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ARTICLE

Production of HMF, FDCA and their derived products: a review of life cycle assessment (LCA) and techno-economic analysis (TEA) studies.

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The chemical industry is increasingly looking to develop bio-based alternatives to petroleum-based platform chemicals, in order to reduce dependence on diminishing fossil resources and to decrease GHG emissions. 5-hydroxymethylfurfural (HMF) and 2,5-furandicarboxylic acid (FDCA) are two examples of bio-based chemicals which could allow for the synthesis of a wide range of chemicals and materials, particularly polymers, from renewable feedstocks. This review paper summarises and critically evaluates results from existing life cycle assessment (LCA) and technoeconomic analysis (TEA) studies of HMF and FDCA synthesis and, by doing this, provides several points of advice for future investigations and assessments of synthetic routes towards these bio-based products. Chemical considerations such as choice of solvent system, catalyst and energy production are reviewed; and methodological issues in LCA, such as treatment of biogenic carbon and allocation methods, are discussed. Overall, results suggest that the production of HMF and FDCA-based products may offer lower impacts from CO_2 emissions than their fossil-based counterparts, but this often comes with an increase in environmental impacts in other impacts categories. Higher operating costs from expensive fructose feedstocks and high energy demands also make HMF and FDCA less economically viable than current chemicals. Moving forwards, further investigation into different lignocellulosic feedstocks, energy production units and the development of new catalytic systems may help in making HMF and FDCA production more favourable than the production of fossil-based counterparts.

1. Introduction

The production of chemicals directly consumes around 10% of our oil and gas resources.[1] This is likely to double to 20% by 2040, as the demands of the chemical industry are set to increase more than any other sector.[1] The chemical sector is also the second largest contributor to industrial greenhouse gas (GHG) emissions; contributing around 16%.[2,3] It is of global interest, therefore, that the chemical industry decreases its reliance on the diminishing stock of fossil resources and that something is done to reduce the impacts of chemical production on the environment. Over the last few decades, a decrease in environmental impacts has come from the implementation of 'best practice technologies', followed by a string of incremental improvements to industrial chemical processes. However, 'game changing' technologies allowing us to replace fossil-derived chemicals with chemicals obtained from renewable biomass are now seen as a route to ensuring the long-term sustainability of the chemical industry.[4] The search for such 'game changers' is now the focus of immense research effort.

In 2004, 2,5-furandicarboxylic acid (FDCA) was highlighted by the U.S Department of Energy (D.o.E) as one of the most promising bio-based chemicals; noting, in particular, it's potential to replace the terephthalic acid (TPA) in future polymer materials.[5] Since then, the search for a commercially viable route to FDCA has been the subject of ongoing research and investment. Now, companies such as Avantium have brought FDCA production to near-commercial scale, largely in response to the interest shown by several global companies in using FDCA-based poly(ethylene furanoate) (PEF) in the manufacture of plastic drinks bottles.[6] Aside from replacing TPA, FDCA can be used to produce succinic acid and a range of other FDCA-derivatives, for use in macrocyclic ligands, antifungal agents, pharmaceuticals and fuels.[5,7,8] The most common route to FDCA is through the oxidation of 5-hydroxymethylfurfural (HMF); which has, itself, been named as a bio-based platform chemical of the future.[9] Aside from FDCA, HMF can also be upgraded to afford a range of value-added chemicals, for use in plastic materials, pharmaceuticals, food products and fuels.[8,10–14] Together, it is hoped that commercial-scale production of HMF and FDCA will provide access to a wide range of bio-based commodity chemicals and materials. While the replacement of petroleum-derived platform chemicals with renewable alternatives is a current strategy for reducing the environmental impacts of the chemical sector, access to a range of bio-based chemicals should enable down-stream sectors (such as packaging, aerospace and construction) to develop and use more sustainable products and materials. The market for PEF alone is expected to increase in volume by 50% following its commercialisation, to reach demands of 81.9 kilotons (worth $129.3 million) – due to demand from packaging, food and construction sectors for bio-based bottles, films and fibers – however PEF production is reliant on efficient routes to HMF and FDCA.[15,16]

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In addition to developing novel routes to bio-based chemicals, the sustainable development of the chemical industry relies on its ability to quantitatively assess its use of energy and natural resources, as well as monitoring the production of waste and greenhouse gases; all of which have associated impacts on the environment. Life cycle assessment (LCA) is an assessment tool which has been developed for this purpose. When it was first established, LCA was used to quantify environmental impacts of realised systems, however LCA is now being used earlier in the development stages of new technologies in order to allow for the early identification of environmental hotspots within systems and to compare the likely impacts of emerging technologies to those of existing processes.[17] Because of its ability to guide sustainable development, LCA has been highlighted as a vital part of the plan to decarbonise the chemical industry – not only as a way of quantifying environmental impacts, but as a way of providing justification for investment into new sustainable technologies.[2] Following chemical production, other sectors may use LCA to consider impacts from product manufacturing, use and end-of-life (EOL), in order to assess how moving away from petroleum-based feedstocks may help them attain their sustainability goals. This may include monitoring impacts on human and environmental toxicity, ozone depletion, water use and air quality; as opposed to focusing solely on GHG emissions.

It must be noted, however, that assessment of the chemical industry should encompass more than just an estimation of environmental impacts; as the sustainability of a technology is also governed by its economic feasibility and potential effects on society. Just as LCA can be used to estimate and compare impacts on the environment, techno-economic analysis (TEA) has been developed as a tool to evaluate a range of economic metrics, and can be used to assess technical aspects of a system such as installation, service life and maintenance requirements, as well as estimating production costs, capital investment and payback periods.[18] Much like LCA, results may be used to highlight economic hotspots, to make comparisons between difference systems and for general decision-making. Carrying out TEA studies early on in the development of new technologies is essential in order to ensure upcoming technologies are competitive with current options and to attract industrial interest to help further the development of the technology.

Given that commercialisation of HMF and FDCA production is well underway, now is an important time to look at the available LCA and TEA studies of HMF and FDCA production, in order to best understand the role that these bio-based platform chemicals could play in the establishment of a more sustainable chemical industry. However, while there are reviews of LCA studies pertaining to bio-ethanol production[19–22], there are no publications that look at reviewing LCA studies of producing any of the other 'Top 10' bio-based platform chemicals, as identified by the U.S. D.o.E.[5] Also, current works reviewing LCA studies of bio-based polymers tend to focus on PLA, TPS, PHA and bio-PET, though no such works have been completed which look at PEF or FDCA-based polymers.[23–27] This paper will provide the first systematic review of the current range of LCA studies addressing the production of HMF, FDCA and their derived products. The review will be structured into the following sections: 1) a brief summary of the methods used to produce HMF and FDCA from various biomass feedstocks, from lab-scale to pilot-scale; 2) a summary of the current LCA studies, specifying the context of the studies and the main conclusions; 3) a summary of TEA studies; 4) a critical discussion of LCA and TEA studies, based on current methodological challenges; and 5) conclusions and outlook towards future production of HMF and FDCA.

1.1. Aims

The aim of this study is to analyse LCA studies assessing HMF and FDCA conversion routes and their derived products, while also presenting a summary of technoeconomic analysis studies, to:

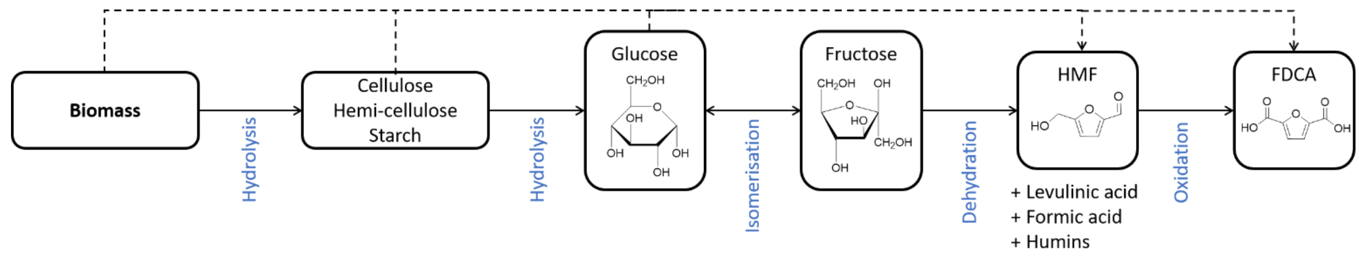
- Assess similarities and differences in terms of environmental impacts and hotspot areas, as well as economic viability and factors affecting minimum selling price.
- Highlight key methodological challenges when conducting LCA studies of FDCA and HMF production and conversion routes.
- Identify key research needs going forward in this area.

2. Routes to HMF and FDCA

While this paper will focus on the assessment of chemical systems, a brief overview of reported routes to HMF and FDCA seems appropriate. Therefore, this section will summarise notable developments in the synthesis of HMF from biomass, and its upgrading to FDCA. For a more comprehensive overview of the systems developed for the production of HMF and FDCA readers are directed to references [11,12,14,28–31] and [7,32–37], respectively.

2.1. Routes to HMF

HMF is obtained, mainly, through the dehydration of hexose sugars. Early routes to HMF involved the acid-catalysed dehydration of fructose, in aqueous solution (relying on simple mineral acids such as H_2SO_4, H_3PO_4 and HCl) (Scheme 1). Maximum HMF yields of around 50-60% were achieved, as a result of hydrolysis of HMF to levulinic acid and formic acid and HMF polymerisation reactions to afford humin by-products. Attempts to reduce these side reactions and obtain greater HMF yields have since steered the development of HMF synthesis. Strategies to increase yields of HMF have aimed to remove HMF and/or water from the reaction mixture or to stabilise HMF, through choice of solvent system. The use of organic solvents such as DMSO, DMF, DMAc and THF afforded higher HMF yields, but some papers reported difficulty in separating the product. The adoption of biphasic systems, where HMF is removed from the aqueous reaction mixture to prevent further hydrolysis has been shown to increase yield and selectivity towards HMF. Systems using water/DMSO as the reaction phase and MIBK/butanol as the extracting phase have



Scheme 1. A scheme showing the stepwise transformation of biomass to HMF and FDCA and indicating possible direct routes (dashed line).

been extensively used and have resulted in higher HMF selectivity and yields.[38]

More recent research efforts have looked at glucose as a feedstock for HMF production. Glucose is a less refined feedstock than fructose, making it both more abundant and cheaper. However, the stability of the glucose ring means that the direct dehydration of glucose to HMF typically results in lower HMF yields. As seen with fructose feedstocks, increased yields and selectivities have been obtained through the use of biphasic solvent systems and ionic liquids.[39] Some notable attempts, resulting in exceptionally high yields, come from Overton *et al*., who reported a 62% yield of HMF from a DMOS/ACN system charged with activated carbon;[40] from Z. Zhang *et al*., who achieved 86% yield of HMF from glucose using polymer-bound sulfonic acid catalysts;[41] and from L. Zhang *et al.,* who have recently reported a 93.6% HMF yield from their biphasic system utilising SAPO-34 catalyst and biomass-derived solvents.[42]

Now, attention has moved towards producing HMF directly from polysaccharides and 'real' lignocellulosic biomass, in order to avoid the energetic and monetary costs associated with biomass refinery and to take advantage of possible waste-feedstocks, which do not compete with food production.[14,43–49] Commonly-used feedstocks are corn stover, wood chips, starch, cellulose, and inulin.[11] In a similar trend to other feedstocks, higher HMF yields from lignocellulosic feedstock have come from the use of ionic liquids and complex heterogeneous catalyst systems. An exciting example has been reported by Overton *et al*. who achieved >80% yield of HMF from corn kernels, in their single-vessel system.[40] Interestingly, higher yields were reported from the more complex feedstocks than from glucose.

Moving forwards, similar challenges of HMF production exist independent of the feedstock choice. Solvent systems need to be developed which supress the side reactions that occur in water, while avoiding expensive ionic liquid solvents. Also, efficient heterogeneous catalysts need to be developed, which don't have the safety issues associated with metal chlorides and highly concentrated acids; and which allow for easy separation of products and simple reuse of the catalyst.

2.2. HMF upgrading to FDCA

Aside from its potential use as a platform chemical, much of the interest in bio-based HMF comes from its role as an intermediate in the synthesis of FDCA. As a result, a lot of attention has been given to developing increasingly efficient catalysts for high yielding FDCA synthesis, from HMF.[50] In general, the ongoing development and use of noble metal (Au, Pt, Pd and Ru) catalysts in basic solution has enabled researchers to achieve high FDCA yields while using O_2 or air as the oxidising agent – under these conditions conversion of HMF is often close to 100%.[33,37] Cheaper, transition metal catalysts (*e.g.* activated MnO_2[51,52]) and non-metal catalysts (*e.g.* nitrogen-doped nanoporous carbon[53]) have since been developed to reduce dependence on precious metals, as well as to avoid the complex removal of leached metal ions from the product stream. Solid alkali and base-free systems also promise to reduce equipment corrosion, increase safety, and reduce the high energy requirements of separation, resulting from the use of liquid alkali solutions.[37]

While these thermocatalytic methods have provided high-yielding routes to FDCA, non-thermal catalytic methods such as electro- and photocatalytic systems are now being considered as a way of reducing energy requirements, increasing safety, and obtaining high atom economy in the oxidation of HMF to FDCA.[37] Some precious metal thermocatalysts are also electrochemically active and can be used with aqueous electrolytes, generating activated oxidising species *in situ*. Taking this even further, Zhou *et al*. have shown how bifunctional Co_3O_4 nanowires can be used to oxidise HMF to FDCA and produce high-purity hydrogen in a coupled electrochemical reaction - which shows the potential of coupled system to increase energy efficiency in biomass conversion processes.[54] Recent advances in catalytic systems for HMF and FDCA synthesis have been covered in review articles.[37,55–57]

2.3. Direct routes to FDCA from sugars and polysaccharides

While much attention has been given to developing high-yielding conversion routes from HMF to FDCA, direct synthesis of FDCA from sugars and polysaccharides could allow for use of cheaper and more abundant bio-based feedstocks and eliminate energy-intensive purification and separation steps. Also, direct FDCA synthesis could decouple HMF and FDCA production, meaning the development of routes to FDCA would not be reliant on the development of efficient routes to HMF; HMF could be produced for a variety of applications but would not compete with growing demand for FDCA.

Direct routes to FDCA currently focus on "one-pot" processes, where FDCA is obtained from a reaction vessel containing the bio-based feedstock, without the need for separation or purification of reaction intermediates such as HMF or furfural.[33,36] Similar trends are seen in the development of such systems as are seen for HMF synthesis; the use of biphasic systems; ionic liquids and fructose feedstocks lead to the most favourable FDCA yields. Yields of between 29-88% have been reported for two-step routes, where HMF is synthesised and oxidised *in situ*.[58–61] Key to advancement of these one-pot processes is the development of efficient heterogeneous catalysts which can be easily removed from the reaction mixture and recycled; as most attempts have involved the removal of the initial acid catalyst, which is replaced by a metal oxidation catalyst for the second step. There are examples, however of multifunctional catalysts containing acid, basic and metal sites which have been used to obtain 64% FDCA yield from fructose.[60] Because current one-pot routes to FDCA proceed *via* HMF, research into the impact of by-products from HMF synthesis on the oxidation of HMF has also become an important area of investigation.[62]

2.4. Large-scale production

Efforts to produce FDCA on a commercial scale are currently being led by the Dutch company Avantium. After successfully demonstrating their YXY technology at pilot-scale, at their plant in the Netherlands, Avantium have received funding for a 5 kilotonne flagship plant – with production planned to start in 2023.[63] Avantium's YXY technology has been developed in partnership with BASF, Coca-Cola and Danone and involves the dehydration of fructose feedstocks to methoxymethyl furfural – a stable ester derivative of HMF - which is then purified and oxidised to FDCA.[7,64] The scale-up of the YXY technology is intended to allow for the incorporation of FDCA in PEF, as well as in the production of future polyesters, polyamides and polyurethanes; coating resins, plasticisers and other chemicals – for applications in packaging materials and textiles.[6] In late 2019, Swedish-Finnish company Stora Enso announced plans for a pilot-scale FDCA plant in Belgium.[65] The company owns patents for FDCA production using heterogeneous, supported noble metal catalysts in water-aprotic organic solvent mixtures and have reported 80-99% FDCA yield from fructose feedstocks.[64] Efforts to produce FDCA on a commercial scale have also been undertaken by Novamont and Petrobras – who also utilise carbon-supported Pt catalysts.[66] Major drawbacks of these methods are the expensive catalysts and demanding reaction conditions. In 2016, AVA Biochem announced that it will also be starting production of FDCA.[67] As for HMF, Swiss company AVA Biochem are currently the world-leading producers and produce HMF on a commercial scale using their hydrothermal process from fructose feedstocks.[68]

3. Methodology

This review aims to discuss all LCA studies pertaining to the production of HMF, FDCA and chemical products derived therefrom. To find these studies, a literature search was carried out using key-word searches. The literature searches were conducted in December 2020, using SciFinder[n] and Google Scholar databases. Search terms included "life cycle assessment" and "LCA", alongside terms narrowing the search to include only reports which included HMF and/or FDCA production within the system boundaries of the study. Environmental assessments conducted using methods other than LCA were not considered. A similar search was conducted when looking for TEA studies; using the search terms 'techno-economic analysis', 'economic assessment', 'TEA' and 'economic analysis'.

4. Review results

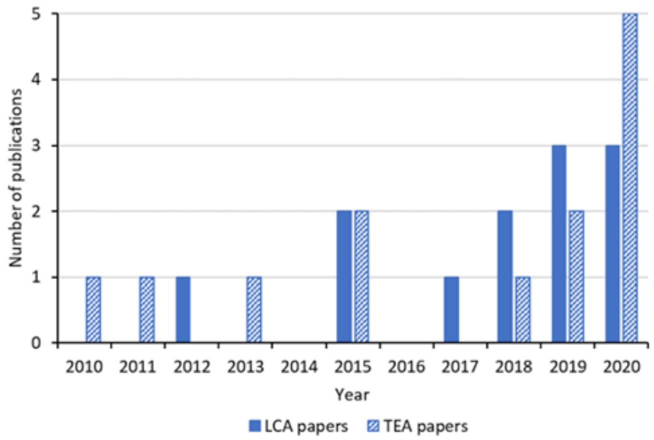
4.1. Summary of LCA studies

LCA is a scientifically accepted methodology for assessing the possible environmental impacts of a defined product or system, and is completed in accordance with standardised frameworks (ISO 14040 and ISO 14044).[69,70] While the frameworks exist to ensure consistency and transparency in the use of LCA as an assessment tool, each study is unique in its purpose and the results from each study are relative only to the specific methodology adopted by the LCA practitioner. With this in mind, the results from LCA studies can be used to recommend actions to decisions makers, highlight the most environmentally impactful areas of a system, as well as aid in the selection of relevant environmental indicators and in the declaration of environmental performance. Practically, though, LCA is an iterative process, meaning that the methodology and data used to complete the LCA may be reviewed and edited to ensure that the results provide a complete and coherent response to the specified goals of the study – although any methodological choices should be made transparent when communicating the results.

Although HMF and FDCA were identified as promising bio-based chemicals just after the turn of the century, the first study found appeared in 2010; and the majority of research in this area has been published within the last 3 years (Figure 1a). A quick survey of these papers highlights how half of the works focus on the production of HMF- and FDCA-derived products (*e.g.* polymers and speciality monomers), rather than the platform chemicals themselves (Figure 1b). While this shows increasing interest in the use and application of HMF and FDCA, studies addressing the development of routes specifically to the bio-based platform chemicals are missing - namely investigations focusing on HMF synthesis and direct routes from lignocellulosic feedstocks. Given that the current industrialisation of HMF and FDCA production is focused on fructose feedstocks, specific studies of these routes to HMF and FDCA, including comparisons with direct routes from lignocellulosic feedstocks, are needed to allow current commercial efforts to be informed by LCA and to guide the development and implementation of the most sustainable technologies.

The following section will provide a summary of research to date, outlining the product systems studied along with the main findings of each report. Table 1 defines LCA terms which will be used throughout the review, and LCA publications considered by this review, are given in Table 2.

a)



b)

		Product		
		HMF	FDCA	Other derived products
Feedstock	Lignocellulosic biomass	1	-	-
	Cellulose	-	2	-
	Starch	-	-	-
	Glucose	-	1	-
	Fructose/HFCS	-	1	6
	HMF	-	1	-

Figure 1. Results of the literature search: a) a graph showing the number of relevant LCA and TEA studies published over the last decade found during the literature survey, and b) a table showing the range of products and feedstocks studied in the LCA works.

4.1.1. HMF and FDCA from fructose feedstocks

The first published LCA study to include FDCA production was provided by Eerhart *et al*., in 2012.[71] This cradle-to-grave study looked at comparing non-renewable energy use (NREU) and GHG emissions for the production of 1 tonne of PEF to those associated with PET production. Various routes to FDCA from fructose and high-fructose corn syrup (HFCS) were studied, in order to assess the different feedstocks and various reaction conditions outlined in patents from Avantium. The results concluded that PEF presents potential savings of between 43 and 51% for NREU and 46% to 54% for GHG emissions, over traditional PET – in the worst- and best-case scenarios. Interestingly, the study showed that impacts from PET production were lower than those for other bio-based polymers such as PLA, PHA and PE.

Table 1. Definitions of LCA terms used in this review (definitions taken and adapted from reference 70).

LCA term	Definition
Functional unit	Quantified performance of a product system for use as a reference unit.
System boundaries	Set of criteria specifying which unit processes are included as part of the product system.
Cradle-to-gate	Partial product life cycle, from material extraction (cradle) to production of the finished product at the factory (gate). Use and disposal phases are not included.
Cradle-to-grave	Complete product life cycle, from material extraction (cradle) through manufacture and use phases to disposal (grave).
Unit process	Smallest element considered in the LCA from which input and output data are quantified.
Product system	Collection of unit processes performing one or more defined functions, and which models the life cycle of a product.
Allocation	Partitioning the input or output flows of a process or product system between the product system under study and one or more other product systems.
Sensitivity analysis	Systematic procedures for estimating the effects of the choices made (regarding methods and data) on the outcome of a study.
Impact category	Class representing environmental issues of concern to which LCIA results may be aligned.

In 2015, Dros *et al*. published an LCA study of hexamethylenediamine (HMDA) production from HMF.[72] While this work did not investigate the synthesis of FDCA, it serves as an example of the production of commodity chemicals through the upgrading of fructose-derived HMF. In this study, two different feedstocks for HFCS production (potato and corn starch) and two different electricity mixes (France and Germany) were compared over the selected routes to HMDA. The route from potato starch with a French electricity mix showed the lowest climate change value of all the bio-based routes and came in just above the value for the traditional fossil-based system. However, results from the sensitivity analysis showed that best case HMF yields (87.7%) and the removal of the energy-intensive feedstock drying process resulted in lower climate change and NREU values than the fossil-based HMDA route – although the bio-based routes remained more impactful in the other impact categories.

Another study comes from Lin *et al*., who assessed the production of *p*-xylene (pX) from HMF *via* Diels-Alder reactions with ethylene.[73] Corn starch-derived HMF was compared to oak-derived HMF and was shown to be much more impactful, as a result of impactful corn cultivation. Most of the process impacts came from high steam requirements, although these impacts were reduced for the oak-based route as waste lignin combustion was used for energy recovery. Sensitivity analysis showed that increasing the selectivity of the corn-to-HMF step had the greatest impact. The study also provided comparisons between economic and mass allocation methods and different lignocellulosic feedstocks.

A cradle-to-gate study of an FDCA-based polymer was published by Isola *et al*., in 2017.[74] This investigation was based on the lab-scale synthesis of a photodegradable polyester consisting of fructose-derived FDCA and a phototrigger – a monomer which, when exposed to UV light, triggers the degradation of the polymer material.[75] The results showed the

Table 2. A table summarising the key features of the reviewed LCA studies.

Paper	Functional Unit	System Boundaries	Feedstock	Energy mix location(s)	Data Sources	Allocation Method	No. of impact categories reported	CO_2 Emissions
Eerhart *et al.*, **2012**.[71]	1 tonne PEF	Cradle-to-grave	Fructose and HFCS	U.S.	PlasticsEurope eco-profile, EcoInvent database, Aspen Plus simulation, literature reports, patents	Mass and economic	2	1.98-2.38 tonne CO_2 eq. per tonne PEF
Dros *et al.*, **2015**.[72]	1kg HMDA	Cradle-to-gate	HFCS	France and Germany	EcoInvent database, literature reports, patents	n/a	9	~4.7-9.9kg CO_2 eq. per kg HMDA.
Lin *et al.,* 2015.[73]	1 ton pX	Cradle-to-gate	Fructose (from corn starch and oak)	US	EcoInvent database, literature reports and U.S. LCI database.	Economic and mass	18	1.1-10.8 ton CO_2 eq. per ton pX
Lam *et al.*, **2018**.[76]	1g converted food substrate	Cradle-to-gate	Food waste	Hong Kong	EcoInvent database, literature reports, Agri-footprint, U.S. LCI database.	n/a	17	n/a
Bello *et al.*, **2019**.[77]	1kg/h FDCA	Cradle-to-gate	Glucose (from wood chips)	Spain	Aspen Plus simulation, literature reports	Economic	11	n/a
Bello *et al.*, **2020**.[78]	1kg/h FDCA	Cradle-to-gate	HMF	Spain	EcoInvent database, Aspen Plus simulation, literature reports	Economic	10	61.5-118.4 kg CO_2 eq. per kg/h FDCA
Isola *et al.*, **2017**.[74]	1g polymer	Cradle-to-gate	Fructose (from corn)	U.S.	EcoInvent database, experimental lab-scale data., Energy Information Administration, literature reports	n/a	13	53 kg CO_2 eq. per gram of polymer.
Garcia Gonzalez *et al.,* **2018**.[79]	1kg polyester	Cradle-to-gate	Fructose (from sugar beet)	Europe	EcoInvent database, primary factory data, literature reports	Economic and energy.	2	1.18 kg CO_2 eq. per kg FDCA 1.75kg CO_2 eq. per kg polyester
Warlin *et al.,* **2019**.[80]	1kg monomer	Cradle-to-gate	Fructose (from sugar beet)	Europe	EcoInvent database, literature reports	n/a	1	1.18 kg CO_2 eq. per kg monomer
Sadhukhan *et al.*, **2019**.[81]	1kg converted dry brown seaweed.	Cradle-to-gate	Fructose (from brown seaweed)	Switzerland and Great Britain	EcoInvent database, model	Mass	3	0.82 kg CO_2 eq. per kg of dry seaweed. 0.32 kg CO_2 eq. per kg FDCA
Kim *et al.*, **2020**.[82]	1kg FDCA	Cradle-to-gate	Cellulose (from wood chips)	Global	EcoInvent database, Aspen Plus simulation, literature reports	Mass	18	2.5 kg CO_2 eq. per kg FDCA.
Kim *et al.* **2020** [83]	1kg FDCA	Cradle-to-gate	Cellulose (from wood chips)	n/a	EcoInvent database, Aspen Plus simulation, literature reports	n/a	18	2.4 kg CO_2 eq. per kg FDCA.

largest contributor to environmental impacts to be the polymerisation of the two monomers, with FDCA production only contributing to between 17-30% of the impacts across the reported impact categories. Noting the reduced impacts associated with potato starch feedstocks over corn starch reported by Dros *et al.*,[72] potato starch was used to test the sensitivity of the impacts to the fructose feedstock material. This time, the potato feedstock resulted in an increase in CO_2 emissions; the authors attributed the difference to different assumptions concerning crop yield and fertiliser use.

Two additional studies of novel monomers and polymer materials come from Garcia Gonzalez *et al*.[79] and Warlin and collegues.[80] The first study covered the production of an FDCA-based polyester binder for potential use in polyurethane coatings, and compared the results of the 100% bio-based material with 75% bio-based and 100% fossil-based versions. When sugar beet derived FDCA was used as a substitute for phthalic acid, reductions of 79% and 60% were seen for GHG emissions and NREU, respectively, compared the fully fossil-based material. Similar results were reported by Warlin *et al*.; their HMF-based spirocyclic monomer showed only 54% and 24% of the GHG emissions reported for other bio-based and fossil-based monomers, respectively.

More recently, Sadhukhan *et al*. presented an LCA study which modelled the possibility of producing FDCA from fructose derived from refined seaweed feedstocks.[81] In this paper, seaweed was refined to produce sugar, protein and inorganic fractions, for upgrading to various chemical products. Compared to the other modelled routes (the production of levulinic acid, succinic acid and lactic acid), FDCA was deemed to be the most suitable chemical for production from the seaweed feedstock.

4.1.2. HMF and FDCA from glucose and other feedstocks

As research into HMF production has shifted its focus towards finding direct synthetic routes from less-refined feedstocks, LCA studies which assess the environmental impacts of these new routes have begun to emerge. In 2019, Bello *et al*. provided a study of a simulated industrial-scale facility for the production of FDCA from glucose, obtained from wood chips.[77] The study was based on a DMSO/water system with Sn-Al_2O_3 catalyst for HMF production, as reported by Kougioumtzis *et al*.,[84] and compared impacts of FDCA recovery through crystallisation and distillation methods, citing previous work done by Triebl *et al*.[85]. The results showed FDCA recovery through crystallisation to be less impactful than the distillation set-up, owing to the lower energy demand.

The first study to look at HMF synthesis directly from lignocellulosic feedstocks came from Lam *et al*. in 2018, where they compared HMF produced in water-organic solvent mixtures, using $SnCl_4$ and $AlCl_4$ catalysts, from waste food substrate such as bread, rice and kiwi fruit.[76] Interestingly, this work includes the first example of a consequential approach to LCA of HMF production; as the recorded HMF yield was used to compensate each route for the avoided impacts of 'traditional' HMF production from fructose syrups – reducing overall impacts by up to 36.86%, in the case of the least impactful scenario.

Finally, the most recent LCA studies come from Kim *et al.* and assess the production of FDCA, while incorporating the direct synthesis of HMF from wood chip-derived cellulose.[82,83] HMF was obtained at 42% yield from a THF/water system, catalysed by H_2SO_4, and converted to FDCA at 93.6% yield. Comparing the environmental impacts to TPA, FDCA proved less impactful in fossil depletion and metal depletion categories, but more impactful in the others – including climate change and ozone depletion. The main contributors to the environmental impacts were shown to be oxygen and electricity requirements, with most of the utility requirements coming from HMF production. Because of this, the study provided comparisons of the effects of different energy sources on the environmental impacts.

Overall, the LCA studies which have been conducted thus far have shown the potential of HMF and FDCA-based chemical products to reduce GHG emissions and NREU by replacing fossil-based counterparts; although these benefits often come as a trade-off to higher impacts in other areas. While most of the studies focus on the production of HMF- and FDCA-derived products, 5 of the studies focus solely on FDCA production and only one focuses specifically on the production of HMF. Moving forward, specific assessment of the production of FDCA and HMF could be useful in providing comparisons between developed routes, especially as potential applications of these bio-based platform chemicals span a wide range of chemical products and industries. LCA work should also continue to assess the growing range of lignocellulosic feedstocks and direct synthesis routes which are being explored in the literature. Keeping up with the synthetic developments is difficult, as LCA studies can take a long time to complete, however it is only by assessing the full range of synthesis options that we can be sure that the most appropriate routes to commercialisation are being selected.

4.2. Summary of TEA studies

4.2.1. HMF production

As with the reviewed LCA studies, the current TEA studies have all taken different approaches to assessing the potential economic performance of industrial-scale HMF and FDCA production (Table 3). The first TEA of HMF production was provided by Torres *et al*. in 2010, where they analysed the economics of a semi-batch, 7000 ton/year biphasic system.[86] The main take-away from this work is that the high price of the fructose feedstock dominated the results – concluding that unless the price of fructose decreased, fructose should be considered an unsuitable feedstock for HMF production, no matter how optimised the system. Another interesting result arising from this study is that replacing MIBK-butanol with THF as the extracting phase resulted in a 9% reduction in HMF cost. This was attributed to the higher partition coefficient, which indirectly lead to decreased energy demands from the extraction and purification units.

In 2011, Kazi *et al.* modelled a plant for the production of HMF from fructose.[87] A biphasic water/butanol system was used alongside HCl to afford HMF at a minimum selling price (MSP: the selling price required to reach the break-even point and make zero profit) of $1.07/kg. The authors concluded that, while this placed the selling price of HMF low enough for use as a commodity chemical, if HMF were to be used for its subsequent oxidation to FDCA then the MSP of FDCA would be too high to compete with the likes of fossil-based terephthalic acid ($0.8/kg). Sensitivity analysis showed that a large reduction in the price of HMF could come from increasing HMF yields, through the optimisation of operating conditions; production of high-value by-products and a decrease in the price of the fructose feedstock.

Results comparing the conversion of fructose and glucose to HMF, reported by Yan *et al*., showed that the cheaper glucose feedstocks afforded HMF at a lower MSP, despite the lower yields and much higher utility requirements; although in this study the difference in price between fructose and glucose feedstocks greater than in other studies.[88] This work also showed that systems optimised towards lower operational costs (from shorter reaction times) allow for a much lower MSP than routes optimised towards higher conversion of feedstock.

A rare study looking at the production of HMF from lignocellulosic biomass in a single step comes from Overton *et al*., who report an 82% yield of HMF from a single-vessel system of ACN/DMSO and activated carbon.[40] From this system, HMF was produced at a MSP of $1105/tonne – lower than the stated MSP of terephthalic acid ($1290/tonne). Optimisation of the system was seen to lower the MSP even further to an impressive $560/tonne of HMF. Just as in other studies, the

Table 3. A table showing the key features of the reviewed TEA studies.

Paper	Product	Scale of plant	Product yield	Feedstock	Result	Cost of fossil-based comparable product
Torres *et al*., **2010**.[86]	HMF	7000 ton/year	42%	Fructose	$1.97-2.16/kg [a]	$1.03/kg *p*-xylene
Kazi *et al*., **2011**.[87]	HMF	300 ton/day of fructose	87%	Fructose	$0.47-1.12/kg [b]	$0.8/kg TPA
Yan *et al*., **2020**.[88]	HMF	10,128 ton/year	70-94%	Fructose, glucose	$0.78-$1.89/kg [b]	n/a
Overton *et al*., **2019**.[40]	HMF	330,000 tonne/year	82%	Corn kernels	$0.56-1.10/kg [b]	$1.29/kg TPA
Aristizábal *et al*., **2015**.[89]	HMF	40,000 tons/year of feedstock	-	Glucose from sugar bagasse and coffee stems	$0.35-0.96/kg [a]	n/a
Triebl *et al*., **2013**.[85]	FDCA	10.5 ton/day of HMF	90%	HMF	$2.71-$4.28/kg [b]	$1.46/kg TPA
Dessbesell *et al*., **2019**.[90]	FDCA	51349 ton/year	31-37%	Starch, glucose, fructose	$1.99-2.04/kg [b]	$1.21/kg TPA
Motagamwala *et al*., **2018**.[91]	FDCA	500 ton/day of fructose	70%	Fructose	$1.44-1.64/kg [b]	$1.59/kg TPA
Dros *et al*., **2015**.[72]	HMDA	165,000 ton/year	n/a	HFCS	€1.1-7.0/kg [c]	€1.84/kg HMDA
Sadhukhan *et al*., **2020**.[81]	FDCA	1,825 ton/year	10%	Seaweed	$2.89/kg [b]	n/a
Kim *et al*., **2020**.[82]	FDCA	2000 ton/day feedstock	~40%	Wood chips	$1.13-1.52/kg [b]	$1.59/kg TPA
Kim *et al*., **2020**[83]	FDCA	2000 ton/day feedstock	~40%	Wood chips	$1.38-2.42/kg [b]	$1.59/kg TPA
Kim *et al*., **2020**[92]	FDCA	2000 ton/day feedstock	~40%	Wood chips	$1.51-1.69/kg [b]	$1.59/kg TPA

[a] minimum production cost, [b] minimum selling price (MSP), [c] full manufacturing cost

main factors affecting the profitability of the modelled production plant were feedstock cost and HMF yield.

4.2.2. Production of FDCA and other products

Lowering the selling price of HMF should allow for the commercial production of FDCA, as Triebl *et al*. showed that HMF production constitutes 54% of the operating costs of producing FDCA.[85] In their study focusing on HMF upgrading to FDCA, the Pt/ZrO_2 catalyst contributed the most to start-up costs. Changing the oxidising agent from air to pure oxygen resulted in a drop in MSP, as the change in oxygen concentration removed the need for large utility-demanding compressors, which made up a large part of the equipment and utility costs. Unlike HMF production, the FDCA yield had no effect on selling price as the lack of side reactions meant that HMF and other intermediates could be recirculated round the system, enabling effective FDCA yields of 100%. Overall, this study did not find FDCA production to be economically competitive with TPA.

HMF yields were highlighted as one of the main factors affecting selling price in a study by Dessbesell and colleagues.[90] In this work, the price of FDCA production was compared when starch, glucose and fructose were used as feedstock (priced at $350/t, $360/t and $453/t, respectively). It was shown that, despite the higher price of the feedstock, the 8% increase in HMF yield from fructose compared to glucose allowed for a lower MSP to be obtained from the more expensive feedstock. The sensitivity analysis showed that where HMF yields were lower, the selling price was increasingly responsive to changes in the price of the catalyst and other reagents. Motagamwala *et al*., showed that the MSP of FDCA from fructose can be decreased by reducing reaction times, as well as lower feedstock prices.[91]

Dros *et al*. showed that the economic feasibility of bio-based HMDA relied mainly on high prices for fossil-based feedstocks and low prices for the HFCS feedstock.[72] The case where these prices were at their extremes was the only scenario which favoured the bio-based routes, however this scenario is not likely. The base case reported manufacturing costs of 2.10-2.50 €/kg for the bio-based routes, compared to 1.84 €/kg for the fossil-based HMDA. The main factors which could lead to lower manufacturing costs were reported to be higher HMF yields and increased recycling of the more expensive reagents (*e.g.* catalysts).

Sadhukhan *et al*. assessed the possibility of producing FDCA from seaweed biorefineries.[81] Seaweed is a form of biomass feedstock which, unlike other terrestrial feedstocks such as woods, can be used to obtain inorganic and protein products alongside various carbohydrate materials. From the carbohydrate fraction obtained from seaweed, the study compares the economics involved in the production of a range of value-added commodity chemicals: FDCA, levulinic acid, succinic acid and lactic acid. When considering only the refinery of sugar products from seaweed, FDCA is produced at a cost of $2620/ton – which lies just above its stated market price of 2450 $/t. However, a hypothetical refinery where the sugar platform is combined with the extraction of protein products provided a lower selling price for FDCA: in fact, all of the chemical products became economically feasible, with FDCA being the most profitable.

Finally, Kim *et al*. have recently reported two economic studies which model the production of FDCA from lignocellulosic biomass and include the co-production of other valuable chemicals.[82,83] The routes considered involve the fractionation of birch wood into cellulose, hemicellulose, and lignin in a gamma-valerolactone (GVL)/water system. In each case, the cellulose fraction is used to synthesise HMF directly, which is subsequently upgraded to FDCA. Hemicellulose fractions are used to produce either bio-based 1,5-pentaindiol, furfural or tetrahydrofurfuryl alcohol and lignin fractions are used for on-site heat and power generation. Humins and other by-products from these reactions are converted to activated carbon, which is also sold. In both papers, the MSP of FDCA is reported to be lower than that of TPA ($1445/ton) when FDCA is produced alongside other chemicals, but the MSP increases when co-products are not considered. This shows that co-production of FDCA and other valuable chemicals is economically favourable, despite the additional production systems and reaction steps leading to greater capital and operating costs. Of all the modelled systems, coproduction of FDCA and 1,5-penaindiol afforded the lowest MSP for FDCA ($1024/ton). In each study, feedstock costs were the main contributors to operating costs while HMF reactors and CHP units contributed most to capital costs. Another work from Kim *et al.* compares FDCA produced *via* cellulose-derived glucose (using GVL/H_2O system) with FDCA derived from HMF produced *directly* from cellulose, in THF and water.[92] Despite having fewer steps, the direct routes had a greater capital cost because of the expensive reactor and lower FDCA productivity. Operating costs were greater for the glucose route because of higher heating and steam requirements, though. Overall, the glucose route provided FDCA at a lower MSP ($1366/ton *vs* $1532/ton).

In 2015, Aristizábal *et al*. also studied the economic impact of co-producing multiple high-value bio-based chemicals and various scenarios for producing ethanol, octane, nonane, furfural and HMF from a biorefinery were assessed.[89] Where more products were produced from the refinery, the production cost of HMF was lower; however, the system configured to produce only furfural and HMF was shown to be one of the more profitable. The authors also showed that the economic margin was more sensitive to the selling price of furfural/HMF than to ethanol/octane. Sugar bagasse was shown to be a more favourable feedstock for HMF production, over coffee stems, as a result of its higher cellulose content.

From these TEA studies, a few salient conclusions can be drawn. Firstly, no consensus has been reached regarding a preferred biomass feedstock. Where fructose is used as a feedstock, fructose price tends to be the main factor in determining the price of the bio-based product. Interestingly, while it is often assumed that the use of cheap, lignocellulosic feedstocks could present a way to more economical production of HMF and FDCA, some TEA studies conclude that - despite lower operating costs and fewer reaction steps – production of HMF and FDCA from lignocellulosic biomass is disfavoured because of low product yields and the need for expensive equipment. In fact, most of the studies highlight high HMF yields as one the most important factors for lowering the price of HMF production. Optimisation of processes - resulting in reduced demand for catalysts, solvents and utilities – will also continue to lower the MSP of bio-based chemicals. Other ways of improving the economics of a particular route could be to establish large refineries which focus on the co-production of several valuable bio-based products or to utilise available sources of renewable energy through on-site energy recovery.

5. Discussion

5.1. Availability and scale of LCA inventory data

One of the main challenges of conducting LCA studies of emerging technologies is the lack of sufficient data for the processes involved. The LCA studies presented in this review have relied on a mix of primary data, obtained by the LCA practitioner or provided by industry partners; or secondary data, found in LCA databases and peer-reviewed literature. However, even when inventory data is available in databases, the differences in impacts seen between the databases can be large, as shown in the work by Lin *et al*. Where data for unit processes could not be found, judgements were made. Chemicals used in minute quantities were assumed to have negligible contributions to the overall impacts and were emitted from the study.[72] Where important chemicals could not be found in databases, data was estimated.[76] However, the main source of missing data was the production of fructose feedstocks. In the fructose-based studies, data for the production of fructose and HFCS was estimated based on impact data for dextrose production; modelled using data from literature sources; or LCA data for other sugar-based production processes were used as proxy.

Another problem encountered in the LCA studies is the lack of understanding and missing data regarding the physical properties of the novel FDCA-based materials and their processing conditions. In the study by Eerhart *et al*., the authors noted that the production of PEF offered notable advantages over PET production, namely the ability to utilise lower temperatures and pressures as well as lower quantities of oxidant and solvent, to obtain a purer product. However, the early-stage of research into PEF production meant that accurate process data was not available, and these advantages were not captured in the results – instead, the process data for PET production was used as proxy. In other studies, the absence of process data for the chosen routes to HMF meant that studies often assumed 100% yield and 100% isolation of products, while catalyst lifetimes and recycling rates were also estimated. Lack of appropriate data was also a reason given for some impact categories not being reported.[72,93]

Also, some of the presented systems incorporate heat and energy recovery through combustion of the humin by-products formed during the production of HMF. As the structure of the humin by-product is not known, it had to be estimated - although different studies have assumed different humin chemical formulae ($C_{12}H_8O$[77,84]and $C_{23}H_{26}O_{12}$[71] – another study in the literature reported a formulae of $C_{17}H_{16}O_5$, $C_{52}H_{40}O_{17}$ and $C_7H_6O_3$[94]). Given that several of the studies concluded that energy and electricity demands were a main cause of process impacts, the estimations used to model these energy-recovery units introduced a significant amount of uncertainty into the studies.

Technologies which have not yet reached commercial scale also suffer from a lack of industry-scale process data. To overcome this, many of the studies have relied on process simulation software such as ASPEN Plus, to produce industrial-scale data from the data available. Despite the associated uncertainties, this approach is recommended – as this allows for preliminary comparisons between upcoming technologies and incumbent processes.[95] Where LCA studies have been conducted using lab-scale data alone, the results are unlikely to be comparable to those obtained from the scaled-up process. Comparisons between lab-scale, pilot-scale and industry-scale LCA studies have shown that general optimisation and increases in process efficiency when scaling up a process can result in a decrease in environmental impacts of >60% and >90%, when comparing lab-scale routes to pilot- and industry-scale routes, respectively.[96] However, early-stage LCA studies have been shown to successfully identify environmental hotspots within the system.[96,97]

Therefore, it is advised that, where it is appropriate, scaled-up models of novel bio-based processes should be made to allow for comparison with incumbent technologies. If this cannot be done, LCA studies of lab-scale routes may allow for the determination of environmental hotspots, but should not be compared to studies of larger-scale systems.[17] Consideration could also be given during ex-ante assessment to testing the sensitivity of lab-scale processes to optimisation of certain steps, as this could help guide the development of the technology.

In the future, solutions to the issues discussed in this section rely on sharing of process and experimental data across all relevant sectors. As more data becomes available, studies should be able to adopt functional units which allow for comparison with other systems; assess a broader range of impact categories; and extend their system boundaries past cradle-to-gate. Results from LCA studies will also become more accurate, as they will not be founded on broad assumptions.

5.2. Theoretical approach to assessing bio-based processes

How to account for the carbon stored within and released from biomass has been a source of disagreement between LCA practitioners – with many methods being developed which take into account different factors.[98–100] These various methods depend on one of two broad assumptions: carbon neutrality or carbon storage. The carbon neutrality approach assumes that the carbon emitted from a bio-based material over its lifetime will be equal to that which was sequestered from the atmosphere before the plant was harvested – resulting in no net change of atmospheric carbon. Criticisms of this approach aim to point out that carbon neutrality does not account for aspects such as the change of carbon levels in the soil and the form of the carbon which is emitted (*e.g*. the difference in impacts between CO_2 and CH_4).[101] The carbon storage approach, however, accounts for the reduction in atmospheric carbon as a result of photosynthesis. Carbon is embedded in the material and whether the impacts caused by the re-emission of this carbon are accounted for, or not, depends on the scope of the study.

This is demonstrated by Eerhart *et al*.'s cradle-to-grave study of PEF, where they mention how the adoption of either of these principles would have produced similar results.[71] This is because the system boundaries included incineration of the PEF material at end-of-life (EOL) – thus, the embedded carbon is re-emitted in both scenarios. For cradle-to-gate studies, where EOL is not considered, the methods chosen by the LCA practitioner have more of an impact on the results. As part of their sensitivity study, Dros *et al*. saw that accounting for the carbon stored within bio-based HMDA reduced the GHG emissions of the bio-based routes by around 31%.[72] This methodological choice would have dramatically changed the results of the study, as this approach largely favoured the bio-based routes over the fossil-based process. Other cradle-to-gate studies chose not to adopt either of these approaches – however attention was given to differentiating between fossil- and biogenic-carbon emissions when reporting the results.[77]

Land use change (LUC) is another factor which may be considered when modelling the use of biomass feedstocks. LUC refers to the change in the amount of carbon stored in the biosphere when land is used for different purposes.[102–104] These impacts can occur either as a direct or indirect result of LUC (dLUC and iLUC, respectively). dLUC refers to the impacts associated to the change in land use (*i.e*. deforestation to clear land for crop production) while iLUC refers to the additional land needed to accommodate any displaced crop production. The only study to consider the potential impacts of LUC was Eerhart *et al*., who estimated that accounting for iLUC caused by increased corn production could increase the results for GHG emissions by around 16%.[71] Other mentions of LUC occur only where the secondary data used in the study happened to included LUC considerations.[79] Studies of various LUC effects may help in the implementation of commercial bio-based chemical production by considering the best placement of the feedstock production processes. For example, one study found in the literature suggests that converting grassland to cropland would result in a large change to the amount of carbon in the soil, and should be avoided.[105] Other studies have clearly shown the difference that accounting for LUC can have on LCA results of bio-based polymer production.[106] By including LUC in the study, land management plans can be devised in order to mitigate potential impacts – although this would require access to relevant LUC data. Where sufficient data is not available, it may be considered best practice to differentiate between fossil- and biogenic-emissions when reporting results.

5.3. Functional unit (FU) and system boundaries (SB)

The FU is the reference output of the system to which all flows to and from the individual processes within the system are scaled. The FU is chosen based on the specific aims of the LCA work (for example, production of x amount of product or processing of x amount of material). The LCA guidelines specify that the FU should represent a performance characteristic of the system, however, in the case of novel bio-based chemicals, the system may have several potential uses or applications. For this reason, most of the studies have chosen to use a specified mass of chemical as the FU (1 g, kg or tonne) – so that the results are not dependent on any specific application of the product. Bello *et al*. adopted a more production capacity-based approach, by choosing to factor time into the FU (kg/h). Where a proposed system focused on making use of novel feedstocks, studies chose a FU based on conversion of that specific feedstock (Table 2).

The SB are set by the LCA practitioner and define which processes and flows are included as part of the product system being assessed – the SB are often shown graphically as a flow diagram encompassing all of the included unit processes. Almost all of the studies set their system boundaries as cradle-to-gate, meaning only processes between the sourcing of raw materials and the delivery of the final chemical at the factory gate were accounted for. While lack of information regarding the applications of the products meant that none of the studies considered impacts of the use stage, 2 studies included EOL options within their study.

These choices of FU and SB are non-trivial, as is it these factors which determine whether one study is comparable with another. Also, it is the FU and SB which help align the study with the intended goals. In some of the studies, the goal was to compare the impacts of the bio-based chemical with those of an incumbent material. Where this was the case, the FU and SB were chosen so that appropriate comparisons between the two technologies could be made. If production of the bio-based technology was not yet at a stage where direct comparisons could be made with established processes, a consequential approach could be taken (the system boundaries could be extended to include the impacts of replacing the incumbent processes), as done by Lam *et al*.. Else, the aim of the study could be to simply highlight environmental hotspots within the system. Where a system has several potential functions, and a single fossil-based equivalent does not exist – as with the production of HMF as a platform chemical – discussion in the literature advises that multiple functional units be used.[95] This allows for comparison between the system and several incumbent processes and may help guide the implementation of the new technology by determining which of the applications provides the greatest environmental benefits.[17] In any case, it would be desirable if FUs and SBs were selected to allow for greater comparability across studies – despite the associated uncertainties which would arise therefrom.

5.4. Energy demands and electricity mix

Around 39% of CO_2 emissions from the UK chemical sector comes from the use of grid electricity.[2] Reducing the energy demands of the chemical industry is, therefore, one of the main tactics which has been implemented in an effort to increase the sustainability of the sector.[107] However, bio-based processes, which rely on the refinement of biomass, tend to involve energy-intensive separation and evaporation steps; and the conversion to value-added chemicals typically relies on demanding process conditions (*i.e*. high temperatures and pressures).[108] It comes as no surprise, therefore, that most of the LCA studies discussed in this review highlight energy demands as one of the main contributors to environmental impacts and conclude that improvements or changes to the amount and/or type of energy used could have a large contribution towards making HMF and FDCA production less impactful on the environment.

Across the LCA studies, energy use is commonly linked to HMF yields, as lower yields increase the required process energy in relation to the functional unit. However, the sensitivity analysis conducted by Dros *et al*. has shown how the removal of energy-intensive steps (HFCS drying) allows for greater reductions in CO_2 emissions than the best case HMF yield. Also, comparisons presented in the work by Lam *et al*. highlighted how increasing temperature and reaction time leads to an increase in HMF yield – however, it is the lower yielding, less energy demanding processes which have lower environmental impacts. This suggests that electricity use is a more important factor than HMF yield, however this may be a result of using a Hong Kong electricity mix, which is heavily reliant on fossil fuels. The effects of changing geographical electricity mix was investigated by Dros *et al*., who compared the impacts of using a French electricity mix to those from a German electricity mix (which relies more on carbon-based sources of electricity generation). The fossil-reliant German mix resulted in large increases in CO_2 emissions and freshwater eutrophication. In the study by Sadhukhan *et al*., impacts for a British electricity mix were compared to a Swiss electricity mix and to a model powered solely by biogas.[81] Change of electricity mix was shown to have a massive impact, with the Swiss mix reducing impacts by 83%, 85% and 53% in the fossil fuel depletion, global warming and freshwater ecotoxicity categories, respectively. The use of local biogas contributed almost zero impacts. Similarly, Kim *et al*. showed that using electricity from renewable resources could reduce climate change and fossil depletion impacts by 21-33% and 27-30% respectively, compared to natural gas. Also, this study shows the massive reduction in energy requirements that can be achieved through heat-integration and optimisation of the system. The same was reported by Lin *et al*., who also showed that increasing stream concentrations can result in reduced heating demands, and thus impacts, of separation processes.

As the production impacts have been shown to be sensitive to electricity mix, methods for on-site electricity production have been incorporated into some of the studies. Several of the works made use of the organic by-products generated during the production of HMF, for energy recovery. The combustion of the non-sellable waste material provided electricity and steam to specified parts of the modelled systems. Dros *et al*. showed how the incorporation of energy-recovery systems within the process model can reduce climate change impacts, however it had less of an effect than scenarios testing higher HMF yields and the removal of energy-intensive processes such as HFCS drying.[72] Results from Bello and colleagues suggest that the renewable energy obtained from burning on-site waste can help to mitigate the impacts of energy-intensive steps, such as the hydrolysis of biomass and HMF production. In this study, the greatest impacts of the system came from energy-intensive processes which were not being supplied by the energy-recovery unit – these processes had a particularly large impact on fossil depletion. Similarly, Lin *et al*. showed that lignin from lignocellulosic feedstocks can also be burned for heat, reducing the need for impactful steam utilities. The results presented by Eerhart *et al.* show that the processes powered by the energy-recovery unit were the least impactful – although, in this study, emissions from the combustion of humin by-product were considered carbon neutral and were not counted in the results.[71] Interestingly, results from this work also suggest that lower product yields result in lower non-renewable energy requirements, because of the increased yield of humins. Assuming the routes have similar conversion of the feedstock, this means that routes with lower product yields have access to more renewable energy – although the paper did not report the conversions or humin yields for the scaled-up modelled processes. Similar results seem to be presented by Lin *et al*., who show that the use of higher lignin-containing bark feedstocks is less impactful than oak. This could be a result of greater renewably energy usage from the combustion of lignin for heat recovery.

In summary, high energy demands are currently one of the main sources of environmental impacts in the production of HMF and FDCA. This is a result of demanding process conditions and the use of fossil resources for electricity generation. Moving forwards, focus should be on the avoidance of energy-demanding processes; as lowering total energy demand has been highlighted as a key factor in reducing environmental impacts. Then, attention should be given to high-yielding routes to HMF, which rely on efficient catalytic system rather than high temperatures and pressures. When routes are to be commercialised, production plants should be located in countries with a low dependence on fossil-based energy. In locations where grid electricity is rich in fossil fuels, on-site valorisation of organic waste products for electricity and heat may help to mitigate impacts. Interestingly, where on-site energy production was used in the production of HMF, systems involved in the production of HMF contributed very little to the overall impacts.[71–73] This is in contrast to studies relying solely on grid electricity, where HMF production was seen to be the major contributor to the reported impact categories.[78] However, more work is needed in order to better understand how to incorporate on-site energy recovery into the system, and which processes would benefit the most by receiving energy from energy-recovery units.

5.5. Solvents and catalysts

As discussed at the start of this work, the development of routes to HMF and FDCA has relied heavily on the development of efficient catalyst and solvent systems. While the use of certain chemicals may lead to increased HMF yields, only certain chemicals and materials are deemed appropriate for use in commercial-scale processes – due to the high environmental and health impacts associated with their production and use. DCM solvent is highlighted by some of the studies as a major source of environmental impacts; contributing up to 99% of ozone depletion impacts.[74,77,78] Impacts associated to THF solvent were the reason some routes were disfavoured when compared to less-impactful acetone and DMSO, in the study be Lam *et al*..[76] In Lin *et al*.'s study, THF and ethylene contributed around 24% towards impacts, once energy-recovery units were incorporated to lower the impacts from steam. Also, by increasing sugar stream concentration, not only did they reduce energy demands but requirements of THF, HCl and NaCl decreased by 44%, 52% and 39%, respectively. Aside from LCA studies, a recent review paper incorporating screening of suitable solvents for HMF synthesis and extraction - based on environmental and chemical considerations - suggests ethyl acetate and methyl propionate as possible solvents of interest.[109]

When systems were modelled at larger-than-lab scale, the systems typically included recirculation or recycling of solvents. Dros *et al*. showed that the impacts of their system were not sensitive to solvent recycling rates and that the use of water as a solvent contributed only 0.003% to the impacts across the different scenarios.[72] In terms of reactants, acetic acid was shown to contribute around 10% to all impact categories in the study by Bello *et al*., while 'lab' reagents such as potassium permanganate and silica incurred large environmental impacts in the work by *Isola et al*..[74,78] Where bio-based alternatives can be used in place of fossil-based chemicals, a decrease in system impacts is likely.[71]

As catalysts are typically used in small quantities, the resulting impacts typically relate to the toxicity of the metals used and the environmental toll of their production: namely, towards acidification, eutrophication and ecotoxicity impact categories.[72,78] In the lab-scale process modelled by Lam *et al*., the $AlCl_4$ and $SnAl_4$ catalysts were used in relatively high amounts. As a result, the choice of catalyst had a large impact on the results. The aluminium-based catalyst showed reduced impacts compared to the tin-based catalyst, because of aluminium's higher abundance and therefore less-demanding preparation. Like solvents, catalysts are typically reused or recirculated when used in industrial processes. The impacts of the system studied by Dros *et al*. were shown to be sensitive to loss of the Ni-based catalyst – as a result of the mining activities associated with nickel.[72]

In all, the main points brought out by the reviewed studies are: 1) solvents such as DCM and THF should be avoided, 2) catalysts should be based on non-precious metals and 3) large-scale systems system should be engineered as to avoid losing catalyst and solvent from the system. It should be noted, also, that a number of catalytic systems which have been reported to give high FDCA yields (*i.e*. non-metal, photochemical and electrochemical systems) have yet to be included in LCA studies. As these technologies mature, LCA comparisons of the different types of catalytic system could provide useful results in the way of directing the development of HMF and FDCA production towards the least impactful routes.

5.6. Allocation methods

Allocation refers to the procedures used by LCA practitioners to partition the impacts of a system across all of its outputs, and is applied when multiple products are obtained from one system.[69,70] In the studies of HMF production, allocation methods have been applied to two distinct areas of the system: 1) the refinement of biomass, where several different carbohydrate fractions are obtained from the crude feedstock, and 2) HMF synthesis, where levulinic acid, formic acid, and other by-products are produced alongside the target HMF product. The specific method used for allocation depends on the underlying relationships between the products of the system. When allocating the process impacts to the various products of the system, most of the studies opted for economic allocation – where flows are partitioned based on the monetary value of the various outputs. 3 of the studies chose to use mass allocation, and 1 study focused on energy allocation (as the purpose of the sugar mill used in this study was assumed to be the production of bioethanol fuel).

While most of the studies employed economic allocation, the contribution of impacts assigned to HMF differed across the studies. Across the studies, HMF was allocated 16.4-27% of the total impacts, as some the modelled systems also produced valuable amounts of lignin or levulinic acid. Fluctuation and uncertainties in estimated market prices for HMF also meant that different market prices for HMF were used in the different studies. Eerhart *et al*. compared their results from economic allocation with those from mass allocation and saw a difference of up to 20% in the NREU and GHG emissions for 1 tonne of FDCA.[71] Lin *et al*. also showed 64-67% differences in results from the use of different allocation methods, with much lower impacts coming from mass allocation. The authors also note that economic allocation typically favours petroleum-based routes, because of the high value of other oil fractions obtained during the fractionation of crude oil. In other published studies of bio-based chemicals, huge differences have been seen for results based on different allocation methods.[110,111] It is for this reason that the ISO standards and other published reviews of LCA studies advise that early-stage LCA studies use and compare results from multiple allocation methods.[69,70,112] Until full commercialisation of HMF and FDCA production has been realised, and more stable market prices can be estimated, it is advised that LCA studies continue to compare results of different allocation methods. This approach offers the greatest transparency in results, which could be used to guide both scientific advancement and other decision making.

5.7. LCA and TEA integration

Techno-economic analysis provides an additional perspective on the sustainability of emerging bio-based material platforms, indicating minimum selling price as a comparator to incumbent technologies. Dros *et al*., Sadhukhan *et al*. and *Kim et al*. address both environmental and economic feasibility in their work, including relative uncertainties and sensitivities. However, there are differences in the ways in which catalyst use, chemical use, and wastewater treatment are accounted for in their analysis. For example, the LCA study performed by Kim *et al*. allocates all environmental impacts to FDCA, while their TEA reports a competitive MSP for FDCA by including co-production of other chemicals. It is also not clear if the same assessment time period (particularly in relation to electricity consumption) is applied across some of the TEA and LCA studies. Dros *et al*. exclude capital cost, calculating full manufacture cost only; whereas Sadhukhan *et al*. include capital costs within their calculation of Net Present Value, as do Kim *et al*. Lack of a standardised approach to TEA makes comparability between studies challenging, and differences in scope and chosen focus of any sensitivity analysis between TEA and LCA studies, carried out on the same process, mean that outcomes from one cannot be directly compared with the other in a meaningful way. This creates particular challenges when evaluating technology at an early stage of commercialisation like HMF and FDCA production, where LCA and TEA together should serve as a useful decision-support method for process design. The need for harmonisation of LCA and TEA guidelines to allow for complete and useful assessment of early-stage systems has been discussed elsewhere in the literature – in works which discuss the creation of specific LCA and TEA guidelines for assessment of carbon capture systems.[113]

6. Conclusions

HMF and FDCA are expected to be key platforms in helping the chemical industry switch from fossil-based to bio-based feedstocks. The studies included in this review have shown that the use of these intermediates in the production of polymer materials could in itself lead to reductions of GHG emissions of between 24-79%, although the widespread impacts of the technologies cannot yet be determined. Despite the mix of results obtained from comparing HMF and FDCA-based products to their fossil-based counterparts, one should feel optimistic regarding the establishment of a bio-based chemical industry. As pointed out by Kim *et al*., petroleum-based products will be forever limited by the very fact that they are derived from fossil resources, whereas the current hurdles toward the mass production of bio-based chemicals – such as low yields and high energy demands – have the potential to be overcome by technological breakthroughs in ongoing research. Environmental benefits, from improved production routes and ongoing use of LCA, will impact not only the chemical industry but other sectors looking to produce novel products and materials which are fit for purpose – that purpose being, alongside other required properties, to offer reduced life cycle impacts.

6.1. Direction for researchers and LCA practitioners

This review has aimed to collate and group the main findings discussed in current LCA and TEA studies of HMF and FDCA production to help advance the development and assessment of promising bio-based chemicals. Although direct comparisons between the studies cannot be made because of the differences in the overall methodology, our findings can be grouped into advice pertaining to synthetic chemists and engineers in order to inform the direction and methodology of ongoing and future LCA and TEA studies (Table 4). It is clear that efficient catalytic systems based non-precious metals need to be developed as a way to increase product yield and process efficiencies. LCA should also be used to assess and compare the growing range of catalytic systems being used for HMF and FDCA production. The use of aqueous or biphasic systems should also be favoured over the bulk use of organic solvents, as this eliminates energy intensive drying of feedstock and reduces the use of impactful solvents (such as DCM and THF). Consideration should also be given to system requirements as routes are scaled up, as elimination of energy-intensive processes (feedstock drying, FDCA recovery through distillation and use of gas compressors) has been shown to improve both environmental and economic performance. Large scale production should be located at sites with access to a low-carbon electricity mix either *via* the grid or through on-site generation (for example, through combustion of organic by-products). These large-scale production systems should also be designed for recovery or recirculation of valuable solvents and catalysts. Where appropriate, the process and reaction data of systems at scale should be made available for use in future LCA and TEA studies. Finally, continued research into direct routes to HMF and FDCA from lignocellulosic feedstocks is likely to greatly reduce the environmental impacts of these bio-based chemicals; however, routes must achieve high yields to ensure that they are economically viable.

For future LCA and TEA assessment of bio-based platform chemicals and their derived products, the development of standardised methodologies which provide specific guidance on the treatment of biogenic carbon, allocation methods and choice of functional unit, within the context of assessing bio-based chemical production, is essential. Until such methodologies are developed, LCA studies should be transparent and show how results are sensitive to methodological choices. To aid the rapid advancement of bio-based technologies, LCA studies should aim to assess current routes to HMF and FDCA platform chemicals to avoid the adoption of potentially impactful technologies. As applications and uses of HMF and FDCA become more defined, consequential LCA could aid in assessing the environmental impacts caused by the widespread adoption of specific bio-based products.

Conflicts of interest

The authors declare no conflict of interest.

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Table 4. Direction for research into new synthetic routes and future LCA and TEA studies of bio-based chemicals

Development of synthetic routes	LCA and TEA considerations
• Efficient, non-precious metal-based catalysts are needed.	• Standardised methodologies specific to the assessment of bio-based chemical products are needed.
• Aqueous or biphasic systems are preferred over the bulk use of organic solvents.	• Until such methodologies are developed, studies should aim to clearly show results from a range of methodological approaches.
• First attempts at commercialisation should aim to utilise renewable energy sources.	• LCA studies should aim to capture discoveries made in the synthetic literature, such as use of different feedstocks.
• Large-scale processes should be engineered as to be highly energy efficient in their use of energy, solvents and catalysts.	• Integration of LCA and TEA should be done in a way that provides relevant and thorough assessment of a given system.
• Continued investigation into direct routes to HMF and FDCA from lignocellulosic feedstocks is required.	
• Process and reaction data should be reported to allow for LCA to be conducted.	

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