis pathway yielded 20 g of furfural per kg of wet sugar beet pulp by employing sulfuric acid as the catalyst and water as the solvent. In contrast, the pyrolysis pathway yielded a significantly higher furfural output of 77 g per kg of sugar beet pulp. The main take-away from this work is that the pyrolysis pathway gave the lowest CO_2 emissions (267 kg CO_2 eq. per ton) and furfural production cost (846 \$ per ton). In contrast, the high water use and low energy-density feedstock transportation in the hydrolysis method resulted in the highest CO_2 emissions (1095 kg CO_2 eq. per ton) and furfural production cost (980 \$ per ton). The sensitivity analysis revealed that biomass conversion rate, drying (only in the pyrolysis pathway), and transportation were the three hotspots that impacted the environmental performance.[66] This study provides valuable insights into the potential improvement directions for the hydrolysis pathway to enhance its sustainability.

Hao *et al.* conducted an LCA study of bio-jet production *via* furfural from corn stalk comparing two processes that differed in how lignin was used. The first process used lignin to generate H_2 for hydrogenation, while the second used the lignin as fuel. Sulfuric acid was the catalyst for furfural and levulinic acid co-production in the aqueous phase. The study employed process simulations using Aspen Plus software, and exergy analysis and LCA were used to evaluate the cumulative exergy efficiency and renewability of the bio-jet fuel production process. The study found that minimizing the consumption of acid and base chemicals and increasing the methanol recovery rate could significantly improve the cumulative exergy efficiency and renewability of bio-jet fuel production. Sensitivity analysis indicated that the conversion efficiency of furfural and levulinic acid to bio-jet fuel and the consumption of stripping steam significantly affected the energy efficiency and exergy efficiency.[67]

Furfural production in biorefinery. Liu *et al.* compared two distinct scenarios of wheat straw biorefinery, each involving different pretreatment methods. As shown in Fig. 10, the first scenario, referred to as the Dilute process, solely focused on ethanol production, while the second scenario, known as the Formiline process, extended its scope to include various derivatives derived from furfural and lignin-based phenol–formaldehyde. The functional unit in this study is 1 ton of ethanol. The LCA outcomes revealed that the Formiline biorefinery exhibited a lower intensity in terms of GWP owing to the

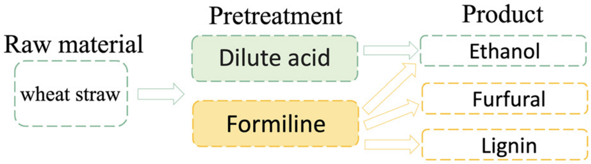

Fig. 10 Formiline and dilute acid processes.

production of multiple products. In the Formiline biorefinery, a furfural yield of 63% was achieved using acetic acid as the catalyst in the aqueous phase, and chloroform as the extracting phase. It is noteworthy that the expanded design within the Formiline process showcased positive effects on all environmental categories, with the exception of ozone layer depletion, which was attributed to the use of chloroform in the extraction process. Sensitivity analysis further revealed that electricity consumption had the most substantial influence on GWP, while the impact of solvents (specifically chloroform) and catalysts (acetic acid/sulfuric acid) remained negligible, accounting for less than 0.14% for both processes. Furthermore, the results indicated that the primary contributors to environmental impact across all impact categories for both the Dilute and Formiline biorefineries encompassed chemical inputs, electricity consumption, direct emissions, and ash landfill, collectively accounting for approximately 75–100% of the overall impact.[68]

Farzad *et al.* presented a case study comparing six biorefinery scenarios expanded from the existing sugar industry. The scenarios differed in the products obtained from bagasse and other sugarcane waste.

Scenario 1: ethanol and electricity (the main products in the biorefinery);

Scenario 2: ethanol, lactic acid, and electricity;

Scenario 3: furfural, ethanol, and electricity;

Scenario 4: butanol and electricity;

Scenario 5: methanol and electricity;

Scenario 6: syncrude and electricity.

Furfural production in Scenario 3 was carried out using a THF/water biphasic system, with NaCl and HCl as additive and catalyst, respectively. However, the results indicated that Scenario 3 had significant challenges in terms of economic competitiveness and environmental friendliness compared to other options. These difficulties mainly resulted from the energy-intensive process of furfural recovery and purification, wherein THF, used as the solvent, emerged as the predominant contributor to the overall impact. To enhance the sustainability of Scenario 3, it is recommended to focus on reducing solvent usage, enhancing internal solvent recycling, and boosting furfural efficiency.[69] This study highlights the intricacies, opportunities, and obstacles associated with integrating furfural production processes into the existing sugar industry.

Pachón *et al.* conducted a comprehensive series of LCA studies, with a specific focus on the production of furfural and other valuable chemicals within the context of a biorefinery. In a 2018 paper, the authors investigated the environmental and economic performance of two integrated biorefinery-sugar mill scenarios: SM-LE (lactic acid and sugar) and SM-LF (lactic acid, sugar, furfural, and surplus). The finding demonstrated that the inclusion of furfural production in scenario SM-LF (2.5 g/38.2 g sugar) resulted in a more favourable economic outcome compared to scenario SM-LE. However, it is important to note that THF used as a solvent in the furfural production process contributed significantly to its poor environmental performance, particularly in terms of climate change impact and fossil depletion.[70] In their subsequent study in 2019, Pachón *et al.* investigated three integrated sugar mill biorefinery scenarios. In scenario SM-FF, furfural was produced in an aqueous phase using sulfuric acid as a catalyst. The study revealed that scenario SM-FF was economically unfavourable due to low furfural and ethanol yields. In addition, furfural production by this process had higher environmental impacts on freshwater ecotoxicity and fossil depletion than the conventional furfural production route, which resulted from using the toxic chemical ammonia in the pretreatment process.[71] Comparatively, in their most recent LCA study, Pachón *et al.* compared two biorefinery scenarios. Furfural (2.5 g/38.2 g sugar) was produced from vine shoots using sulfuric acid and NaCl in THF/water in Scenario 2. The study found that furfural produced in biorefinery is less environmentally harmful than the conventional furfural conversion processes, which is different from the early LCA study in 2019.[72] The differences in results across the studies conducted by Pachón may be attributed to variations in feedstock and scope. Changes in the scope of an LCA can significantly influence the environmental outcomes. As such, it is not feasible to conclusively determine which technique is more environmentally friendly until comprehensive LCAs, covering cradle-to-gate or cradle-to-grave perspectives, are thoroughly analyzed.[39]

Ng *et al.* conducted a prospective gate-to-gate LCA on the co-production of furfural and glucose from empty fruit bunch biomass, using an Aspen Plus simulated database. The analysis revealed that the furfural and glucose recovery units had the most significant environmental impacts, accounting for 50–80% of the total across multiple categories, including GWP, acidification potential, and eutrophication potential. The product purification stage emerged as a critical phase due to its substantial energy demands, primarily met by high-pressure steam and hot water supplied to the reboiler. This energy-intensive process led to emissions of sulphur oxides, nitrous oxide, nitric oxide, nickel, cadmium, and palladium, all contributing to acidification potential, eutrophication potential, and human toxicity. Furthermore, sulfuric acid used for converting hemicellulose in EFB to xylose was a key contributor to acidification potential. The co-production process also required significant quantities of steam and hot water, resulting in considerable consumption of liquefied natural gas (LNG). The combustion of LNG released contaminants and contributed to GWP. The study further highlighted that substituting diesel with LNG increased the carbon footprint by 16%, whereas replacing diesel with hydrogen led to a substantial reduction in the carbon footprint by 47%.[73]

Khounani *et al.* conducted a cradle-to-gate LCA of furfural production in a poplar wood-based biorefinery, analyzing variations in mannitol concentration (ranging from 0–15% w/w) and different catalyst types ($FeCl_3$, $FeCl_2$, $CuCl_2$, $AlCl_3$, and $MgCl_2$). The study was based on lab-scale data, excluding the impacts of catalyst recycling, as well as wood cultivation and transportation. The results revealed that furfural production using $AlCl_3$ with a 5% w/w concentration of mannitol exhibited the most favorable environmental performance among all the conditions assessed. Specifically, the use of $AlCl_3$ led to a 45–79% reduction in environmental burdens across all impact categories when compared to the other catalysts. Furthermore, it was observed that the use of fossil-based electricity was a significant contributor to the overall environmental impacts of the process.[9]

Different feedstock for furfural production. Putra *et al.* conducted an environmental assessment of the co-production of furfural and dissolving pulp from non-woody biomass waste empty fruit bunches (EFB) obtained from oil palms as a potential substitute for wood as a feedstock. Three scenarios were proposed and compared. In the first scenario, 50% of wood consumption was substituted with EFB. The second scenario involved a complete replacement of wood consumption with EFB. Lastly, the third scenario not only replaced 100% of wood consumption with EFB but also substituted sulfuric acid with water. This adjustment aimed to enhance overall environmental performance while maintaining identical cooking and bleaching conditions as implemented in the other scenarios. The majority of the inventory data used in this study originated from laboratory-scale experiments conducted by Pytra's research group. Furfural was produced in an aqueous phase with 6 wt% sulfuric acid under mild reaction conditions of 98 °C and 1 h, and 400 kWh t^{-1} of furfural production was used. This study highlighted the importance of prehydrolysis which breaks down the carbohydrates in biomass to provide sufficient xylose for furfural co-production, furfural is a valuable by-product that can increase revenue. The study presented the potential of food waste EFB as a substitute for wood within the dissolving pulp industry, with the additional advantage of furfural co-production, thus further enhancing the economic viability and environmental benefits of the process.[74]

Separation techniques for furfural isolation. Contemporary methodologies employed in furfural production suffer from high energy consumption. The purification step in particular is well known for its substantial energy consumption.[75] Three LCA studies have been conducted to comprehensively evaluate the procedures of furfural separation. Bello *et al.* investigated the production of high-value chemicals from beech woodchips rather than fossil resources, integrating organosolv fractionation. Furfural, as a C_5 sugar valorisation product, was prepared in ethanol/water (50% v/v) with 1.25% sulfuric acid. A traditional distillation method and a hybrid extraction-distillation method for furfural recovery were compared, using extractive solvents including benzene, toluene, and butyl chloride. The results identified benzene as the most effective option for furfural recovery, while toluene was determined to be the least efficient. Among the alternatives evaluated, including butyl chloride and exclusive distillation, the hybrid process utilizing benzene demonstrated the most favourable outcomes based on the LCA analysis. However, benzene poses significant carcinogenic risks, which must be carefully considered in its applications. In addition, the hybrid extraction-distillation method exhibited superior environmental performance compared to distillation alone because it used less energy. The use of fossil-based solvents for furfural recovery increases the contributions to climate change, ozone depletion, and fossil fuel depletion.[76]

The published LCA studies about furfural synthesis have produced several similar results. The traditional method of furfural production in reviewed LCA studies commonly employed water as the solvent and sulfuric acid as the catalyst, respectively. Another commonly used design was a two-phase reaction system in a batch or continuous reactor with *in situ* extraction of the organic phase, which can lead to a higher yield and selectivity for furfural. This is due to the inhibition of the rehydration of furfural in the reaction phase, and the addition of an extractive phase can improve the separation of furfural and increase the recyclability of the reaction phase. THF has been frequently used, but THF has a strongly negative environmental impact because its production requires much more energy than other organic solvents.[77] As a result, improving the reaction system and looking into different solvents may result in more benign ways to produce furfural.

Long-distance transportation of feedstocks and high energy consumption for production and separation were the major contributors to the environmental impact of furfural manufacturing.[64] To reduce the environmental impact of the biorefinery, it is essential to shorten transportation distances, implement milder reaction conditions, and adopt energy-efficient separation systems. Additionally, the heavy reliance on fossil-based electricity significantly contributes to the environmental footprint of the process. Transitioning to renewable electricity would substantially mitigate these impacts, particularly in terms of GWP.

Furfural separation has been more extensively studied in LCA research compared to HMF separation. These studies demonstrate that furfural separation plays a significant role in both the production cost and the overall environmental impact of its production process. Additionally, two Eco-indicator 99 studies conducted by Zarazúa *et al.* provide further insights into its environmental impact. In 2021, Zarazúa *et al.* compared eight distillation methods for purifying furfural and its co-products, using extractive distillation with butyl chloride as a solvent (see Fig. 11). These methods included direct, indirect, direct thermally coupled (DTC), indirect thermally coupled (ITC), thermally coupled equivalent direct (TCED), thermally coupled equivalent indirect (TCEI), direct intensified (DIS), and indirect intensified alternative (IIS) distillation. These methods differ in terms of the separation process and the equipment and technology used. Specifically, direct methods are traditional separation methods, while indirect methods require adding another fluid to the column to improve energy efficiency. Intensified methods build upon traditional

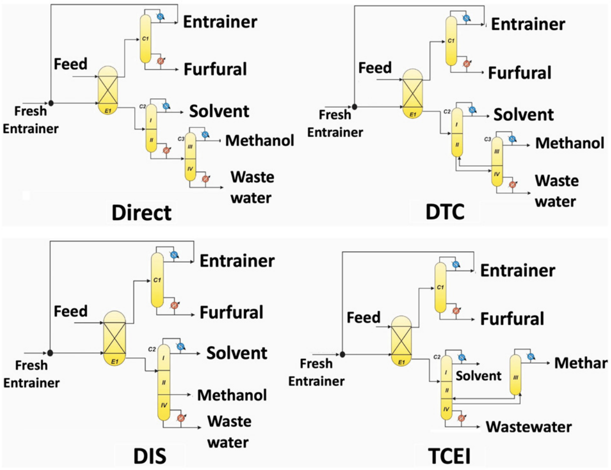

Fig. 11 Four distillation methods. Adapted from ref. 75 with permission from Elsevier,[75] copyright 2021.

methods to achieve greater efficiency and lower costs. The study revealed a direct correlation between cost, environmental impact, and energy requirements.[75] When comparing the seven separation methods, it was concluded that IIS stands out as the best option, offering the lowest environmental and economic impact. Based on Zarazúa's findings, it is clear that further advancements in furfural and HMF separation techniques are essential, with a focus on reducing energy consumption through methods such as membrane technology or crystallization. In 2022, Zarazúa *et al.* conducted a comprehensive analysis using Eco-indicator 99 and total annual costs to evaluate two pretreatment methods (acid pretreatment and ammonia fibre explosion (AFEX)) and four purification techniques (conventional Quaker Oats process, thermally coupled process, divided wall column scheme and extractive liquid–liquid process) for producing furfural from four types of agricultural residues (corn stover, wheat straw, sorghum bagasse and sugarcane bagasse). The assessment, based on data simulated through Aspen Plus within the context of a biorefinery (see Fig. 12), revealed that wheat straw using dilute acid pretreatment and thermally coupled separation gives the lowest cost and lowest harm.[78]

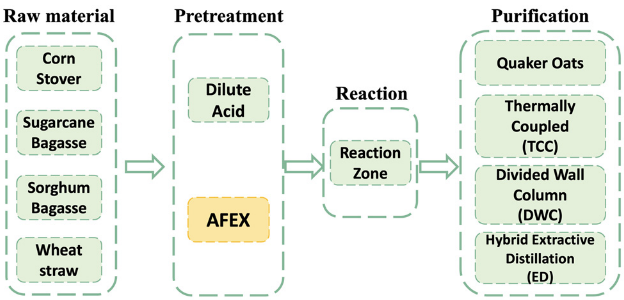

Fig. 12 Diagram illustrating the different possible scenarios studied by Contreras-Zarazúa *et al.* Adapted from ref. 78 with permission from Elsevier,[78] copyright 2022.

The choice of feedstock is crucial in determining both the environmental impact and the final cost and yield of a product, influencing these factors both directly and indirectly. For instance, biomass feedstocks have a carbon sink capacity that can partially offset the greenhouse gas (GHG) emissions generated during their conversion. A notable example is cornstalks, whose growth can offset 83% of the GHG emissions associated with furfural production. However, it is important to recognize that agricultural biomass often depends on agrochemical fertilizers, such as urea, which contribute to environmental issues like global warming, acidification, eutrophication, and human toxicity.[79] The selection of biomass significantly impacts the LCA results for furfural production indirectly.[74] Some feedstocks, like EFB, require lower energy inputs and less intensive processing conditions to produce furfural. This is particularly significant, as energy consumption—encompassing electricity and steam—accounts for more than 60% of the total environmental impact in conventional wood-based processes. As such, selecting feedstocks that require milder processing conditions is a key strategy for mitigating the environmental impact of furfural production.

Technology comparisons by LCA not only facilitate the evaluation and screening of novel, environmentally friendly furfural production techniques but also enable purposeful improvement of methodologies through an analysis of environmental sensitivity. Such studies have shown that expansion of a biorefinery's multi-production spectrum, such as furfural and ethanol co-production, has the potential to enhance both the environmental and economic aspects. Additionally, reducing energy consumption *via* optimization or redesign would be advantageous.[76] Future process and technology advances, such as catalysts, process routes, green solvents, and reaction conditions, will necessitate more LCA studies.

3 TEA studies

TEA is a systematic approach to evaluating the technological and economic viability of a product or process. This methodology typically involves five key steps: process design, mass and energy balance calculations, cost estimation, profitability analysis, and sensitivity analysis. Once capital expenditures (Capex) and operational expenditures (Opex) are determined, a cash flow analysis is performed over a defined lifetime to assess various economic indicators, such as internal rate of return (IRR), net present value (NPV), payback period (PP), and minimum selling price (MSP).[83,84]

Recent research focusing on TEA for furfural and HMF production has explored simulated plant designs, experimental setups, and integrated processes utilizing different feedstocks. Common studied feedstocks for TEA of furfural production often include bagasse, corn cobs, oil palm empty fruit bunches, switchgrass, waste hemicellulose, birch hydrolysate, and mixed feedstocks,[83,85–91] while HMF production primarily utilizes raw materials like fructose, bagasse, high-fructose corn syrup, glucose, starch, miscanthus, and corn. TEA studies on furfural production often incorporate the generation of co-products such as glucose, ethanol, HMF, levulinic acid, and levoglucosenone.[92–97] TEA studies for HMF production typically focus on standalone production or on processes where HMF is synthesized alongside furfural, ethanol, levulinic acid, or as an intermediate for FDCA production. Through these TEA studies, it was discovered that key elements impacting the economic feasibility of furanic production across studies include feedstock cost, transportation logistics and availability, process efficiency and yield, energy consumption, solvent and catalyst recycling, and the scale of production facilities.

Furfural has been commercially established for over a century, with its market price typically falling between US $1000 and US$1500 per metric ton. TEA study of furfural production consistently presents potential for further lower MSP estimates relative to market values. Minimum selling prices (MSP) for furfural are estimated to range between US$366 and US$625 per ton.[83,85–90] A study even showed that a continuous biphasic reactor system for furfural production achieves a remarkably low MSP of US$366 per ton—approximately 75% below the prevailing market price. Another example is an integrated switchgrass-based production system, which cites an MSP of US$625 per ton alongside a 10% internal rate of return (IRR).[98] Given that, the research for furfural production focus will be on leveraging of environmental and economic performance of the furfural process as well as on leveraging its production with by-product production to improve the overall environmental and economic performance of the biorefinery.[92]

However, the large-scale commercialization of HMF production continues to face challenges related to HMF MSP. In contrast to furfural, MSP for HMF varies widely, from approximately US$1000 per ton to as high as US$3000 per ton, influenced by factors like feedstock selection, production scale, and geographic region.[92–97] A TEA of HMF production was conducted by Torres *et al.* in 2010, who evaluated a semi-batch biphasic system with an annual capacity of 7000 tons. Their study reported an MSP of $1968 per ton of HMF from fructose. Reducing the MSP of HMF is critical. Without this adjustment, HMF will struggle to compete with fossil fuel alternatives, making it the primary challenge that must be addressed for its economic viability. This study showed that feedstock alone can account for over 80% of the MSP of HMF.[93]

Glucose is a good alternative to fructose for HMF production. The difference between using fructose and glucose as feedstocks was further investigated by Yan *et al.* in 2020. Their work demonstrated that fructose dehydration catalysed by HCl in water, with 2-MeTHF as an extractant, achieved an HMF yield exceeding 94%. Additionally, they confirmed that glucose could also be converted to HMF with a high yield (close to 70%) using HCl and $AlCl_3$ as catalysts in water, with MIBK as the extractant. A subsequent techno-economic analysis indicated that HMF could be produced at an MSP of $1716 per ton from fructose and $1215 per ton from glucose, based on a plant capacity of 10 128 tons per year. In this study, feedstock cost remained the largest contributor to the MSP, accounting for 42%.[94]

Lignocellulosic feedstocks such as miscanthus, bagasse, or corn are much cheaper than fructose and glucose, it has been proposed to be a promising feedstock. HMF produced from woody residues under catalytic hydrothermal conditions has been reported to have a selling price of $2160 per ton regardless of IRR of 44%, and a payback period of 2.25 years.[95] Another study estimated a total investment of 257 million euros for a plant processing spruce to produce 5 kt of HMF annually. The MSPs were estimated at 1930 € per ton for HMF. The profitability analysis showed an IRR of 16%, indicating that the process is both viable and profitable.[96] A TEA study proposed using milled corn kernels as feedstock, achieving over 80% molar yield of HMF within 3 min of reaction time. For a facility with an annual production capacity of 330 kilotons, the MSP of HMF was estimated to be $1105 per ton. Further analysis suggested that with very high solvent recycling efficiency (99%), the MSP could be reduced to as low as $560 per ton. However, it should be noted that this analysis is overly optimistic from a technical perspective.[97]

4 Catalysts

4.1 Homogeneous catalysts

Homogeneous catalysts, commonly used in furanic compound production, commonly include inorganic and organic acids such as HCl, H_2SO_4,[99–103] formic acid, acetic acid, maleic acid, and succinic acid.[104–107] In addition to these acid catalysts, metal salts such as $AlCl_3$, $CrCl_3$, $FeCl_2$, $FeCl_3$ and $CuCl_2$ [108–113] are widely employed. Conveniently, these homogeneous catalysts are commercially available and reasonably stable.

The use of H_2SO_4 in the traditional furfural production process causes concerns for the environment and equipment.[114] H_2SO_4, the most commonly used acid, contributes significantly to terrestrial acidification, water depletion, and depletion of metal resources.[64] Researchers have explored ways to reduce the negative effects on the environment as well as equipment corrosion caused by homogeneous acidic catalysts such as H_2SO_4 and HCl while maintaining high yields.[115,116] Alternative acids, such as organic acids like formic acid[117] and acetic acid, have been explored as less toxic and safer options for handling.[118] However, the use of organic acids as milder acidic catalysts requires careful evaluation, as their application may result in higher electricity consumption due to longer reaction times and elevated operating temperatures. Maintaining mild reaction conditions is essential for the efficient use of organic acids, highlighting the need to balance their more benign nature with potential increases in energy demand.

Metal chlorides, such as $FeCl_3$, NaCl, and $AlCl_3$, have been recognized as excellent catalysts for the synthesis of furanic compounds. Reduced corrosiveness, commercial availability, and lower cost make metal chlorides more appealing as catalysts.[119] Particularly, the synergistic effect of combining Lewis and Brønsted acids significantly promotes HMF production. Specifically, Lewis acids can facilitate the rate-determining isomerization, in which aldose is converted into ketose, by promoting the formation of an enol intermediate. On the other hand, Brønsted acids catalyse the hydrolysis and dehydration reactions. The significance of this synergistic effect has been demonstrated in several studies.[60–62] The metal catalyst has the most significant impact on terrestrial acidification, freshwater eutrophication, freshwater ecotoxicity, and marine ecotoxicity.[50]

Numerous investigations have conclusively demonstrated that metal chlorides, particularly trivalent cations, represent the most promising catalysts in aqueous solution. Mao *et al.* reported that a combination of 60 mM $FeCl_3·6H_2O$ and acetic acid (2 to 4 wt%) produced a good furfural yield of 73% directly from corncob at 190 °C in seawater.[119] This is because of the nucleophilic properties of Cl^-, which prove advantageous in furfural synthesis. Additionally, it has also been proven that Cl^- as well as Br^- and I^- can promote the selective dehydration of glucose, thus improving the selectivity of HMF. Nevertheless, the use of metal chlorides may give rise to environmental concerns owing to the presence of metals and halogens. Bello *et al.*, for instance, reported that the most noticeable impacts resulting from the use of metal catalysts were terrestrial acidification, freshwater eutrophication, freshwater ecotoxicity, and marine ecotoxicity, with impact contributions of 21, 14, 29, and 28%, respectively.[50] Different metals have diverse impacts on the environment. For instance, Lam *et al.* in their investigation of HMF production from bread waste, employed $AlCl_4$ and $SnCl_4$ catalysts, revealing that the selection of catalyst had a noticeable impact on LCA results. The aluminium-based catalyst exhibited reduced effects compared to the tin-based catalyst, largely due to the higher abundance of aluminium.[42] In support of this, Khounani *et al.* emphasized that using an appropriate catalyst, specifically $AlCl_3$, can significantly reduce the environmental impact of furfural production, achieving a reduction of 45% to 79% compared to alternative catalysts such as $FeCl_2$, $FeCl_3$, $CuCl_2$, and $MgCl_2$.[9]

4.2 Heterogeneous catalysts

Various heterogeneous catalysts, including zeolites,[120–125] modified zeolites,[126–130] metallic oxides,[131] and ion exchange resins[132–137] are commonly used in the synthesis of furans from carbohydrates. Compared to homogeneous catalysts, heterogeneous catalysts are easier to separate from the product and solvent after the reaction. Catalyst recovery is an essential consideration in chemical and fuel-based industries, with the catalyst and its required reaction equipment often accounting for more than half of total equipment investments.[138] Easy solvent-catalyst separation improves the feasibility and economic viability of furanic compound production.

In addition, the effective inhibition of the undesired polymerization of furanic compounds, leading to the formation of humins, is crucial for achieving higher yields of furanic compounds. Heterogeneous catalysts like zeolites with appropriate pore size are effective in achieving this goal. Gürbüz *et al.* examined various solid acid catalysts for the conversion of xylose into furfural in GVL. These catalysts included zeolites such as H-mordenite, H-beta, and HZSM-5, modified zeolites, Sn-SBA-15, and sulfated varieties. The heterogeneous catalysts exhibited significantly higher yields (>70%) of furfural compared to the use of 0.02 M H_2SO_4.[139] In another study, Lessard *et al.* reported a furfural yield of 98% from xylose using a mordenite catalyst in a toluene–water biphasic system.[140] A kinetic analysis showed that the use of ZSM-5 zeolites with pore sizes in the range of 0.8 to 1.0 nm could mitigate the undesired reaction of furfural converting into humins in the aqueous phase. Specifically, the appropriately sized pores of the ZSM-5 zeolites spatially hindered humin formation by limiting the space available for furfural to polymerize with itself or side products.[141,142] The regulation of catalytic sites in zeolites, coupled with precise control over pore size, holds significant potential for the development of improved catalysts for furanic compound synthesis.

Zeolites have been widely used in the synthesis of furanic compounds, but the preparation of the catalyst itself contributes to environmental harm. The production of zeolite A, a commonly used zeolite, involves various chemical inputs, with aluminum hydroxide being the primary contributor, followed by silica and sodium hydroxide.[143] The Bayer process is the primary method of manufacturing aluminum hydroxide used in commercial applications and involves the digestion of bauxite in a caustic solution of NaOH at high temperatures, followed by separation of the resulting waste and precipitation of aluminum hydroxide from the remaining solution.[144] However, the resulting insoluble bauxite residue known as "Red Mud", which consists mainly of iron oxide and residual NaOH, has a significant environmental impact, particularly on freshwater ecotoxicity and human toxicity. Storage of "Red Mud" in lagoons has historically presented a range of challenges, highlighting the need for effective management strategies to mitigate its adverse effects. The intricate relationship between zeolite synthesis, aluminum hydroxide production, and the associated environmental impacts necessitates careful consideration and exploration of alternative approaches to enhance sustainability and mitigate the environmental footprint of zeolite production.[145,146]

An environmental study for metallic oxide γ-Al_2O_3 production demonstrates lower GHGs compared to ZSM-5, while its modified metallic oxides, including CoMo/γ-Al_2O_3 and Pt/γ-Al_2O_3, exhibit GHGs similar to that of ZSM-5, as depicted in Fig. 13. However, it is worth noting that even a small amount of metal loaded in the catalyst can have a significant environmental impact. For example, platinum constitutes only 2% of the catalyst mass, yet it contributes about a third of the catalyst's GHG intensity due to the high GHG intensity for its production. Platinum production is an energy-intensive process.[147] This observation highlighted the critical role of metal selection in catalyst design, where the environmental impact of individual metals must be considered alongside their catalytic performance.

Furthermore, the catalyst consumption rate and the inputs for producing the catalyst together determine the environ-

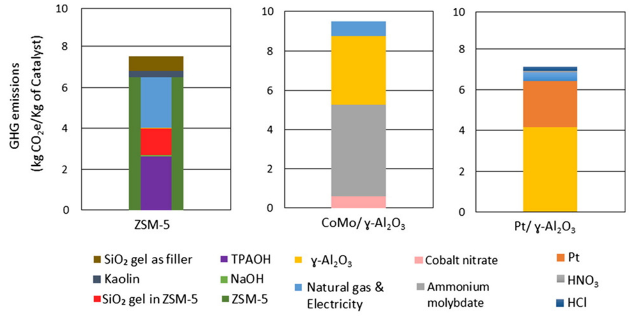

Fig. 13 Cradle-to-gate GHGs for the synthesis of ZSM-5, CoMo/γ-Al_2O_3, and Pt/γ-Al_2O_3. Adapted from ref. 147 with permission from Elsevier,[147] copyright 2017.

mental impact of furanic compound production. Despite the lower GHGs associated with ZSM-5 production, its higher consumption rate compared to the bimetallic catalyst CoMo/γ-Al_2O_3 makes the overall production of furanics more GHG intensive. This is because the recovery of spent ZSM-5 catalyst is generally deemed economically infeasible and not widely practiced. The difference in catalyst consumption rates is substantial, with ZSM-5 exhibiting a consumption rate 22–36 times greater than that of CoMo/γ-Al_2O_3. Consequently, the use of ZSM-5 in the production of renewable gasoline significantly contributes to GHGs, potentially accounting for up to 14% of these emissions.[147]

Thus far, limited literature exists regarding the LCA of ion exchange and carbon-based catalyst production. Despite that, numerous examples have demonstrated the exceptional performance of such catalysts for HMF production. For instance, Amberlyst-15 powder with a size range of 0.015–0.053 mm demonstrated 100% HMF yield at high fructose concentrations (50 wt% in DMSO) at 120 °C for 2 h.[148] Carbon-based catalysts have also shown promising results, with the highest HMF yield of 94% being achieved using sulfonated graphitic carbon nitride (S-GCN) with glucose as the substrate and water as the solvent at 200 °C for 5 h. S-GCN possesses amphoteric properties by having both Brønsted base and Brønsted acid sites.[149] Carbon-based heterogeneous catalysts such as biochar and bio-carbon-based heterogeneous catalysts produced particularly from carbon waste could potentially offer a more promising approach for the production of environmentally benign catalysts. This potential is attributed to the dual advantages of employing waste carbon-based materials and various unique functional groups on their surface, such as oxygen-containing species (carbonyl groups, phenolic hydroxyl groups, and carboxylic acidic groups).[150]

Heterogeneous catalysts encounter challenges when it comes to the hydrolysis of raw biomass. This limitation arises due to the restricted contact area between the catalyst and the feedstock, impeding the hydrolytic depolymerization of raw biomass and subsequently resulting in diminished mass transfer and low yield.[131,151] To illustrate, Chareonlimkun *et al.* studied the conversion of corncob to furfural in the presence of TiO_2–ZrO_2 and water at 573 K, achieving a small yield of 10%.[131,151] Consequently, raw biomass necessitates additional pretreatment to facilitate the hydrolysis of polysaccharides into monosaccharides, then monosaccharides rapidly diffuse into the inner pores of heterogeneous catalysts through suitable external pores and channels, benefiting from their high solubility in solvents. As a result, the transformation of monosaccharides would not be constrained by mass transfer limitations, enabling their conversion into furanic compounds by specific catalytic active sites located within the internal pores.

The need for new catalysts or additional pretreatment is anticipated to address this limitation of heterogeneous catalysts. New recyclable and green catalysts have been studied to overcome heterogeneous catalysts' poor catalytic performance for lignocellulosic biomass. For instance, a new recyclable polytriphenylamin-SO_3H solid acid catalyst (MSPFR) was developed. MSPFR could wrap around untreated biomass, which increased the contact area and mass transfer between the catalyst and biomass feedstock material. Yields of 43% furfural and 31% HMF were obtained from cornstalks using MSPFR. The MSPFR could then be regenerated through a washing process employing water and acetone.[152] In addition to MSPFR, CO_2 was also used to produce furfural as a non-toxic, recyclable gaseous catalyst. Morais *et al.* reported, for the first time, that xylose conversion of more than 83 mol% and furfural yield of 70 mol% were obtained at 180 °C and a pressure of 50 bar of CO_2 as a catalyst in THF/water mixture.[153] One advantage of using CO_2 as a catalyst lies in its potential to serve as an extractant during downstream treatment processes, facilitating the separation and purification of furanic compounds. This is achieved by introducing additional CO_2 into the biphasic mixed reaction medium containing water and organic solvents subsequent to the reaction, thereby forming an extraction layer.[154] Catalysts like MSPFR and CO_2 are both easily recovered and able to react with solid biomass, which is a winning combination for the conversion of raw biomass.

In summary, the use of catalysts in industrial-scale biofuel production has a minimal impact on GHGs during the conversion stage, generally ranging from 0.5% to 5% depending on the co-product treatment method applied.[155] Despite their small usage, catalysts have a significant impact on chemical reactions in terms of both the economy and the environment. Their manufacturing, recycling, lifetimes, metal loading, and consumption rate are major drivers of process economics, sustainability and greenness.[147] However, this information is often undisclosed.[156] Because there are not enough in-depth insights, further research is required before we can make precise recommendations for catalyst development.

5 Feedstocks

5.1 The starting materials for HMF production

The feedstocks for HMF synthesis can be categorized into three groups: monosaccharides (*e.g.*, glucose and fructose), polysaccharides (*e.g.*, cellulose and starch), and raw biomass (*e.g.*, lignocellulosic biomass and waste, algae). Using fructose and glucose, monomeric C_6 sugars derived from raw biomass, in HMF synthesis results in a superior yield of HMF, particularly fructose as it is an intermediate in the HMF production pathway. However, the process of obtaining monosaccharides also required more energy, chemicals, and additional processes such as pretreatment.[64] Furthermore, fructose lacks the reserves and viability of glucose and cellulose. Given that, fructose is less favourable than glucose. Comparatively, raw biomass, such as corn stover, hardwoods, conifers, and sugarcane, is cheaper than monosaccharides. The economics of HMF production using raw biomass as a feedstock hinge on various factors, including taxes, feedstock price, transportation, electricity, technology, and infrastructure investment.[64] Raw biomass gives a lower HMF yield, resulting in low material and energy efficiency.

The industrialization of HMF is facing significant impediments attributed to two fundamental factors, namely the inflexible structure of cellulose and the instability of HMF. The high degree of polymerization and the crystalline structure of raw cellulose makes it harder to depolymerize and convert to HMF than hemicellulose. In natural cellulose, there are three hydrogen bonds per glucose unit in the same sheet (Fig. 14). The main force between each sheet is the van der Waals interaction, which contributes greatly to the stability of cellulose. Cellulose is a component in lignocellulosic polymers, and the number of glucose units in one polymer chain can reach 10 000 or more.[157] Although glucose monomers and glucose oligomers are hydrophilic, cellulose is insoluble in water due to its high molecular weight (solubility is usually inversely proportional to polymer chain length). In addition, the flexibility of cellulose polymeric chains is relatively low.[158] The hydrogen bonds between molecules and the van der Waals interactions between the top and bottom layers of the hydrophobic plane cause the cellulose chains to pack together tightly, resulting in cellulose being insoluble in water and most hydrophilic solvents and resistant to hydrolysis. As a result, more severe reaction conditions, such as high temperature and high pressure, are required to achieve effective cellulose hydrolysis.

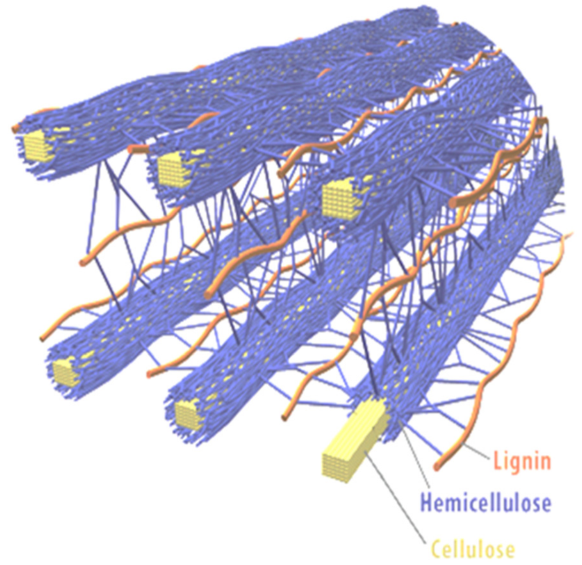

Fig. 14 Spartial arrangement of cellulose, hemicellulose and lignin in the cell walls of lignocellulosic biomass. Adapted from ref. 161 with permission from the U.S. Department of Energy Genomic Science program,[161] copyright 2011.

However, HMF, being a kinetic product, can readily further react to produce humins in an acidic environment or under severe reaction conditions such as high temperature and high pressure.[159] HMF contains two reactive functional groups: an aldehyde group and one hydroxyl functional group, while furfural has only one functional group: the aldehyde group. The two active functional groups on the HMF ring are readily involved in isomerization, condensation, and cross-polymerization, which cause the instability of HMF. Because of this instability, HMF generally needs to be refrigerated and stored away from light. Galkin *et al.* reported that HMF oil (97–99% purity) was placed at room temperature for two weeks and found that part of the HMF oligomerized into dimers and oligomers.[160] The instability of HMF and the recalcitrance of cellulose result in a low yield and a high selling price for HMF.

The direct and indirect effects of the choice of feedstock on the economic feasibility and environmental impact have not been comprehensively discussed in published reviews. The high cost of some feedstocks poses a significant hindrance to their industrial application in HMF production. A techno-economic analysis (TEA) conducted by Torres *et al.* in 2010 concluded that fructose is an unsuitable raw material for HMF production, as its high price outweighs the benefits of any optimization of the production system.[93] A thorough investigation of the TEA aspects involved in the successful synthesis of HMF and furfural from mixed-sugar hydrolysates was presented by Gogar *et al.* They cleverly combined chemical and enzymatic catalysis. Within the scope of this study, a thorough sensitivity analysis proved that feedstock sugar cost and overall furan yield were the dominant determinants of the selling price.[162] A TEA of a low-cost, high-efficiency method for FDCA synthesis from starch, glucose, or high-fructose corn syrup using HMF was conducted by Dessbesell *et al.* Sensitivity analysis revealed that, across all scenarios, the feedstock (high-fructose corn syrup, glucose, or starch) had the most effect on the discounted payback period.[163]

A considerable number of LCA studies have been conducted to evaluate the environmental impacts of HMF production from various raw feedstocks. These studies emphasize the substantial influence of material and energy inputs related to feedstock cultivation on the overall environmental performance of HMF production. Key factors include the use of fertilizers and pesticides, irrigation water, and diesel fuel for plantation operations. The variability in these inputs across different feedstocks highlights the importance of carefully selecting and managing raw material supply chains to minimize the environmental footprint of HMF production systems. Wang *et al.* elucidated that raw feedstock has a carbon sink capacity during growth, offsetting GHGs from ethyl levulinate production.[82] Dros *et al.* suggested that using potatoes as the feedstock instead of maize could minimize GHGs, primarily due to the higher crop yield achieved in potato production.[45] However, Isola *et al.* reported that fructose from potatoes negatively impacted GHGs but significantly reduced freshwater eutrophication and human toxicity. These varying outcomes among studies can be attributed to diverse assumptions regarding crop yield and fertilizer use.[47] Lin *et al.* evaluated the environmental impacts of *p*-xylene production from different feedstocks, and they observed that the cultivation and processing of maize starch had a substantial influence on most impact categories, accounting for 75% of impacts in marine eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, agricultural land occupation, and urban land occupation. In comparison, oak cultivation predominantly impacted the categories of agricultural land occupation and urban land occupation.[46] It should be noted that repurposing land use is a critical factor, particularly when evaluating biofuels in comparison to fossil fuel alternatives. Repurposing land may disrupt global market dynamics and influence the prices of goods. Consequently, this could potentially trigger land use conversion in other regions, leading to deforestation and the subsequent release of carbon into the atmosphere.[165,166]

The choice of biomass feedstock significantly influences reaction conditions and process design, which in turn impact both the cost and environmental footprint of furanic compound production. For example, EFB exhibit higher delignification efficiency compared to wood, allowing the use of environmentally friendly, sulfur-free pulping systems to remove lignin. In conventional wood-based processes, energy consumption (primarily electricity and steam) accounts for more than 60% of the total environmental impact. As an alternative feedstock, EFB offers substantial energy savings during prehydrolysis and soda cooking processes, while also reducing the need for nitric acid, leading to a lower overall environmental impact.[74] A comprehensive study by Zarazúa *et al.* evaluated furfural production from various agricultural residues, including corn stover, wheat straw, sorghum bagasse, and sugarcane bagasse. The results showed that wheat straw had the lowest environmental impact and cost, followed by corn stover, sugarcane bagasse, and sorghum bagasse. This ranking can be attributed to the higher water requirements of sugarcane and sorghum bagasse, which increase separation costs and energy consumption. These findings highlight the importance of careful biomass selection to minimize the environmental footprint and cost of furfural production.[78]

In summary, feedstock selection is crucial as it directly and indirectly influences the technical, economic, environmental, and social performance of furanic compound production in biorefineries. Ideally, raw materials with desirable characteristics such as agricultural wastes (*e.g.* corn stover and corncob), low polymerization and high carbohydrates, large and stable production, less land use, high carbon sink capacity, short transportation distances, less water usage and reasonable cost, are recommended.

5.2 The starting materials for furfural production

As with HMF, the starting materials for furfural production can be divided into monosaccharides (such as xylose, arabinose, and C_5 hydrolysate), polysaccharides (such as hemicellulose and xylan), and raw biomass (such as lignocellulosic and marine biomass). LCA studies showed that different feedstocks (such as monosaccharides and lignocellulosic biomass) have diverse effects on climate change, freshwater eutrophication, and human toxicity. For example, the preparation of furfural from agricultural waste corncob involves land use, pesticides, fertilizers, diesel, and electricity consumption during corn growth. However, corn growth is also a carbon sequestration process, which offsets part of the GW of the final product.[64] Comparatively, monosaccharide production requires more material and energy input than raw materials such as lignocellulosic biomass, even though a higher furfural yield could be obtained from monosaccharides. Studies show that use of monosaccharides can substantially increase furfural yields, potentially 80% to 90%, by employing diverse solvent systems such as biphasic or monophasic mixtures, ionic liquids, and deep eutectic solvents (DESs).[167–169] However, the cost of feedstock is a key factor in determining the market price of furfural; the industrial furfural synthesis is much more economical produced from lignocellulosic biomass than with isolated monosaccharide and polysaccharide feedstocks. The traditional “one-pot” furfural production method, which uses lignocellulosic biomass as the main feedstock and sulfuric acid in an aqueous environment to produce furfural, is one of the conventional methods used in its production on an industrial scale. This method gives a furfural yield of between 40% and 50% by mass fraction. Notable examples of these lignocellulosic biomasses comprise corncobs, corn straw, oat husks, wheat straw, and wheat husks.

6 Solvents

6.1 Green solvent selection

In today's chemical industry, solvents are used in large quantities. In particular, large amounts are used per mass of final products in fine-chemical production. Therefore, solvents define a significant part of the environmental performance of a chemical process.[60] One of the most efficient and essential strategies for minimizing the environmental impact of HMF and furfural production on an industrial scale is the appropriate selection of solvent.

The LCA studies reviewed demonstrate that the solvent affects not only environmental and economic performance but also product yield, cost, energy consumption, and safety of HMF or furfural production, even when compared to the choice of catalyst and feedstock. The selection of a solvent is pivotal in refining downstream separation processes, directly influencing factors such as reaction selectivity, extraction efficiency, phase dynamics, and overall operational performance. Strategic solvent choices tailored to interact specifically with solutes can dramatically enhance separation efficiency during stages like extraction or crystallization, simplifying the isolation of the desired product from impurities. An optimal solvent not only facilitates smoother process operations but also streamlines energy-efficient techniques such as liquid–liquid extraction and distillation. Moreover, a well-chosen solvent contributes to improved sustainability metrics, including superior *E*-factor values or reduced process mass intensity. This is achieved by optimizing the selectivity of HMF or furfural during the reaction stage, enhancing their separation efficacy during extraction, and minimizing energy consumption during purification.

In addition, solvents that can be used in various processes, such as biomass pretreatment and the production of HMF and furfural, provide considerable advantages. Their versatility contributes to supply chain stability and improves the adaptability of chemical process design. For example, the use of a single solvent across multiple reaction units can streamline operations, reduce energy consumption, and minimize solvent and product losses. This approach enables direct use of the product in its solvent medium for subsequent reactions without the need for intermediate separation, thereby optimizing resource efficiency. Furthermore, the integration of such a continuous chemical process can eliminate the additional costs associated with separation equipment, contributing to improved economic and environmental sustainability of the overall production system.

Numerous solvents have been explored and applied in studies related to furfural and HMF. This review paper places strong emphasis on identifying environmentally sustainable and greener alternatives among these options, given that the solvent selection greatly impacts the environmental and economic aspects of the process, both directly and indirectly. Significant strides have been made through extensive research into green solvents, marking notable advancements in this field. Prominent frameworks frequently referenced include the Conductor-like Screening Model for Real Solvents (COSMO-RS),[170,171] the CHEM21 guide,[172] and the GSK guide,[173–175] all of which align with Green Chemistry principles. The CHEM21 guide and GSK guide offer thorough evaluations encompassing health, safety, and environmental considerations, but tend to emphasize the impacts of the solvent itself rather than the impacts of the solvent's manufacture. Thus a good score in CHEM21 does not guarantee a relatively benign life cycle. COSMO-RS facilitates predictions about solvent extraction efficiency using molecular-level parameters like structural features, molecular affinities, and dissolution properties.

Table 3 presents a selection of solvents that are considered relatively green, safe, and less toxic for HMF and furfural synthesis, as well as biomass pretreatment, based on these screening solvent studies. THF is included for comparison. The ideal solvent should exhibit high performance (COSMO) and be known for its safety, low toxicity, and environmental sustainability, as defined by established frameworks such as the GSK guide and CHEM21. In addition, these solvents should possess exceptional versatility to potentially facilitate not only HMF and furfural synthesis, but also biomass pretreatment, downstream reactions for the synthesis of various other products, and their purification.

6.2 Solvents for the preparation of HMF and furfural

Historical attempts to synthesize HMF were primarily conducted in water with the aid of various minerals or organic acids as catalysts, spanning a century-long period from 1875 to 1977. Despite ongoing efforts to optimize reaction conditions such as temperature, reaction time, and starting materials, HMF yields have remained disappointingly low, with fructose typically yielding less than 50% HMF. To address this challenge, it is necessary to prioritize the development of cleaner and more efficient chemical processes. In this regard, solvents play a critical role in enabling more sustainable and environmentally friendly production of HMF, because a proper solvent can enhance HMF yields, whether from raw feedstocks or monosaccharides.

In the furfural industry, water is the primary solvent used in the traditional furfural synthesis method, specifically in industrial applications using sulfuric acid and steam. However, studies have shown that, as water is used alone as a solvent, it is challenging to increase furfural yield only by increasing the catalyst loading or the temperature. Many studies indicated that adding additional organic solvent could effectively improve the furfural yield by improving the furfural formation rate and decreasing the furfural degradation rate.[125,177,178] Therefore, a proper solvent can also promote the effective hydrolysis of raw biomass and polysaccharides.

Therefore, this section critically discusses the selected green solvents for HMF and furfural production, which allow effective cellulose and untreated lignocellulosic biomass breakdown and efficient HMF and furfural production in a one-step or multi-step (including biomass pretreatment) reaction process.

Monophasic solvent systems. The addition of water-miscible organic solvents (polar organic solvents) to water, making a monophasic solvent system (Fig. 15), can improve the selectivity and production rate of furanic compounds by affecting the solvent shell around the sugar and the catalyst.[179] These interactions between solvent and reagent result in changes in reaction rate, reaction pathway, and product distribution.[180] In this regard, the conventional practice includes the use of a monophasic system composed of water and hydrophilic solvents, including DMSO,[105,133,181–194] GVL,[20,178,195–204] THF,[198,205–218] acetone,[219–223] *n*-butanol,[133,219,224–230] and ethanol,[149,220,231,232] have been employed in HMF and furfural synthesis and can be broadly classified into two categories: protic and aprotic solvents. DESs[233,234] and ionic liquids[235–237] have also been employed in HMF and furfural synthesis due to their desirable properties such as thermal stability, non-flammability, high customizability, *etc*. Many of these solvents can form a monophase reaction medium when mixed with water or a biphasic reaction medium when salts or pressure are introduced. An aqueous blend of water with a hydrophilic solvent (particularly THF, *n*-butanol, and acetone) could generate a biphasic state

Table 3 Comparison of selected organic solvents

Solvent	GWP for solvent production (kg CO_2 eq. per kg)	Solvent production CED per kg solvent (MJ-eq.)	Health[d] ref. 175,176	Safety[d] ref. 175,176	Env.[d] ref. 175,176	Number of published papers until 2024	Cost[e] ($ per kg)	BP (°C) and product recovery	Vaporization enthalpy (kJ kg^{-1})	Water solubility [g per 100 g] at 20 °C	Comments from ref. 172, 175 and 176
THF[c]	5.2–6.5	271	6	3	3	Furfural: 40 HMF: 118	2.4–2.6	65 Distillation	450	30	Problematic
MeTHF[b]	5.6	n/a	4	3	4	Furfural: 9 HMF: 8	0.5–3.5	79 Distillation	375	14	With minor issues
MIBK[c]	3.0–4.5	64	6	7	2	Furfural: 57 HMF: 89	1.3–2.0	117 Distillation	406	2	Recommended
n-Butanol[b]	4.6	97	5	8	5	Furfural: 8 HMF: 8	1.7–2.7	118 Distillation	581	6.3	Recommended
GVL[a]	3.5	25	n/a	n/a	n/a	Furfural: 63 HMF: 49	2.6	207 Distillation	548	Miscible	Problematic
DMSO[c]	1.2–1.3	n/a	7	2	5	Furfural: 25 HMF: 179	1.5–3.5	189 Extraction and distillation	665	25.3	Problematic
[TEA][HSO_4][a]	0.1	0.17	n/a	n/a	n/a	Furfural: 5 HMF: 5	1.1–1.2	91 Extraction and distillation	n/a	Miscible	n/a
[Bmim][Cl][b]	6.4	n/a	n/a	n/a	n/a	Furfural: 8 HMF: 86	26.0–30.0	n.a. Extraction and distillation	1380	Miscible	Problematic
Ethyl acetate[c]	1.3–2.7	96	8	4	4	Furfural: 3 HMF: 17	0.4–0.9	84 Distillation	352	3.3	Recommended
Ethanol[c]	0.4–2.1	50	8	6	3	Furfural: 7 HMF: 4	0.9	79 Distillation	841	Miscible	With minor issues
Acetonec	1.39–2.81	74.6	8	4	3	Furfural: 2 HMF: 5	1.2	56 Distillation	539	Miscible	With minor issues
ChCl-based DESs[b]	1.62–4.30	n/a	n/a	n/a	n/a	Furfural: 29 HMF: 33	Choline chloride: 1.2	>265 Extraction and distillation	n/a	Miscible	n/a

THF as reference solvent. The related papers are published from 2012 to 2024. [a] Self-modeling based on CML2001 using Gabi. [b] Reported literature. [c] LCA data from Ecoinvent 3.1 database. [d] Solvent has health, safety (flammability/explosion and reactivity/stability), and environmental criteria (Env.) (waste, environmental impact, life cycle). Specifically, health, safety and Env. range from 0 to 10. A number below 3.5 is undesirable; a number from 3.5 to 7.5 is acceptable; and a number over 7.5 is preferred. [e] The commercial solvent price is sourced from a website (Alibaba.com) and reflects the cost of industrial bulk chemicals.

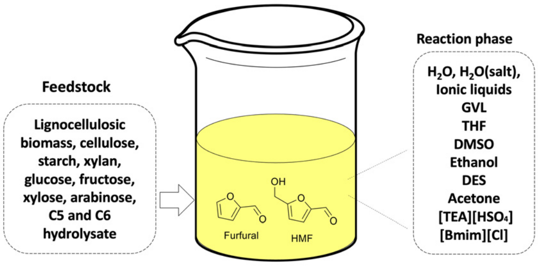

Fig. 15 Monophasic solvent system.

as a result of the addition of salts at room temperature. Such phase separation arises from the salting-out effect of kosmotropic salts.

In the realm of hydrophilic organic solvents such as DMSO and GVL, DMSO provided an encouraging reaction environment to boost HMF production and selectivity because aprotic solvents can accept hydrogen bonding, which facilitates the stabilization of transition states and products in the dehydration reaction.[210,238–240] It has been found that DMSO hinders the degradation of HMF by creating a solvation shell around the HMF, thus considerably reducing the degradation that ensues from the interaction of water with the sugar, a finding that has significant implications for the efficient synthesis of HMF.[239,241] In 1983, Musau and Munavu achieved a milestone in the synthesis of HMF by effecting its dehydration from fructose in DMSO at 150 °C for 2 h using sulfonated silica as the catalyst, which furnished the product in a remarkable 92% HMF yield.[242] Subsequently, it has come to light that the highest HMF selectivity (92%) from fructose could be obtained in DMSO without any additive or catalyst, employing microwave as a heating medium, by heating at 150 °C for 4 min, a surprising discovery that drew considerable attention.[243] With the use of a catalyst, HMF selectivity could be pushed to reach 100%. Notably, a 10% w/w proportion of SiO_2–SO_3H was used for the preparation of HMF from fructose, resulting in a 100% conversion in a microwave reactor during a 10 min interval at 150 °C in DMSO, with 100% selectivity for HMF, and the SiO_2–SO_3H could be recycled three times, adding an eco-friendly aspect to the synthesis.[244,245]

DMSO is also a representative solvent used in furfural production research. Studies indicated that DMSO may act as a catalyst in the conversion of sugar to furanic compounds through their dissociation or degradation behavior.[246,247] Notably, DMSO enables higher furfural yields by stabilizing intermediates of xylose and restraining the condensation of xylose and furfural.[248] Moreover, another study demonstrated that the conversion of xylose in DMSO was fast, and side reactions accounted for a large proportion of the feedstock.[249] For instance, Lin *et al.* conducted a comparative study effect of DMSO, dimethyl formamide (DMF), isopropanol (ISO), GVL, and γ-butyrolactone (GBL) on xylose conversion under catalyst-free conditions. Without any catalyst, the increasing order of xylose conversion in a pure solvent system is GVL < GBL < H_2O < ISO < DMF < DMSO. Remarkably, water and DMSO gave 34% and 30% furfural yield, respectively, at 180 °C in 2.5 hours. The yield of furfural could be further boosted with the aid of the catalyst. The highest furfural yield in DMSO was 53% when *p*TSA and $CrCl_3·6H_2O$ were combined in a 10 : 1 molar ratio and reacted at relatively mild reaction conditions (60 min at 120 °C).[250]

DMSO offers several advantages, such as a low selling price, and low GWP for DMSO production in the range of 1.2–1.3 kg CO_2 eq. Nevertheless, its application in the production of furanic compounds is constrained by the significant amount of energy required for the subsequent separation. Román-Leshkov and colleagues evaluated the energy requirements associated with HMF separation from MIBK and DMSO. The result demonstrated that the use of MIBK, a low boiling point solvent (116 °C), instead of DMSO, a high boiling point solvent (189 °C), led to a 10% reduction in HMF loss and a 40% decrease in energy requirement during vacuum evaporation. Given that energy savings and reductions in HMF loss have substantial economic and environmental implications for HMF industrial production, the choice of solvent significantly impacts process efficiency. Alternatively, a low-boiling-point solvent could be used as an extractive solvent to remove HMF from DMSO. For instance, Bello *et al.* reported a separation method using DCM/water (9/1) to isolate HMF (96.7%) from DMSO. It should be noted that DCM, employed in the recovery of HMF, has been identified as a primary contributor to climate change and ozone depletion, accounting for roughly 50% and 98% of the environmental impact associated with HMF production, respectively.[43] It has also been banned in the US for many applications.

Dumesic's research group first synthesized and studied GVL in the production of furfural and HMF. Analogous to DMSO, the introduction of aprotic solvents such as GVL greatly enhances the selectivity and conversion of HMF and furfural.[220] Given that GVL is an excellent solvent with good application prospects, it is widely used in the production of furanic compounds. In a study by Song *et al.*, the effect of aprotic and protic hydrophilic solvents (GVL, acetone, dioxane, methanol, and ethanol) on glucose and fructose conversion was compared in hot-compressed solvent/water mixtures (90 : 10 v : v) at varying temperatures without any catalysts or additives. The results demonstrated that the GVL/water solvent mixture led to the highest HMF yield (50%) and selectivity (69%) from fructose of all the other solvents tested. Subsequent analyses of HMF production in GVL/water mixture revealed that the highest HMF yield of 94% from glucose was reported by Zhang *et al.* using SAPO-34 as the sole catalyst at 170 °C for 40 min.[251] A GVL/water mixture was also employed in pretreatment for lignocellulosic biomass, leading to an enhanced glucose yield of nearly 80% by dissolving lignin, which was double the glucose yield obtained using water alone.

The traditional furfural industrial production methods using sulfuric acid (1 to 7.5 wt%) as the catalyst in water achieve 40 to 50% furfural yields in a "one-pot" method.

However, furfural's rapid degradation in water limits the increase in its yield. Because the stabilization of acidic protons by polar aprotic solvents (GVL) reduces the activation energy for acid-catalysed reactions, the addition of hydrophilic organic solvents (GVL) not only reduces the required amount of sulfuric acid but also increases the final yield of furfural by accelerating the dehydration rate of C_5 sugars and decreasing the rate of furfural degradation.[178] Furthermore, it was also found that GVL effectively reduced the activation energy of lignocellulose biomass hydrolysis, which provided favourable energy conditions for lignocellulose biomass hydrolysis to effectively release monosaccharides.[176] The highest furfural yield of 99.5% from raw lignocellulosic biomass corncob was obtained in GVL in the presence of 0.1 wt% sulfuric acid at 190 °C for 20 min.[114] From a technical standpoint, GVL exhibits promising potential as a solvent for biomass pretreatment and the production of furanic compounds within the context of a biorefinery setting.

These results suggest the potential of GVL as a promising solvent for HMF and furfural production, as well as biomass pretreatment. GVL emerges as an environmentally friendly and sustainable solvent. But there is unfortunately no LCA study on GVL production. To further understand GVL potential from an environmental perspective, we employed published GVL industrial-scale production Aspen simulation data to build an LCA model for GVL production.[252] Additional details are provided in the SI. The use of GVL derived from agricultural waste corncob has substantial promise for enhancing sustainability due to its carbon dioxide absorption capability during its growth stage, which contributes to the mitigation of GWP and makes GVL a more sustainable and eco-friendly solvent option. Our LCA finding reveals that GVL is like MIBK and DESs in the GWP for solvent production.

Nevertheless, it is important to acknowledge that the relatively high boiling point of GVL (207–208 °C) necessitates a greater energy input for the separation of HMF and furfural compared to low-boiling solvents like acetone. Investigations specifically targeting furfural recovery *via* distillation remain relatively scarce. Only two papers have addressed the topic thus far. Ding *et al.* reported that 80% of furfural could be recovered by distillation from GVL/H_2O.[253] Similarly, Morais *et al.* demonstrated that distillation from a DES/GVL mixture can recover 90% of the furfural.[254] Regrettably, these studies failed to provide comprehensive details concerning the energy consumption entailed in the process of furfural recovery. Therefore, future studies aimed at investigating low-energy methodologies for achieving a high recovery rate of furfural from GVL become imperative, particularly considering the growing demand for large-scale applications of GVL.

DMSO and GVL with their high boiling points have been shown to require a greater amount of energy for their subsequent separation.[255] Despite that concern, in the field of HMF and furfural production research, these solvents have so far made significant progress, enabling admirable yields. Besides, from a safety perspective, such solvents are safe for storage and transportation purposes. Thus, there is a need for further exploration and optimization of HMF and furfural separation from DMSO and GVL. In addition, research efforts should focus on identifying other alternative solvents that can reduce energy requirements while maintaining high yields of HMF and furfural.[255]

In the process of solvent selection, in addition to boiling points, the vaporization enthalpy is another important aspect that deserves consideration, as vaporization enthalpy directly influences the energy required for solvent vaporization. For instance, organic solvents, as opposed to water, have considerably lower vaporization enthalpies, although small alcohols such as ethanol and *n*-butanol exhibit higher vaporization enthalpies due to their ability to form hydrogen bonds. Aprotic solvents like MIBK, THF, MeTHF, acetone, ethyl acetate, or those with higher boiling points require less energy when they are removed by distillation or evaporation. Low vaporization enthalpy is essential to ensure an economically viable procedure.[256]

In addition, the use of protic organic solvents, including *n*-butanol, acetone, and ethanol, has exhibited promising potential in reducing the amount of catalyst required, owing to their capacity to decrease humins formation. Moreover, this approach was also associated with an average reduction in the mass of formed humins by approximately 60%. Studies have demonstrated that the incorporation of water as the solo solvent resulted in a furfural yield of 36–52%, which could be improved up to 90% by supplementing the reaction mixture with ethanol. The suppression of humins formation is due to the diminished availability of free carbocations in the presence of ethanol.[257]

From an economic and environmental perspective, ethanol also emerges as a highly advantageous solvent for industrial processes due to its cost-effectiveness, renewability, and high solubility. Moreover, ethanol possesses several environmentally friendly qualities, including low toxicity, biodegradability, low emissions, renewability, and overall sustainability. Ethanol's advantageous characteristics place it in a superior position among organic solvents, not only as a solvent for furfural and furfural derivatives but also as a co-product in biomass biorefineries.

Given that, ethanol as an alternative solvent has garnered the attention of academia and industry. Notably, the Agency for Science, Technology, and Research (A*STAR) of Singapore has led the development of a fructose dehydration process to produce HMF in a solvent mixture of ethanol and water, achieving an impressive HMF yield of 60% using HCl as the catalyst, a reaction temperature of 100 °C, and a reaction time of 4 h.[232] In a separate study, recyclable heterogeneous catalysts (Sn-beta (Si/Sn = 230) and Amberlyst-15) in an ethanol and water solvent system led to a 53% HMF yield.[232] Additionally, Novamont S.P.A., an Italian company, achieved a 93% yield with a purity of 97.6% using ethanol and THF solvents for HMF separation and purification. However, it is essential to acknowledge that ethanol's compatibility with other solutes does not come without limitations. The use of ethanol can lead to unwanted byproducts, such as ether, 2-diethoxymethylfuran or acetal, reducing overall HMF and furfural output.[257] Therefore, the development of sustainable industrial processes for HMF and furfural production in alcoholic solvents, including *n*-butanol and ethanol, requires further investigation into suppressing side reactions. Selecting the appropriate reaction conditions that maximize the production of furfural while simultaneously minimizing accompanying side reactions is significant.[258,259] Future investigations into the synthesis of HMF in ethanol should prioritize strategies to mitigate the formation of humins, a challenge extensively highlighted by Thoma *et al.* in their critical review of sustainable approaches to converting biomass into HMF.[137]

Despite being a low-cost and easily recoverable organic solvent, acetone has received surprisingly little attention, as evidenced by the limited number of publications on the subject. Pioneering studies conducted by distinguished researchers, including the investigations led by Dumesic and colleagues, have shed light on the considerable potential of acetone in HMF production. Acetone has a range of advantageous characteristics, notably its ability to decrease the activation energy required for C_6 sugar dehydration. Specifically, the activation energy for fructose dehydration in an 80 : 20 v/v acetone/water mixture was determined to be 90 kJ mol^{-1}, significantly lower than that in water (130–140 kJ mol^{-1}).[221,260] Acetone mixed with LiBr hydrate could obtain 93% of HMF yield from fructose, and 37% of HMF yield from cellulose even without catalysts.[261] A momentous achievement in the path towards the industrialization of HMF production was published by Dumesic and colleagues. HMF can be produced cost-effectively in an acetone/water mixture, with a high HMF recovery rate (96%) and purity (>99%). Remarkably, this study demonstrated the successful separation of HMF, a thermally unstable molecule, from this low-boiling solvent while maintaining high recovery and purity. These findings have significant implications for the industrial-scale production of HMF and demonstrate the remarkable potential of acetone as a solvent for HMF production, particularly when using fructose as a feedstock. The resulting HMF can be obtained at a minimum selling price (MSP) of US$1710 per ton, and further reduction in the MSP can be achieved by using glucose as a feedstock, resulting in an MSP of US$1460 per ton.[262] Published results suggest that acetone is the most commercially feasible and environmentally friendly solvent in which to produce HMF and furfural.[42,61]

Biphasic systems. As previously mentioned, water is the solvent employed in conventional methods for HMF and furfural synthesis, especially in industrial applications. However, furfural and particularly HMF are unstable in acidic aqueous solution and often react further to form by-products such as humins (water-insoluble polymeric by-products).

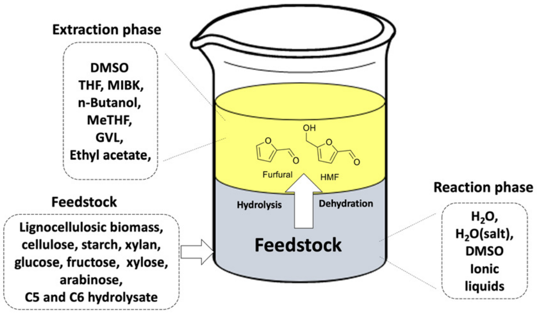

Fig. 16 Biphasic solvent system.

In 1977, a biphasic reaction system was first introduced for the synthesis of HMF, marking a significant development (Fig. 16).[263] In this system, HMF is initially formed from water-soluble C_6 sugars within the aqueous phase, and from there it partitions into the organic phase (MIBK), consequently slowing the further conversion of HMF to humins. A kinetic investigation revealed that the organic solvent in the biphasic system protects the HMF by simultaneously extracting it away from the active aqueous phase.[264] The presence of a limited quantity of organic solvent molecules within the aqueous phase additionally serves to inhibit the kinetics of unfavourable side reactions of C_6 sugar, such as fructose, *via* interaction with sugars and the active species.[264] Weingarten *et al.* reported that an 85% furfural yield could be obtained from fructose using HCl as the catalyst in a MIBK–water biphasic system, which can be compared to the 30% furfural yield that is obtained in a monophasic system (water).[265] Furthermore, another benefit of using a biphasic system is that organic solvents can be recycled and reused multiple times, and the catalyst in the aqueous reaction layer can continue to be used in the next reaction run as well.[19,119]

A diverse range of solvents have been employed as the extractive phase in a biphasic system, including THF,[266,267] *n*-butanol,[268–271] MIBK,[272] MeTHF,[106,109,264,273–278] acetone,[266,279,280] ethyl acetate,[130,281,282] and ionic liquids.[283,284] MIBK and ethyl acetate are hydrophobic solvents that can naturally establish a two-phase solvent system without the addition of salts. Conversely, the other solvents under consideration are hydrophilic and require the presence of salts to achieve phase separation. Biphasic solvent systems are frequently preferred due to their natural phase separation at room temperature. Following the reaction, the organic phase, which predominantly contains a high concentration of HMF and furfural, can be readily separated from the aqueous phase.

In the extant literature, THF, a well-studied solvent capable of generating a biphasic reaction environment by adding salts, has attracted a great deal of interest due to the advantageous partition coefficient of HMF between THF and water, cost-effectiveness, and low boiling point, all of which help to significantly reduce energy consumption and increase economic viability. In addition, the unique chemical composition and characteristics of THF have a significant impact on lignin solubilization, allowing for the fractionation of lignocellulosic biomass and the production of furanic compounds. Furthermore, the THF co-solvent exhibits excellent performance in the pretreatment of raw biomass due to its high lignin-dissolving ability, extracting lignin with a recovery rate of over

90% as a fine powder.[285] Because lignin content can be significantly decreased *via* the THF/H_2O system, it effectively mitigates the cross-condensation reaction through bond cleavage between lignin and amorphous cellulose.[286] As a result, more soluble monosaccharides were released from raw biomass, allowing their efficient use; thereby, THF/H_2O delivers good HMF and furfural yields in a one-pot method even when lignocellulosic biomass is used as the starting material without any pretreatment.[286] Sun *et al.* employed NH_2SO_3H as the catalyst and microwave heating to attain a 52% HMF yield from bamboo in THF/water.[287] Similarly, Cai *et al.* obtained a 51% HMF yield and 95% furfural yield from maple wood and a comparable yield from corn stover in THF/water, using $FeCl_3$ as the catalyst at a reaction temperature of 170 °C with conventional heating.[285]

Yang *et al.* further corroborated the feasibility of THF/H_2O as a furfural production medium by producing furfural from diverse feedstocks in a water–THF biphasic medium containing $AlCl_3·6H_2O$ and NaCl, generating high furfural yields of 75% (xylose), 64% (xylan), 55% (corn stover), 38% (pine wood), 56% (switch grass), and 64% (poplar wood).[288] Despite these benefits, comprehensive LCA studies have revealed that THF does not meet the standards for environmentally friendly solvents due to the high energy consumption required to manufacture THF and the need for large amounts of THF during the synthesis of HMF.[42,46,60] THF employment should be avoided unless significant progress is made in reducing its ecological footprint and minimizing the energy consumption associated with its production.[81]

MeTHF has emerged as a highly promising candidate to replace THF as the preferred solvent of choice for both biomass fractionation and HMF and furfural production in biorefinery applications. MeTHF exhibits chemical properties similar to THF, while its physical properties resemble toluene and MIBK.[268,289] Furthermore, MeTHF is regarded as safer than THF in terms of handling and storage. While MeTHF has a lower tendency to form peroxides compared to THF, the potential risk should not be entirely overlooked. Appropriate precautions must be taken during its handling and storage to minimize any associated risks (see Table 4).[290] Additionally, MeTHF–water demonstrates a stable biphasic system across a broad temperature range, positioning it as a highly promising solvent system for biorefinery operations, particularly concerning lignin softening processes.[291] Xu *et al.* conducted a comparative investigation involving three biphasic systems: THF/H_2O, MeTHF/H_2O, and butanol/H_2O. The research team employed a cost-effective heterogeneous catalyst, HZSM-5, and discovered that THF/H_2O and MeTHF/H_2O produced roughly equivalent HMF yields of 61% and 50%, respectively, when glucose was subjected to optimal reaction conditions of 160 °C and 90 min.[278] In another study, MeTHF exhibited praiseworthy efficiency in HMF synthesis. At 150 °C and 20 min, sulfuric acid catalyzed a reaction that produced 91% HMF in MeTHF and water.[274,277] Additionally, an unprecedentedly high HMF selectivity and yield of >90% were realized using salted diluted thick juice from sugar refining as the feedstock with H_2SO_4 as the catalyst. This feat was recorded in a biphasic MeTHF/water solvent mixture at 150 °C.[277]

Table 4 Various properties of THF and MeTHF[290]

	THF	MeTHF
Price	Low	High
Peroxide	High	Moderate
Boiling point	Low	Moderate
Flammability	High	High
Water miscibility	High	Low
Feedstock	1,4-Butanediol	Renewable resources
Acid stability	Low	Moderate

Xu *et al.* achieved an 82% furfural yield from xylose using $CrPO_2$ as a catalyst in a biphasic system consisting of MeTHF and water.[292] This study of the conversion efficiency of biphasic systems also found that MeTHF, with its wonderful xylose conversions and furfural yields, could be ranked above butanol and MIBK but slightly below DCM.[292] Some researchers have reported MeTHF as the extracting solvent in furfural production with reactive phases such as DESs and ILs.[254,293] For example, using a renewable glycine-based ionic liquid with MeTHF as the extractive phase, a 90% furfural yield was attained from sugarcane bagasse acid hydrolysates.[293]

MeTHF is a bio-derived solvent obtained through catalytic hydrogenation of furfural or levulinic acid and possesses the dual advantage of being more economically feasible and environmentally benign than THF. Notably, MeTHF has been found to effectively aid in the biomass fractionation of substrates like bamboo and birch wood as well.[289] Furthermore, MeTHF facilitates rapid phase separation, high selectivity and partition coefficient values for furanic compounds (furfural and HMF), and easy azeotropic drying at atmospheric pressure. These physical advantages reduce solvent consumption, carbon dioxide/VOC emissions, and energy consumption. Moreover, MeTHF significantly reduces the environmental footprint and production costs, as Table 3 shows. Given these advantages, several global corporations have initiated programs to replace traditional solvents with MeTHF.[294] However, despite these promising experimental results and advantages, MeTHF as a solvent in HMF production has been less well-studied than THF, and further research on this topic is necessary.

n-Butanol, known as a low boiling point solvent, has potential applications in furanic compound production in biorefinery from both an ecological and economic standpoint.[269,270] Most production of *n*-butanol is from fossil fuels, but it used to be made by fermentation of biomass. It can form a monophasic or biphasic reaction system in depending on the conditions. For example, *n*-butanol and water are completely miscible at temperatures above 125 °C. However, below that upper critical solution temperature, a miscibility gap exists.[295] 2-Butanol has also been used in a monophasic system, the highest recorded HMF yield of 99.1% from fructose was achieved using a mild reaction condition of 120 °C and 120 min in the presence of 2-butanol as the solvent. A heteropoly acid salt of an IL-forming cation functionalized with propane sulfonate as a "reaction-induced self-separating" recyclable catalyst.[225] In the biphasic system, 2-butanol, as an extraction solvent, has been found to possess a remarkable ability to achieve optimal partition coefficients for furanic compounds.[268] Román-Leshkov *et al.* used 2-butanol as the organic extraction agent for HMF production and reported an impressive HMF yield of 88% from a high fructose concentration (10 to 50 wt%) at a reaction temperature of 180 °C.[271] Moreover, a good HMF yield could also be obtained in butanol using $RuCl_3$ as the catalyst, with a high yield of 83% and selectivity of 88% in a NaCl–butanol/water biphasic system.[229]

Zhang and colleagues achieved 97% xylose conversion and 44% furfural yield in 3 h at 170 °C in the co-solvent system comprising 1-butanol and water. Additionally, their findings suggested that the ratio of 1-butanol to water could influence the furfural yield.[269] Subsequently, Enslow *et al.* looked into the effect of reaction conditions and modifiers on furfural degradation in *n*-butanol. They achieved a xylose conversion of 95% and furfural selectivity of 88% using a biphasic system of *n*-butanol and water and mild reaction conditions of 5 hours at 140 °C.[296] In a recent study, Wang *et al.* recycled the catalyst, solvent, addition, and products in a *n*-butanol/NaCl/water system in recent research. The maximum furfural yield from xylose was 78%, while the xylose conversion was 99.7% after 30 min of reaction at 180 °C using modified MCM-41. Yields from poplar and corncob were 76% and 67%, respectively. After the reaction, the organic and aqueous phases were separated. The organic phase was distilled under vacuum and at a moderate temperature (30–50 °C) to remove the *n*-butanol from the furfural. The NaCl in the aqueous phase was recovered by drying.[297] Furthermore, *n*-butanol exhibits a high capacity to remove lignin and hemicellulose, leading to improved enzymatic hydrolysis in biomass pretreatment processes. This broadens the application range of this solvent in biorefinery.

As aforementioned, the potential for acetone in industrial applications is quite substantial, but acetone reactivity may result in unwanted polymerization with furfural when employed as a monophasic solvent in conjunction with acidic, basic, or metallic catalysts.[298,299] To address this issue, the adoption of a biphasic solvent system presents a potential solution, wherein acetone is employed solely as the extractive phase through the addition of secondary solvents like DESs or water with salts such as NaCl.[279] For instance, a biphasic system comprising acetone and DES (choline chloride and EG) gave a furfural yield of 75% using $AlCl_3$ as a catalyst. Widsten *et al.* also reported that acetone and brine (35 wt% NaCl in water) biphasic solvent system yielded 62 mol% furfural, with 1% H_3PO_4 as the catalyst.[266] Furthermore, if more than 90% of the furfural were partitioned into the extractive phase (acetone), the energy required for furfural and acetone separation would be much less than the energy required for removing high boiling solvents.[280]

MIBK has been extensively studied for HMF production. MIBK (944 $ per ton (ref. 300)), a non-toxic, low-boiling renewable solvent, is comparable in price to acetone (970 $ per ton (ref. 300)) from an economic and environmental standpoint.[301] One notable advantage of MIBK lies in its inability to form peroxides, rendering it a safer alternative to ether solvents like THF. MIBK, sometimes blended with other solvents (water, DESs, and ionic liquids), has been used in many HMF syntheses that resulted in high yields.

The best HMF yield of 98.6% from fructose was achieved in a biphasic system where [BMIM][Cl] served as the reactive phase and MIBK as the extractive phase under mild conditions of 112 °C and 24 min using sulfonated wood pulp catalysts.[302] Another example with a high HMF yield of 93% from fructose was published by Desir *et al.* employing the simple catalyst HCl at 200 °C for 2 s in a MIBK/water biphasic microreactor.[303] The low boiling point of MIBK makes it an effective solvent for the separation of HMF. This is due to the ease with which HMF in the MIBK phase can be separated by vacuum evaporation or distillation, which is accompanied by solvent recovery. Studies have shown that vacuum evaporation technology can effectively separate 99.5% of MIBK and 97.5% of HMF under conditions of 13 mbar and 70 °C.[304] These results demonstrate the efficiency of MIBK as a solvent for HMF separation and the potential for its application in biomass conversion processes. The use of MIBK could thus contribute significantly to the development of sustainable and cost-effective strategies in HMF production.

Monosaccharides, polysaccharides, and lignocellulosic biomass could be effectively converted into furfural with a high yield in a mixed solvent containing MIBK. Then, furfural in the MIBK phase can be readily separated by vacuum evaporation or distillation.[304–306] Employing monosaccharides as raw materials can yield furfural with remarkable efficiency, exceeding 90% in product yield. Tao *et al.* presented an efficient and simple approach for furfural production from xylose; a high xylose conversion of 95% with a high furfural yield of 92% was achieved in only 25 min at 150 °C in a water–MIBK biphasic solvent system using a Brønsted acidic ionic liquid catalyst $[C_4SO_3Hmim][HSO_4]$[307] Moreover, lignocellulosic biomass can be used directly as a raw material for furfural production without the need for pretreatment for the feedstock. Rivas *et al.* employed MIBK as an extraction solvent and H_2SO_4 as a catalyst for the dehydration of birch hemicelluloses by two-step processing, achieving a noteworthy furfural yield of 75% from hemicellulosic saccharides that were derived from the autohydrolysis of Pinus pinaster wood.[230] Additionally, Morais *et al.* introduced a novel approach to producing furfural from lignocellulosic biomass in a biphasic system with water/MIBK/THF. Under the reaction conditions with 50 bar of initial CO_2 pressure, at 180 °C for 60 min, wheat straw-derived hemicellulose hydrolysate dehydration yielded 43 mol% of furfural with a selectivity of 44 mol%.[308]

In addition, MIBK has garnered attention for its use as a pretreatment solvent, aimed at enhancing the enzymatic digestibility of biomass. In detail, the pretreatment process involves the removal of hemicellulose and lignin from the cell wall, followed by enzymatic saccharification of the cellulose-rich solid residue. Following the filtration step, which separates the solid and liquid fractions, the pretreatment liquid is mixed with water, thereby leading to the phase separation and recovery of lignin-rich MIBK from the aqueous alcohol solution containing hemicellulose and soluble sugars.[309] The MIBK/water system has shown practical effectiveness in the removal of hemicellulose from raw biomass without the need for additional catalysts. The creation of fermentable sugars and the production of "clean" lignin are potential benefits of this pretreatment technique using MIBK. In the context of biorefinery, MIBK's unique properties give it versatility as a solvent in a variety of processes, including biomass pretreatment and furfural synthesis.[289,310]

Ethyl acetate has been identified as a promising solvent for HMF and furfural extraction from aqueous solutions owing to its remarkable performance. The addition of ethyl acetate as an extractive phase, either before or after the reaction, has been shown to effectively enhance the equilibrium yield of HMF, especially at high initial feedstock concentrations.[282] This property of ethyl acetate allows for the reduction of the required solvent quantity and a decrease in energy demand during the purification.

Sulfonated carbon–titanium dioxide composite nanofiber tube catalysts have also demonstrated excellent performance in preparing HMF using fructose, glucose, and cellulose as raw materials, with a good yield of 76% under a mild reaction condition of 150 °C and 180 min in an aqueous/ethyl acetate biphasic solution.[311] At a very low temperature of 65 °C, a biphasic acetone–water/ethyl acetate medium gave a high HMF yield of 50% using a mordenite catalyst for 9 h.[130] Additionally, the incorporation of ethyl acetate in the HMF industry confers multiple benefits, including cost-effectiveness, reduced emissions of greenhouse gases, and low boiling point. The use of a minimal quantity of ethyl acetate for HMF separation leads to decreased energy consumption during the purification of the concentrated HMF solution, thus resulting in reduced HMF production costs.[50] Notably, ethyl acetate has also demonstrated efficacy in the purification and separation of HMF, yielding HMF crystals with a purity of 95%.[281]

Trimble *et al.* have conducted a pioneering investigation exploring the feasibility of furfural extraction from aqueous solutions using ethyl acetate as a steam-saving alternative to azeotropic distillation.[312] Importantly, the superior stability of furans, including furfural and HMF, in ethyl acetate constitutes a significant economic advantage in downstream separation processes.[279] Due to its propensity for hydrolysis under acidic and aqueous conditions at elevated temperatures, ethyl acetate typically serves as an extractive medium after the reaction.[279] For instance, Zhang *et al.* have reported a remarkable furfural yield of 94% from xylan obtained by $H_3PW_{12}O_{40}$ at 160 °C in [BMIM][Cl], with ethyl acetate employed as the extractant for furfural from [BMIM][Cl].[313]

The solubility of lignin in ethyl acetate has been investigated, and it has been found that a mixture of ethyl acetate, ethanol, and water can result in 59% lignin recovery, 44% xylose yield, and 85% glucose enzymatic yield. These results demonstrate the effectiveness of ethyl acetate not only as a solvent for the production and purification of HMF but also in the process of biomass pretreatment. The implications are profound, as they highlight the potential of ethyl acetate as a versatile and valuable solvent capable of finding diverse applications in the biorefinery context.[314] However, it has been acknowledged that ethyl acetate's solvent recovery and recycling would be affected by its vulnerability to hydrolysis in acidic environments; therefore, it is crucial to take this characteristic into account for its effective use in biorefinery operations.

Aside from water and the organic solvents mentioned above as a reaction phase, ionic liquids and DESs could be applied for HMF and furfural production as a reaction phase in either a biphasic or a monophasic system. The reactive phase (ionic liquids and DESs), containing HMF and/or furfural, could be extracted in real-time or post-reaction using organic solvents. The use of ionic liquids and DESs in biomass conversion processes offers a multitude of advantages, including low vapor pressure, thermal stability, recyclability, and designability. Furthermore, their chemical properties can be tailored by manipulating the anion and cation components, thereby meeting the needs of experiments.

The use of ionic liquids in the catalytic dehydration of fructose, glucose, and other biomass sources into HMF has a rich research history dating back to 1983.[283,284] Ionic liquids have been found to effectively hydrolyze polysaccharides into monosaccharides, which are subsequently converted to HMF in a one-pot synthesis.[315] Ionic liquids consist of anions and cations that interact with the hydroxyl group of cellulose to cleave the α- and β-1,4-glycosidic bonds. The anion interacts with the proton of the hydroxyl group, while the cation interacts with the oxygen of the hydroxyl group, thus facilitating the cleavage of both the intramolecular and intermolecular hydrogen bonds of cellulose.[316] Notably, ionic liquids have demonstrated good selectivity for HMF in the presence of metal chlorides or acidic catalysts.[317] For instance, Zhang *et al.* have achieved HMF yields of 62% and 52% from cellulose and pine wood, respectively, in [BMIM][Cl] using $AlCl_3$ highlighting the effectiveness of ionic liquids in the catalytic dehydration of polysaccharides and raw biomass sources to HMF.[316]

[Bmim][Cl] is also a commonly used ionic liquid for furfural production. Zhang *et al.* have widely studied the potential of this solvent for furfural production from monosaccharides (xylose and arabinose), polysaccharides (xylan), and raw lignocellulosic biomass (corncob, grass, and pine) using homogeneous catalysts ($AlCl_3$) and heterogeneous catalysts (Amberlyst-5 and NKC-9). The highest furfural yield of 94% was obtained from xylan using $H_3PW_{12}O_{40}$ catalyst at 160 °C for 10 min in [Bmim][Cl]. When corncob, grass, and pine were used as the feedstock, the furfural yields were 12–27% over different solid acids. In addition, the [Bmim][Cl] could be recycled and reused after ethyl acetate extracted most of the furfural from the [Bmim][Cl] mixture.[313]

Nevertheless, the adoption of ionic liquids, as mentioned, has been hindered by their higher cost and potential environmental impacts, thus limiting their industrial applicability when compared to the aforementioned organic solvents. For example, a comparative LCA between toluene and [Bmim][Cl] shows that the environmental impact of producing [Bmim][Cl] is approximately 2 to 100 times higher than that of toluene across all assessed environmental categories. This difference is especially large in categories such as terrestrial, freshwater aquatic, human, and marine aquatic ecotoxicity potential.[318,319] Despite the hindrances posed by the relatively higher cost of ionic liquids compared to organic solvents and the associated environmental concerns, it is important not to overlook the significant potential that ionic liquids hold as a viable option. Ongoing research and advancements in ionic liquid technology are continuously addressing the challenges associated with cost and environmental concerns, presenting opportunities for the broader use of ionic liquids in the pursuit of sustainable and economically viable strategies for large-scale HMF production.

Considerable attention has been directed towards the exploration of new alternatives, focusing on new ionic liquids, or DESs, that offer greater affordability and greener profiles. For instance, Hallett *et al.* pointed out that acidic ionic liquids (AILES) are potentially more efficient and cheaper than ordinary ones. AILES could be used as a solvent and a catalyst, often called a bifunctional ionic liquid.[320,321] For instance, Gschwend *et al.* pretreated miscanthus in triethylammonium hydrogen sulfate ([TEA][HSO_4]) at 120 °C for 24 h to obtain 40% furfural without any additional catalyst.[322] Importantly, [TEA][HSO_4] proves to be an economically viable and environmentally friendly solvent. Aspen HYSYS modeling estimates a minimum commodity price of $1.24 per kg.[322,323] Its price is close to the industrial selling price of organic solvents such as acetone and toluene and 40–70 times lower than the common ionic liquid commodity prices ($40–81 per kg).[322,323] Additionally, an LCA of [TEA][HSO_4] production showed that in terms of human health, ecosystem quality, and resource availability, [TEA][HSO_4] is equivalent to acetone.[324]

As ionic liquid equivalents, DESs have received more attention than ionic liquids on furanic compound production topics and biomass pretreatment. Many review papers have been published about DESs for furanic compound production and biomass fractionation.[325–329] The unique characteristics of DESs are garnering attention in the scientific community. Not only do they share the same advantages as ionic liquids in terms of application-specific tunability, designability, nonflammability, various viscosities, low vapor pressure, safe transportation, and thermal stability, but they also effectively address the issues of cost, purification, and biocompatibility, as highlighted in previous studies.[177] DESs are economical and straightforward to synthesize, requiring only a mild temperature and a specific duration for mixing two or more components. In addition, most raw materials used for the synthesis of DESs can be derived from biomass, except for urea and thiourea, which are traditionally sourced from petroleum-based feedstocks. The synthesis process for DESs is relatively straightforward, often eliminating the need for complex multistep procedures, extensive separations, or the use of additional organic solvents.

DESs have emerged as notable liquid mixtures comprising two or three compounds that form a liquid state below 373 K. These compounds can be classified into two categories: hydrogen-bond acceptors (HBA) such as quaternary ammonium salts with amides and carboxylic acids, and hydrogen-bond donors (HBD) such as urea, thiourea, glycerol, or oxalic acids.[326,327,329] Among the diverse range of DESs, choline chloride (ChCl) and urea have garnered significant attention as environmentally benign DES components. ChCl-based DESs can be obtained by mixing EG, glycerol, lactic acid, and glutaric acid.[177] Four representative ChCl-based DESs (ChCl with EG, ChCl: glycerol, ChCl: citric acid, and ChCl: glucose) and reline DES were evaluated using LCA. This LCA study revealed that, in general, the studied DESs have lower environmental impacts than DCM and ethyl acetate but higher impacts than methanol and ethanol. Among the four studied ChCl-based DESs, ChCl/citric acid DES had the highest environmental impacts due to the high-water consumption and greenhouse gas emissions caused by fermentation to synthesize the citric acid.[330]

DESs can form biphasic systems when mixed with organic solvents listed in Table 3, such as MIBK, acetone, ethyl acetate, MeTHF, THF, DMSO, and GVL, for HMF production. A notable example of this is the use of an ultra-low sulfuric acid loading at 190 °C for 10 min in a ChCl–H_2O–acetone solution with a mass ratio of 1 : 2 : 3, resulting in a competitive HMF yield of 73%.[331] Additionally, Zuo *et al.* reported that noteworthy HMF yields of 55–65% were obtained from various feedstocks from monosaccharides (glucose), polysaccharides (starch), food waste (rice waste), and food waste (bread waste) at 130 °C in the DES/MIBK biphasic system.[332] Interestingly, the mixture of DES and isopropanol was found to be the most effective solvent system for the conversion of fructose into HMF catalyzed by [HNMP]Cl with an HMF yield of up to 89% after 3 h of reaction at 25 °C.[333]

Furthermore, a ChCl/MIBK biphasic system was able to achieve effective biomass fractionation and furfural production in a one-step reaction, yielding up to 84% furfural while preserving over 90% of the cellulose pulp, which can subsequently be hydrolyzed into glucose.[334] Wang *et al.* received a 70% yield of furfural from *Eucalyptus urophydis* under the best conditions (at 140 °C for 90 min) in DES (choline chloride–oxalic acid)/MIBK biphasic system using the $AlCl_3$-catalyzed reaction.[233]

Notably, DESs demonstrate multifunctionality, serving not only as Brønsted acid catalysts and solvents in HMF and furfural production but also as pretreatment solvents for lignin extraction and facilitators of saccharification enhancement. Significant removal of hemicellulose (100%) and lignin (91%) was achieved in DESs using Eucalyptus as feedstock under the optimized conditions (150 °C, 30 min, 0.2 M $Al_2(SO_4)_3$, 0.075 M H_2SO_4), further highlighting the versatility and potential of DESs in biomass pretreatment and biorefinery.[335] At a similar loading of acid, over 70% of lignin can be removed in organic solvents (methanol, ethanol, acetone, acetic acid, THF, MIBK, ethyl acetate, MeTHF, *n*-butanol, GVL at 120–220 °C), ionic liquids (at 50–130 °C) and DESs (at 70–150 °C) compared to 20% lignin removal in the aqueous phase with dilute acids (such as sulfuric acid, 180 °C).[289,310] More details were shown for pretreatment reaction conditions using the aforementioned solvents in the review papers from ref. 335–350.

DESs were used as agents for both raw biomass pretreatment and furanic compound production. DESs first segregated raw biomass under particular reaction conditions, and then the reacted mixture comprising released monosaccharides could be efficiently transformed into furanic chemicals with the addition of additional catalysts. In this two-step process, cellulose, xylan, and cellulose were isolated and ready for use in further high-value product manufacture.[289,310]

The viability of DESs integrated in a biorefinery for the one-step or two-step production of furfural and other products from switchgrass was studied by Zang *et al.*[351] and Chen *et al.*[352] Zang and colleagues analyzed the economic performance of a reaction system in which the ChCl functioned as the reaction medium for biomass pretreatment and hemicellulose conversion, while MIBK was used as the organic phase for the extraction of furfural. This analysis specifically investigated the feasibility of using a biphasic solvent mixture consisting of ChCl and MIBK, with sulfuric acid as a catalyst, to establish an integrated biorefinery for the simultaneous production of furfural (18%), lignin (16%), and ethanol (15%) from switchgrass with roughly 49% of total carbon. The minimum furfural selling price was $625 per ton, which is about 37% lower than the furfural market price. The sensitivity analysis highlighted the significance of technical parameters, such as reaction temperature and solid loading, in influencing the minimum selling price of furfural, as opposed to economic factors like material and installation costs. To enhance the economic performance of the process, it is crucial to minimize ChCl consumption, increase solid loading during pretreatment, and enhance the ChCl recycle ratio. These findings have important implications for the development and optimization of cost-effective and sustainable DES-based biorefinery processes.[351] Chen and colleagues developed a two-step method that effectively maximizes the xylan and furfural production from switchgrass. Initially, a ChCl : EG pretreatment was implemented, creating an acidic environment to facilitate the dissolution of xylan from switchgrass. Remarkably, this approach results in a xylan recovery rate of up to 94%. Subsequently, a 1.5% concentration of $AlCl_3$ is introduced to the ChCl : EG system, catalysing the conversion of xylan into platform chemicals and giving an overall furfural yield of 91–92%. To efficiently extract the produced furfural, the addition of MIBK as an extractive phase was employed to extract 92% of the produced furfural, while its immiscibility with the aqueous ChCl : EG phase facilitates its easy separation.[352] The recovery of MIBK from the organic phase was facilitated by its relatively low boiling point. It was suggested that the application of a low-boiling solvent system such as MIBK and acetone is energetically more advantageous, provided that more furfural can be removed from DESs using less extraction solvent.[352,353]

The reusability of DESs in biomass processing is an important factor in their practical implementation. The ability to reuse DESs not only holds the potential to significantly reduce the cost associated with biomass conversion processes but also contributes to minimizing their environmental impact, thereby rendering them more sustainable and economically viable options. ChCl, in particular, has exhibited good recyclability and reusability with minimal degradation even after multiple uses. Chen *et al.* conducted a study highlighting the reusability of ChCl : Gly, which demonstrated its ability to undergo at least five additional pretreatment cycles (120 °C, 60 min) while consistently retaining its effective pretreatment capability.[354] Additionally, Mankar *et al.* reported a promising yield of HMF ranging from 71 to 83% for five consecutive recycling runs using the catalytic system ChCl: lactic acid. These significant results highlight the suitability of DESs, in particular ChCl-based DESs, for repeated application across multiple cycles while successfully maintaining their catalytic activity and selectivity.[355]

7 Discussion

Mass production of bio-based chemicals currently faces economic and environmental challenges, solving these challenges can be likened to solving a complex “multivariate equation.” This involves the careful selection of starting materials, solvents, catalysts, and process routes, all of which are interdependent and can simultaneously impact the economic and environmental performance of the synthesis. Leveraging economic and environmental factors is a critical consideration for future green technology development and industrialization of furanic compounds.

This review consolidates and categorizes recent studies on LCA and technological advances in furanic compound production. It concludes that improving the efficiency of material and energy use emerges as the key approach to enhancing the environmental and economic impacts of the final products. While general optimization efforts have predominantly aimed at maximizing product yields, it is crucial to acknowledge that optimization objectives should extend beyond just boosting yield. They must also include higher feedstock loading and enhanced efficiency in the use of solvent and catalyst. Driving resource and energy efficiency, as well as waste minimization, should be considered as one of the optimization objectives.

In addition to LCA studies, incorporating green metrics can serve as a rapid tool to enhance the sustainability and environmental friendliness of a process, particularly in early stage of technique development. However, it is crucial to emphasize that LCA should not be overlooked, even if green metrics indicate the process is potentially greener or more sustainable. LCA remains the definitive method for evaluating the overall environmental performance of a product or process. Frequently used green metrics can generally be categorized into mass-based metrics, such as the *E*-factor, atom economy, and process mass intensity (PMI), and energy-based metrics like energy intensity.[356–360] These metrics are practical tools for quickly assessing both resource and energy efficiency as well as waste generation. They allow for specific assessments, such as determining how much material is consumed per gram of product during the reaction phase and how much is used during the purification stage. A potential method is to evaluate the energy demand per gram of purified product, such as furfural or HMF, by analyzing the total electricity used during the reaction and separation phases in a lab-scale purification process to identify the most efficient furanic production approach in the early research stage. In brief, these metrics play a fundamental role in conducting preliminary analyses of material and energy efficiency within chemical processes, offering valuable insights into reaction system development, process design and process optimization.

Some strategies that can be used to increase mass use efficiency include:

1. Enhancing yield can effectively reduce the environmental impact. Notably, variations in HMF yield, ranging from 49% (worst case) to 88% (best case), resulted in emissions of 8.6 and 5.7 kg CO_2 eq. per kg HMDA, respectively.[48] Furthermore, studies have shown that if the furfural yield is increased from 45% to 55% by mass, the overall environmental impact of producing 1 ton of furfural and furfuryl alcohol will be reduced by about 13% and 11%, respectively, and their total cost will also be reduced by 5%.[164]

2. Reducing solvent loading and increasing solvent recycling rates bring about multiple simultaneous advantages. For instance, achieving recycling rates above 95% contributes to lower capital costs, reduced electricity consumption, and decreased working capital requirements.[361] However, recycle rates much higher than 95% may be challenging due to issues including solvent losses and accumulating impurities.

3. Selecting solvents with high distribution coefficients of furanic compounds relative to water as the reaction medium represents an effective strategy for improving solvent use efficiency.[362]

4. Reducing the demand for catalysts, solvents, and utilities, or focusing on boosting their recycling for catalysts, solvents, and utilities can further contribute to lowering the manufacturing cost of bio-based chemicals.

5. Co-production within biorefineries offers compelling benefits, including the maximization of value derived from biomass resources, enhanced economic viability, and improved environmental performance. For instance, the integration of value-added products derived from lignin can generate additional profits and enhance the economic feasibility of biorefinery technologies.[361,363]

As demonstrated by LCA studies, electricity consumption had the most substantial impact on the GWP in the production of furanic compounds. Therefore, it is imperative to use green electricity and improve energy efficiency in the pursuit of developing economically and environmentally sustainable processes for production and separation. The choice of energy sources used in industrial processes can significantly influence the overall environmental impact. Studies have consistently shown that shifting from fossil-based energy systems to low-carbon or renewable energy sources drastically reduces greenhouse gas emissions associated with industrial production.[52,364] Consequently, the adoption of renewable primary energy sources for electricity generation would contribute to the sustainability goals of furanic compound production. Furthermore, improving electricity efficiency is a key approach to improving environmental performance. For instance, if the advanced power consumption level (400 kWh t^{-1} furfural) replaces the power consumption (600 kWh t^{-1} furfural), the overall environmental impact of producing one tonne of furfural will further decrease by about 7%.[164]

To reduce energy use impact or increase energy efficiency, other approaches have been suggested:

1. Investigating energy-efficient approaches for the production and separation of furanic compounds, focusing on strategies like utilizing low-temperature, short-duration synthesis processes and implementing advanced energy-saving separation techniques.

2. Process intensification strategies, including the integration of reactions with *in situ* extractions, reactive extractions, reactive distillations, and microwave heating, which not only enhance material efficiency but also improve energy efficiency.

Feedstock, directly and indirectly, affects the reaction conditions, process design, and economic and environmental performance of furanic compound production. Given that, the choice of biomass should be carefully studied based on a thorough understanding of the technical perspective, and the economic and environmental impacts of using different lignocellulosic feedstocks in biorefineries to produce furanic compounds. These investigations will be urgently needed in the future study.

Among the many different feedstocks, we want to highlight the numerous benefits of using macroalgae as a new substrate for the synthesis of furanic compounds. Macroalgae offers several advantages that lignocellulosic biomass lack. To begin with, macroalgae can grow across diverse aquatic ecosystems, avoiding not only the use of agrochemicals such as pesticides and fertilizers but also extensive land use. Land-use changes can greatly influence the global carbon cycle, leading to substantial greenhouse gas emissions by altering carbon stored in soil and vegetation.[52] Notable life cycle assessment studies confirm the advantages of macroalgae for HMF production, highlighting their distinct suitability in this context.[365] Secondly, macroalgae growing in water could maintain an uninterrupted reproductive cycle throughout the year. This ensures a steady and consistent supply of feedstock. Thirdly, macroalgae have a significant carbohydrate content that ranges from 25% to 80%, and they have a structural rigidity that is greatly reduced, making them easily converted into furanic compounds. They lack lignin, which makes it unnecessary for lignin or its breakdown products to be removed. Compared to microalgae, macroalgae are much easier to remove from the water they were raised in. Fourthly, macroalgae play a wide variety of ecological roles that go beyond just serving as a source of food. They also effectively improve wastewater with a high CO_2 burden, providing a method for sequestering carbon.

A study presented that the net "cradle-to-gate" carbon emission of agar from seaweed is −1.11 $kgCO_2$ eq per kg, indicating a net positive environmental impact.[366] Carbon-negative agar could be further converted into HMF and levulinic acid using acid/alkali catalysts under hydrothermal condition, indicating the potential for macroalgae valorisation into valuable platform chemicals such as HMF.[367] Furthermore, Pereira *et al.* developed an integrated biorefinery system that utilized macroalgae *Ulva lactuca* in combination with spent coffee grounds to produce HMF alongside alternative fuel precursors. In this study, C_6 sugars were converted into HMF through hydrothermal liquefaction, achieving yields of 46.6 g kg^{-1} HMF, 78.2 g kg^{-1} biocrude, and 390 g kg^{-1} biochar under optimized conditions.[368] This finding highlights the feasibility of employing *Ulva lactuca* in an integrated HMF biorefinery system. Similarly, Mondal *et al.* proposed a detailed processing methodology using *Kappaphycus alvarezii* seaweed to produce HMF from κ-carrageenan, employing $Mg(HSO_4)_2$ as a catalyst. The process delivered calculated yields of 0.18 tons of HMF per ton of granular biomass, illustrating another viable pathway for macroalgae-based HMF production.[369] Macroalgae hold significant potential as a valuable raw biomass source for future biorefineries. However, further research is essential to advance the synthesis of furanic compounds derived from macroalgae.

The selection of solvents holds the key to advancing green production and facilitating mass and energy-efficient separation of furanic compounds, thereby playing a pivotal role in the development of sustainable and environmentally friendly production processes. The choice of solvents influences several critical aspects, including reaction kinetics, product yield, energy consumption, separation efficiency, and overall process economic and environmental performance. Low boiling-point green solvents, including MIBK, MeTHF, butanol, ethyl acetate, ethanol, and acetone, could efficiently reduce the energy required for product separation. Studies for furanic compound synthesis using other solvents other than MIBK are not yet sufficient. Green solvents with high boiling points, such as GVL and DMSO, require more energy during the post-reaction separation process. However, from a safety perspective, these solvents prove to be more suitable for storage and transportation purposes because they are not flammable or prone to vapor emissions. Importantly, extensive research on GVL and DMSO as reaction solvents has been conducted, with promising results in terms of target product yields. As a result, GVL and DMSO with effective and low-energy product separation processes would be more attractive in the manufacture of furanic chemicals in the setting of biorefineries.

Among selected green solvents, due to versatility, greenness, sustainability, recyclability, and modifiability, DESs are worthy of further investigation. The biorefinery industry may wish to use them more widely, giving DESs a prominent position in the future of biorefinery operations. DESs could function as agents for both raw biomass pretreatment and furanic compound production, or as catalysts for the production of furanic compounds. Due to their unique properties, DESs offer significant potential for developing a green and sustainable process for producing furanic compounds. The process begins with DESs fractionating raw biomass under specific reaction conditions. Following this, the biomass-derived mixture containing monosaccharides can be further transformed into furanic compounds using additional catalysts within a biphasic solvent system. Environmentally friendly, low-boiling-point solvents such as MIBK, acetone, ethyl acetate, and MeTHF could be employed as extractive solvents in this system. These biphasic solvent systems boost the production of HMF and furfural by rapidly extracting them from the reaction phase, thereby reducing their participation in side reactions. Additionally, DESs improve the stability of furanic compounds.[370] Furthermore, the use of low-boiling extraction solvents potentially facilitates an easy, mass- and energy-efficient separation and purification process for furfural and HMF. Given the significant potential for furans production in DES, it's surprising that there's a scarcity of LCA and TEA research applicable to many popular DESs that consider the implications of recyclability, extraction efficiency, and varied raw materials. As a result, the future requires a broader range of experimental studies, LCA and TEA research using DESs as solvents for pretreatment and furanic chemical manufacturing inside biorefinery frameworks.

Because they are used in very small amounts, catalysts typically have a lower environmental impact than electricity consumption and solvents. Some catalysts even achieve 100% yields of furanic compounds, demonstrating remarkable efficacy. Impressively, at high fructose concentrations (50 wt% in DMSO) for 2 h at 120 °C, Amberlyst-15, with particle sizes ranging from 0.15 to 0.053 mm, was used to facilitate an exceptional HMF yield.[148] Both homogeneous and heterogeneous catalysts play significant parts in the production of furanic compounds. However, in LCA studies, the evaluation of the influence of heterogeneous catalysts is sometimes hampered by a lack of data on their production, recycling and regeneration processes, so the environmental harm caused by those steps must be unjustifiably disregarded. Without this information, it is difficult to ascertain how green catalytic processes are. In addition, it is critical to provide relevant information in LCA studies on catalyst loadings, lifetimes, and specific compositions to examine their long-term implications thoroughly. Water, as a green and abundant solvent used in biorefinery operations, provides numerous advantages in terms of cost-effectiveness, practicality, and environmental performance. An outstanding breakthrough for the low-cost and green production of furanic compounds in water could be achieved by recyclable water-tolerant catalysts and waste-based catalysts, but it will require more attention and development. A sulfonated graphitic carbon nitride heterogeneous catalyst in the presence of glucose as the substrate and water as the solvent, for 5 h at 200 °C, gave an outstanding HMF yield of 94%. Sulfonated graphitic carbon nitride exhibits amphoteric characteristics, harbouring both Brønsted base and Brønsted acid sites.[149] Because of the presence of diverse functional groups on their surface, carbon waste-based heterogeneous catalysts such as biochar and bio-carbon-based heterogeneous catalysts created from carbon waste may offer a more viable alternative for green catalyst synthesis.

Homogeneous catalysts, that involve both inorganic and organic acids, as well as metal salt solutions, are examples of commercially available catalysts with reliable supply chains. Despite this, homogenous acids cause significant terrestrial acidification, water depletion, and metal resource depletion. Furthermore, the question of recyclability presents a new challenge for these homogeneous catalysts. In contrast to heterogeneous catalysis, homogeneous catalysis faces the challenge of evenly mixing the solvent and catalyst, which complicates catalyst recycling and product separation, increasing costs and operational inefficiencies. To address this, efforts have been directed toward developing homogeneous catalysts while being adaptable for reuse in multiphase systems. For example, biphasic systems could offer a practical solution by allowing the catalyst to remain in one phase while facilitating the extraction of products into another phase.[371] There is still a need for further LCA and TEA research to determine how many times these homogeneous catalysts can be reused and, if recycling is feasible, to evaluate the environmental and economic implications of the recycling process. Efforts should focus on avoiding high energy demands during the recycling of homogeneous catalysts, as seen with recovery boilers using for recycling cooking chemicals and generate energy in the Kraft pulp industry, which heavily impact the overall environmental performance of process and product.

Heterogeneous catalysts, on the other hand, include a wide range of solid acids, such as zeolites, modified zeolites, metallic oxides, and ion exchange resins. The use of heterogeneous acid catalysts has numerous benefits in biorefinery and chemical processes, including improved control over reaction kinetics, improved catalytic stability and reusability, and increased environmental sustainability. However, a common challenge persists in the hydrolysis of raw biomass feedstocks, which detrimentally affects the production of furanic compounds from abundant sources such as lignocellulosic biomass. To overcome this barrier, novel catalysts (MSPFR and CO_2) or supplemental pretreatment techniques could be investigated.

The recycling of solvents and catalysts holds the potential for further reducing the environmental impacts associated with HMF and furfural production. A recent LCA study by Barman *et al.* demonstrated that heterogeneous catalyst recycling can notably lower environmental impacts compared to processes that do not incorporate catalyst recovery.[53] However, it is crucial to recognize that recycling is not universally beneficial. In certain scenarios, the material and energy demands associated with the recycling process itself can be substantial, potentially offsetting the environmental advantages of the recycling process. This highlights the importance of conducting LCA studies to evaluate the trade-offs associated with solvent and catalyst recycling. Such assessments are necessary to determine whether recycling strategies contribute to net environmental benefits under specific process conditions and to guide the development of more sustainable production pathways.

The early stages (feedstock cultivation and transportation) also play a critical role in shaping the overall environmental outcomes, as demonstrated in several studies.[372–375] A LCA conducted for large-scale furfural and furfuryl alcohol production, with an annual capacity of 60 000 tons, highlighted that the feedstock production and transportation stages exerted significant environmental impacts, primarily due to the direct emissions of heavy metals, phosphates, and phosphorus associated with corncob cultivation and handling.[376] Furthermore, feedstock cultivation involves several operations, including fertilization, irrigation, sowing, land preparation, and harvesting. Among these, traditional fertilization was found to be the largest contributor to various environmental impacts, especially in categories such as ecotoxicity and GWP. Transportation of feedstock also introduces environmental burdens, including emissions of CO_2, CO, NO_x, and hydrocarbons, which are particularly relevant to GWP, acidification, eutrophication, and human toxicity indicators.[374] This holistic perspective is essential for identifying key impact drivers and potential opportunities for improving the sustainability of HMF and furfural production systems.

Research on LCA of HMF and furfural separation technologies remains relatively scarce. However, LCA studies have reported that the energy consumption associated with separation processes exceeds 50% of the total electricity use.[68] Various studied distillation techniques present minor differences in environmental performance, further emphasizing the need for a deeper investigation into emerging separation technologies and their environmental investigations.[43,65] Separation technologies such as membrane-based methods present several advantages, including lower energy consumption, a smaller footprint, and enhanced selectivity. Membrane processes, by maintaining the integrity of heat-sensitive molecules like HMF, avoid the degradation risks commonly associated with distillation, thereby enhancing both yield and purity.[377] In addition, another approach to reduce the energy used for separation and purification involves the design of reaction processes that eliminate the need for HMF and furfural separation. For instance, HMF can be directly routed into subsequent stages along with the solvent, thus avoiding the losses typically incurred during traditional separation and purification steps. This approach not only reduces the loss of HMF yield but also does not demand additional energy, offering a more sustainable solution for industrial applications while minimizing environmental impacts.[63]

A promising strategy for accelerating the industrial-scale production of furanic compounds involves integrating their production into newly established biorefineries or existing industrial infrastructures, such as sugar mills and pulp mills. For instance, the conversion of existing sugar mills into versatile biorefineries capable of producing a diverse range of products including food, biochemicals, and energy has enormous potential for fostering a paradigm shift towards a more sustainable industrial landscape in South Africa.[378] This approach offers notable advantages, including reduced capital investment requirements and minimized environmental impacts. Furthermore, the Canadian and Nordic forestry sectors have faced a consistent downturn over the past decades, with sawmills and paper mills enduring the majority of recent closures. However, the development of new biorefineries has opened opportunities to recover lost production capacity and revitalize the industry.

8 Conclusions and perspectives

In conclusion, with the increasing needs for sustainable biorefinery development, production of furfural and HMF in biorefinery context requires further research. The research need for furfural would be leveraging economic and environmental performance and upgrading to high-value biobased products either in a stand-alone plant or in a biorefinery plant. In contrast, HMF production still needs to overcome the economic barriers to before its commercialization.

In this review, we have concluded that the choice of feedstock and solvent determine whether the process will be sustainable and economic, because they directly and indirectly determine the deployment of the process, equipment selection, energy requirements, solvent and chemical recyclability, transportation distance, feedstock availability, energy efficiency and mass efficiency. Therefore, thoughtful selection of feedstock and solvent will be the first and key step for furfural and HMF economic and green production. Some essential approaches have the potential to improve the environmental and economic aspects of furanic chemical production. These approaches include a lower *E*-factor or higher PMI, shorter transportation distances, the use of more energy-efficient and milder reaction and separation conditions, improvement of solvent and catalyst recyclability, *etc*. These parameters have had a favourable impact on the overall performance of furanic compound production by lowering energy requirements, resulting in better environmental and economic outcomes. Notably, using energy-efficient and less harsh reaction conditions in furanic chemical synthesis reduces energy consumption, expenses, and GHGs. It is important to stress, however, that recommendations for improvement should be based on a comprehensive study of each instance using LCA and TEA approaches.

Furthermore, conventional LCA and TEA were used primarily to evaluate established technologies. However, conducting LCA and TEA at early stages with a Technology Readiness Level (TRL) of 1 to 2 allows for greater flexibility in optimizing innovative techniques in terms of environmental and economic performance. The outcomes of these studies can directly support decision-making aimed at reducing environmental and economic impacts, then fostering more sustainable and cost-effective chemical production practices. As a result, the growth of *ex-ante* LCA and TEA approaches is as a critical research avenue for efficiently assessing the potential life cycle environmental and economic implications of furanic chemical synthesis technologies during their development stage. *Ex-ante* LCA and TEA comprise estimating energy consumption, input–output material data, various costs after the industrialization of new technologies, using mathematical models that include reaction processes, chemical process simulations, artificial intelligence, and other computer approaches. Simulated process design has proven to be very useful to fill in the data gaps for technology with TRLs below 5 but higher than 2–3.[49] This method combines upstream and downstream data from industrial chains, making it easier to identify and analyze potential environmental and economic impact hotspots. The resulting conclusions provide invaluable insights and recommendations, as well as green and cost-effective guidelines for future experimental attempts and process design efforts.[369–383]

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Supplementary information (SI) is available, it contains the life cycle inventory (LCI) of [TEA][HSO_4] and GVL production. See DOI: https://doi.org/10.1039/d5gc03729h.

Acknowledgements

This research is supported by Shenzhen Science and Technology Program (No. KCXFZ20211020172542001).

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