Chem Soc Rev

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Cite this: *Chem. Soc. Rev.*, 2020, **49**, 6329

Biomass-derived chemical substitutes for bisphenol A: recent advancements in catalytic synthesis†

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Bisphenol A is an oil-derived, large market volume chemical with a wide spectrum of applications in plastics, adhesives and thermal papers. However, bisphenol A is not considered safe due to its endocrine disrupting properties and reproductive toxicity. Several functional substitutes of bisphenol A have been proposed in the literature, produced from plant biomass. Unless otherwise specified, the present review covers the most significant contributions that appeared in the time span January 2015–August 2019, describing the sustainable catalytic synthesis of rigid diols from biomass derivatives. The focus is thereupon on heterogeneous catalysis, use of green solvents and mild conditions, cascade processes in one-pot, and continuous flow setups. More than 500 up-to-date references describe the various substitutes proposed and the catalytic methods for their manufacture, broken down according to the main biomass types from which they originate.

Received 28th February 2020

DOI: 10.1039/d0cs00179a

rsc.li/chem-soc-rev

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1. Introduction

There is no doubt that plastic materials are central to our society. Plastics are widespread in everyday products that we use for housing, personal care, packaging, clothing, transport, adhesives and electronics.[1] There is equally no doubt that, just because of their versatility and ubiquity, today plastics are also a source of concern. Multiple issues relate to plastics.[2,3]

Plastics are usually synthetic polymers recalcitrant to biodegradation. They accumulate in the environment if discarded, thus representing important pollutants.[4,5] Plastics may contain or release toxic components or volatile organic compounds dangerous to human health and the habitat.[6,7] Most plastics

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d0cs00179a

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Carmen Moreno-Marrodan studied Chemistry in the University of La Rioja, Spain. In 2008 she won a Leonardo da Vinci European Programme Fellowship in the chemical industry in Cork, Ireland. In 2009 she was awarded a Marie Sklodowska Curie Fellowship and joined the ITN Nano-HOST in the Institute of Chemistry of Organo-Metallic Compounds (ICCOM), Florence, Italy. In 2013 she received her PhD in Chemistry from the University of Florence. Currently, she is a Permanent Researcher in the Italian National Research Council (ICCOM) in Florence. Her research interests focus on biomass valorisation through the development of heterogeneous catalysis and flow technologies.

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are manufactured from oil, which contributes to the carbon footprint of the process industry and to the depletion of exhaustible raw materials.[8,9] Not all plastics can be recovered and reused, or have significant recycling economic value; therefore, they are liable to end up in landfills or the environment.[10,11]

To overcome, at least in part, these problems, considerable efforts have been devoted in recent years to the development of compostable and bio-based polymers,[12,13] and to the synthesis of alternative monomers.[14,15] Transnational strategies have been launched to this aim,[16,17] including the United Nation Sustainable Development Goals (SDG 13 Climate Action, SDG 12 Responsible Consumption and Production),[18] the European Strategy for Plastics in a Circular Economy,[19] and the United States Sustainable Materials Management Program Strategic Plan.[20] Research agendas[21,22] and position papers[23,24] have been made available from European Technology Platforms and Consortia.[25]

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, BPA) is a component of several plastic materials, from which it may leach under certain circumstances. Unfortunately, BPA is considered a hazardous compound.[26] A number of chemicals have thus been proposed as substitutes for BPA, some of them obtainable from plant biomass derivatives.

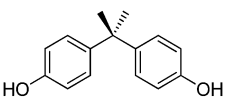
The present manuscript reviews the most significant contributions that appeared in the last five years' literature, describing the catalytic synthesis of functional monomer substitutes of BPA, which are manufactured from biomass or from biomass-derived compounds. The synthetic processes are illustrated according to the raw materials used and the corresponding value chains. The topic was partially covered by previous surveys,[27,28] particularly in relation to the synthesis of epoxy monomers.[29,30] The aim of the present review is to provide the reader with the basic concepts behind chemical substitution, and with an analysis of the advancements proposed for the sustainable synthesis of BPA replacements from renewable feedstock. The focus is thereupon on heterogeneous catalysts enabling multistep reaction sequences in one-pot, use of green solvents, mild conditions and continuous flow setups. Strategies, challenges and prospects in the field are discussed. No functional substitutes other than diols are considered (*e.g.* epoxides, amines), neither petroleum-derived chemicals, nor biocatalytic processes will be detailed.[31,32]

2. BPA

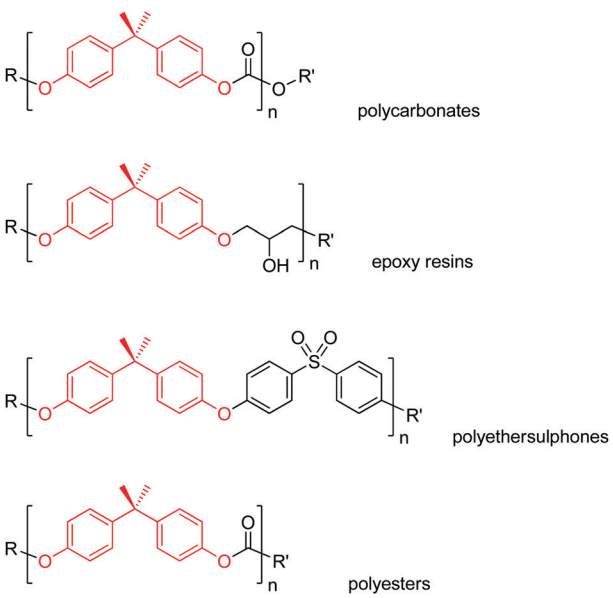
2.1. Properties and uses

BPA (CAS No. 80-05-7) is a diphenylmethane derivative bearing two hydroxy groups in the *para* positions. The chemical structure of BPA is reported in Scheme 1. BPA is industrially produced by the acid-catalysed condensation reaction of phenol with acetone, using an excess of phenol.[33] All by-products of the BPA synthesis, including unreacted phenol, are toxic.[34,35] An environmental profile associated with the production of BPA as a monomer is available from plastic manufacturers.[36] Lab-scale yields up to 96% were reported for this process.[37] A purity greater than 98% is required for most uses of BPA.[38,39]

BPA is largely incorporated as a monomer in a variety of polymers, namely polycarbonates, epoxy resins, polyethers, polysulphones and polyesters.[40] Representative structures are shown in Scheme 2. End-user applications of polycarbonates include food and beverage containers, optical lenses, electronic and household appliances, safety helmets, telephones,



Scheme 1 Structure of bisphenol A (BPA).



Scheme 2 Representative structures of some BPA-based polymers.

Pierluigi Barbaro

Pierluigi Barbaro was born in 1962 in Firenze. He obtained his PhD in Chemistry from the University of Firenze, then he spent a two-year post-doctorate fellowship at ETH Zurich. Presently he is the Researcher Director at the Istituto di Chimica dei Composti Organo Metallici, Consiglio Nazionale delle Ricerche (Italy). He was a member of the Network of Excellence IDECAT and a Coordinator of the Initial Training Network NANO-HOST (European Commission VII FP). He is a member of the Board of Directors of the European Research Institute of Catalysis, Brussels. His activities are in the fields of green chemistry, catalysis and flow processes for biomass valorisation.

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automotive components, construction parts, medical equipment and toys. Epoxy resins are primarily used for the production of consumer and industrial coatings, paints and adhesives.

The extensive use of BPA justifies for a global BPA market above 6 million tons in 2017, with an expected compound annual growth rate of *ca.* 6% over the period 2019–2024.[41,42] This makes BPA one of the highest volume chemicals produced worldwide. To date, the manufacture of polycarbonates and epoxies accounts for about 68% and 30% of the production capacity of BPA, respectively.[43] The remaining market is shared among other polymers and the components of antioxidants, flame retardants, colour agents and thermal papers. In 2018, the amount of BPA used for thermal papers in the EU market was around 3 ktons.[44]

In addition to its double functionality and intrinsic stability,[45,46] one other reason for the massive use of BPA in polymer manufacture is its rigid structure. The limited degrees of freedom associated with the BPA molecule are believed to endow the resulting polymers with excellent thermal and mechanical properties, including stiffness, toughness and hardness.[47,48] Indeed, BPA-based plastics usually feature high flexural strength,[49] glassy moduli, glass transition temperatures (T_g),[50,51] tensile moduli,[52,53] and tensile and impact strength.[54,55] A detailed description of the synthesis and properties of the resulting polymers is outside the scope of the present review. The reader may refer to the above cited specialised reviews for this purpose.

BPA's physico-chemical properties, potentially relevant to toxicological and exposure aspects, are its low solubility in water (300 mg L^{-1})[56] and volatility (5.3×10^{-6} Pa),[57] and its significant octanol/water partition coefficient ($\log K_{ow}$ 3.42).[58] These parameters result in a high tendency for BPA sorption to soil and sediments, which ultimately controls the fate of BPA in aquatic and terrestrial environments.[59,60]

BPA-derived resins and polycarbonates are sensitive to hydrolysis[61,62] and temperature.[63,64] Together with the presence of monomer residues, due to incomplete polymerization,[65,66] or the incorporation of BPA as an additive,[67] this may cause the release of BPA from BPA-containing materials and related plasticware, including bottles,[68,69] dental sealants,[70,71] textiles,[72] papers,[73,74] food packaging[75,76] and cans.[77,78] Consequently, significant levels of BPA are detected in air, dust, wastewater, drinking water, food,[79,80] and human fluids and tissues,[81,82] particularly in infants.[83]

2.2. Health and environmental effects

A plethora of studies have been carried out on the diverse effects of BPA on human health. Several reviews are available in the literature.[84,85] Exposure to BPA occurs mainly through ingestion, although inhalation and dermal absorption may contribute significantly.[86,87] BPA is recognised as an endocrine disrupting and estrogenic chemical.[88,89] Data have indicated BPA as potentially responsible for a variety of health problems, such as obesity,[90,91] diabetes,[92,93] carcinogenesis,[94,95] neurobehavioral and neurological disorders (autism, anxiety, cognitive deficits, hyperactivity),[96,97] and reproductive[98,99] and developmental impairment.[100,101]

The risk associated with BPA exposure was assessed in the aquatic, sediment and terrestrial compartments,[102,103] suggesting significant toxic potential for vertebrates, invertebrates and algae.[104,105] The need for further information and testing was highlighted, however.[106,107]

On the above basis, several regulations have therefore been enforced worldwide on the production and use of BPA.[108]

Use of BPA in the manufacturing of baby bottles has been banned in Europe since 2011.[109] The marketing of any packaging, container and utensil containing BPA, intended to come into direct contact with food, has been prohibited in France since 2015.[110] In 2017, following the European Union Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation,[111] the European Chemical Agency (ECHA) placed BPA on the Candidate List of Substances of Very High Concern (SVHC),[112] classifying it as toxic for reproduction (Article 57c) and endocrine disrupting (Article 57f).[113] In December 2016, the EU published a new regulation stating that BPA "shall not be placed on the market in thermal paper in a concentration equal to or greater than 0.02% by weight after 2 January 2020".[114] In July 2019, the General Court of the European Union confirmed "the inclusion of Bisphenol A as a substance of very high concern on account of its properties as a substance toxic for reproduction".[115]

BPA is on the List of Chemicals Known to the State of California to Cause Cancer or Reproductive Toxicity (Proposition 65), because it is considered harmful to the female reproductive system.[116] Since July 2013, the manufacture, sale or distribution of bottles or cups that contain BPA above 0.1 ppb has been prohibited in California, if they are designed as containers for food and beverages used by children.[117] Other twelve US states and the District of Columbia have enacted law restrictions on BPA since 2009.[118] According to the U.S. Food and Drug Administration, the use of BPA-based polycarbonates and epoxy resins in baby bottles, sippy cups and infant formula packaging has been abandoned since 2012.[119,120] In 2014, the U.S. Environmental Protection Agency released a report on BPA alternatives in thermal paper, for stakeholders interested in chemical substitution.[121]

Starting from 2010, baby bottles containing BPA polycarbonate have no longer been manufactured advertised, sold and imported in Canada.[122]

3. Chemical substitutes of BPA from biomass

3.1. Principles of chemical substitution

The increasingly restrictive rules concerning the use of chemicals of risk to human health and the environment have become a major driver for their substitution in both research and industry.[123,124]

Chemical substitution is "the replacement or reduction of hazardous substances in products or processes by less hazardous or non-hazardous substances, or by achieving an equivalent functionality *via* technological or organisational measures".[125,126]

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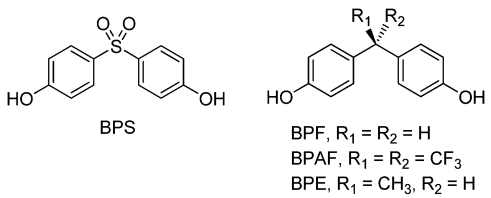
Therefore, chemical substitution is considered as a primary prevention strategy, rather than a mere reduction of the risk associated with a hazard.[127,128] Research in chemical substitution is "solution-oriented": the target is not the replacement with a specific compound (*e.g.* drop-in chemicals),[129,130] but the functions that the chemicals may provide.[131,132] Whenever structure–activity data are available, "safety-by-design" chemicals may be proposed for substitution.[133,134] In case that large volume chemicals are targeted for substitution, economic assessment attributes, other than hazard and functional performance, shall be considered for optimal replacement: capital investment, costs, technical feasibility, environmental impact of manufacture, life-cycle of chemicals.[135,136] Substitution using non-fossil feedstock is certainly a preferred option and a priority from a circular economy perspective.[137,138] Support and assessment tools are available online for chemical substitution.[139,140]

3.2. Proposed substitutes for BPA

A number of "bisphenol analogues" have been produced to replace BPA in various applications.[141,142] The largest market shares are held by BPF (4,4′-methylenediphenol), BPS (bis-(4-hydroxyphenyl)sulfone) and BPAF (2,2-bis(4-hydroxyphenyl)-hexafluoropropane), whose structures are shown in Scheme 3. However, they are neither considered safer than BPA,[143,144] nor synthesized from renewable sources.[145,146] Therefore, they will not be discussed further in the present review. Reports and databases are available on the viability of these monomers as BPA substitutes.[147,148]

Lignocellulose, together with cellulose, hemicellulose and lignin, accounts for around 80% (non-edible portion) of plant biomass (Fig. 1).[149,150] Terpenes, terpenoids and triglycerides account for *ca.* 10%.[151] These matters can be used as alternative carbon sources for the manufacture of most materials currently obtained from oil. In contrast to biofuels, the estimated amount of feedstock available from biomass is enough to produce high value-added chemicals that we need in everyday life,[152,153] including solvents, pharmaceutical building blocks, agrochemicals, food additives, hygiene and cosmetic components, and monomers for bio-plastics.[154,155] A limited number of functional molecules, called platform chemicals,[156] can be produced through biomass conversion and usable as bulk chemicals in this direction.[157,158] Examples include 5-hydroxymethylfurfural (HMF), sorbitol, furfural, and xylitol.[159,160] The upgrade of these intermediates usually requires multi-step sequences of dehydration, isomerisation, esterification, oxidation or hydrogenation reactions that, for their economic feasibility, each should be performed with high selectivity and a safe environmental profile.[161,162] In practice, the best way to achieve this goal is through catalysis: chemical and biocatalysis each have their role to play.[163,164] Excellent reviews are available covering most aspects of catalytic valorisation of lignocellulosic biomass.[165,166] From an industrial point of view, heterogeneous catalysts are preferred due to the easier catalyst/product separation, catalyst reuse and integration in existing reactor equipment.[167,168] This, however, often requires the immobilisation of tailored catalysts onto appropriate insoluble support materials.[169,170] On the other hand, multi-step processes are most efficiently achieved in one-pot by using truly bifunctional catalysts, *i.e.* a combination of well-defined supported acid and metal sites acting under the same reaction conditions, notably metal catalysts immobilized onto solid acids.[171,172] The strategy has been successfully applied to the upgrade of bio-derived platform molecules.[173,174] A step forward in sustainability and process intensification is provided by performing catalysis under continuous flow conditions, because of the considerable advantages compared to conventional batch operations: increased safety and reactor volume productivity, simpler downstream processing, smaller hold-up volumes, improved heat transfer and process control.[175,176] Continuous refreshes of the catalyst surface may also reduce active site inhibition due to the adsorption of (by)products.[177] Facilities integrating "biomass conversion processes and equipment to produce fuels, power, heat and value-added chemicals from biomass" are called biorefineries.[178,179] A 4th generation of biorefineries, focusing on economically feasible technologies, production of unconventional platforms and use of advanced catalysts, is currently under development.[180,181]



Scheme 3 Structures of BPF, BPS, BPE and BPAF.

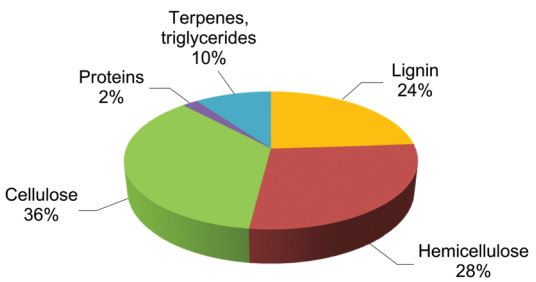


Fig. 1 Composition of plant biomass.

Several studies have been devoted to the catalytic synthesis of alternative monomers for plastics from renewable resources, particularly from lignocellulose.[182,183] The finished polymers are often referred to as "sustainable polymers" or "renewable polymers".[184,185] Metrics to evaluate the sustainability of bio-derived polymers are available.[186,187] Functional substitutes of BPA from biomass and its derivatives have also been proposed, mainly from cellulose and lignin and a few from terpenoids and hemicellulose.[188] Schematic representations of the main BPA substitutes from biomass found in the literature are reported in Fig. 2.

Cellulose is a linear-chain homopolysaccharide consisting of a well-defined sequence of D-glucose units linked by β(1,4) glycosidic bonds.[189] Cellulose is the main component of the cell walls of green plants and many algae, and the most

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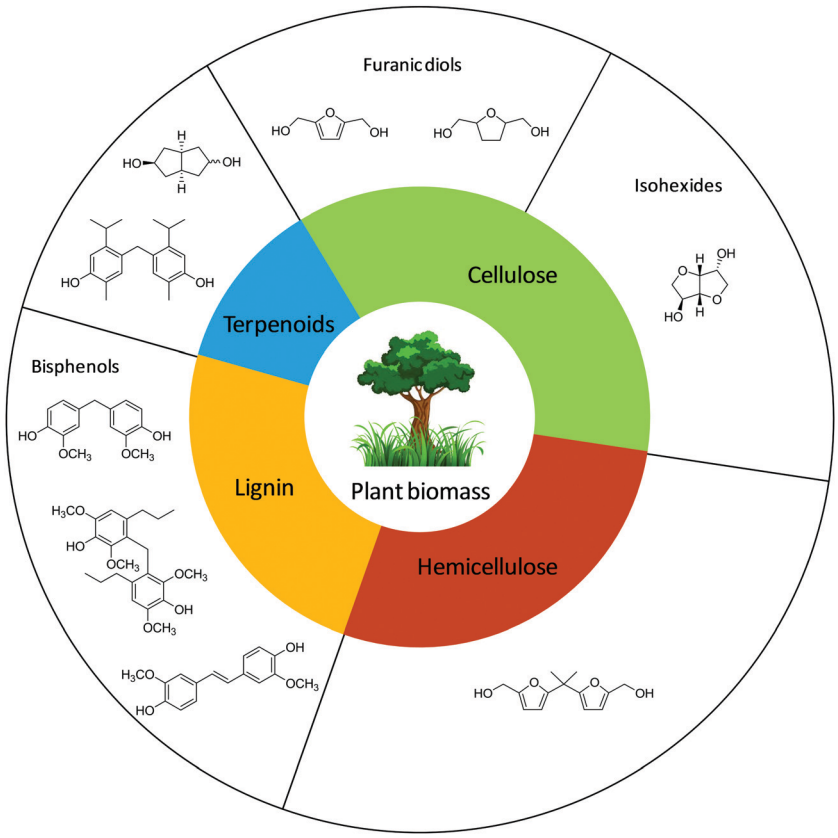
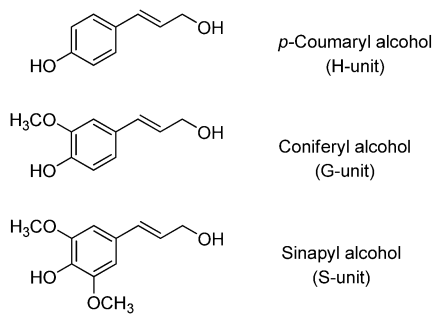


Fig. 2 Sketches of the main BPA substitute types recently proposed from biomass.



Scheme 4 Structures of H, G and S monolignol subunits of lignin.

abundant organic polymer in nature.[190] Unlike cellulose, lignin is a very complex, cross-linked polymer reducible to three main methoxylated 4-hydroxycinnamyl alcohol building blocks, known as monolignols (Scheme 4).[191] They form a variety of structural and functional motifs, whose composition depends on the plant from which lignin is extracted.[192,193] Lignin is considered a waste material from the paper and forestry industries, with a production of around 100 million tons per year.[194,195]

It is generally agreed that the proposed monomer BPA substitutes from biomass shall be bifunctional and have a rigid structure, either due to a ring scaffold or due to the inhibition of rotational flexibility.[196,197] The present paper reviews the substitutes based on rigid diol units which are obtained by catalytic methods. No linear diols will therefore be considered.[198] The syntheses of these compounds will be reviewed in the following sections, according to the main biomass feeds from which they originate: cellulose, lignin or others.

4. Substitutes from the cellulose depolymerisation chain

Cellulose is a source of C6 carbohydrate platform molecules. Upon full acid-catalysed hydrolytic depolymerisation, cellulose affords glucose,[199,200] from which two important platform molecules can be obtained *via* catalysis: sorbitol[201] and HMF.[202,203] These materials are the starting materials used in industry to produce a variety of useful chemicals, including isosorbide and furanic diols, also through catalytic methods.[204,205] The overall value chain is outlined in Scheme 5. Isosorbide, as well as isohexides in general, and bis(hydroxymethyl)furans have been investigated as BPA replacements. Routes to these compounds from glucose (or cellulose) involve sequences of two or more acid-catalysed dehydration (hydrolysis) and metal-catalysed reduction steps. Use of upstream substrates, other than sorbitol or HMF, is clearly more attractive owing to the intensification,[206] reduced complexity and cost of the overall process.[207] However, its drawbacks are the high pressures and temperatures usually needed, and the significant amounts of mineral acids reported to overcome the recalcitrance of glucose, cellulose and the

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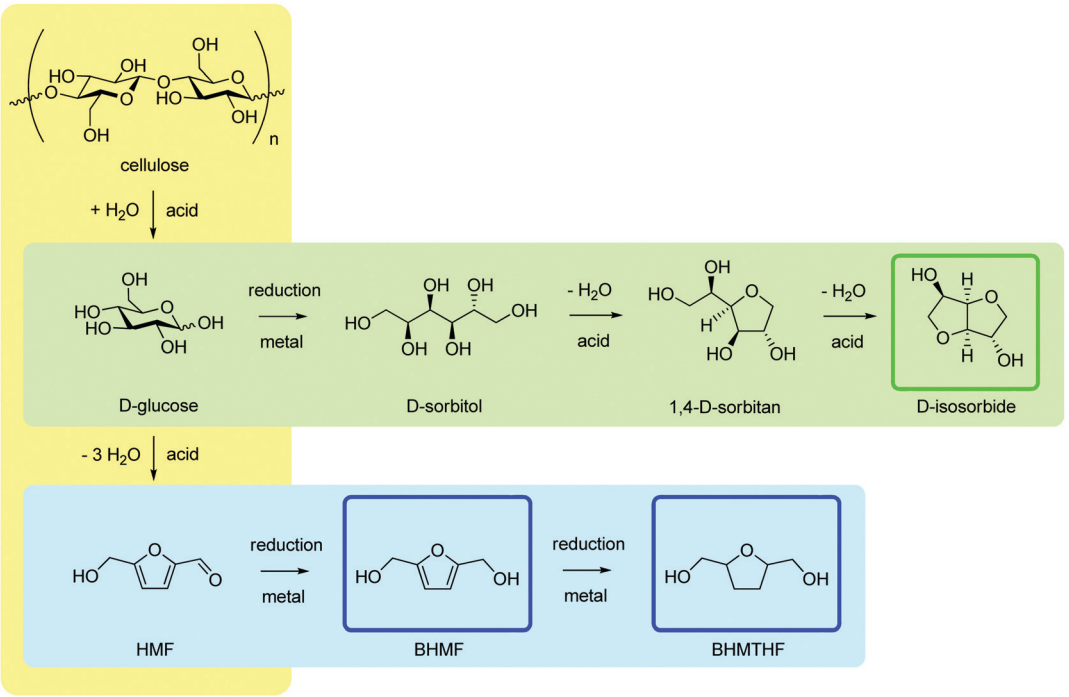


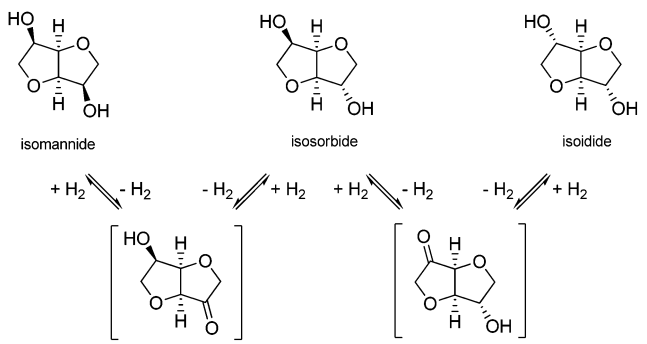
Scheme 5 Simplified reaction pathways for the catalytic conversion chain of cellulose to isosorbide and furanic diols.

non-edible biomass in general.[208] Process selectivity under such harsh conditions is often moderate, leading to variable quantities of (humin) by-products, partly because of the suboptimal catalysis used, whose stability may be an issue as well.[209]

Therefore, improved catalysts and processes shall be developed, in order to convert efficiently and selectively original cellulose-derived feeds to the desired bio-based building blocks.

4.1. Isohexides

Isohexides are chiral V-shaped diols consisting of two fused tetrahydrofuran units, with secondary hydroxyl groups in *endo*/*endo* (isomannide), *exo*/*endo* (isosorbide) and *exo*/*exo* (isoidide) configurations (Scheme 6). Their very low toxicity (Table S1, ESI†), rigid bicyclic structure, acceptable chemical stability, different stereochemistries and potential for selective functionalizations make them very attractive for several applications,



Scheme 6 Structures and epimerization of isosorbide, isomannide and isoidide.

including synthesis of pharmaceutical intermediates (*e.g.* isosorbide dinitrate);[210] synthesis of fuel additives, surfactants, chiral auxiliaries;[211,212] and bio-based plastics.[183] The preparation and properties of polymers (polycarbonates, polyesters or polyamides) based on isohexides,[213] particularly isosorbide,[214,215] scaffolds have been reviewed earlier. The *exo*/*exo* configuration of the least sterically hindered isoidide results in polymers with the highest molecular weights, whereas the *endo*/*endo* configuration of isomannide provides polymers with higher thermal stability, compared to the other isomers. Importantly, biodegradable polymers based on isohexide units have been developed.[216,217]

Synthetic methods and applications of isomannide and isoidide are yet limited. Due to the poor availability of their sugar alcohol precursors (L-iditol for isoidide, D-mannitol for isomannide), and the low selectivity of the associated dehydration processes, they are still produced on a bench scale.[182,218] Recently, an unprecedented 63% yield of isomannide from mannitol was achieved over solid acid Hβ zeolite catalysts having a Si/Al ratio of 75.[219] The efficiency of the catalysts was attributed to the structural properties of the zeolite and to the balanced acid loading and hydrophobicity of Hβ-75. Based on density functional theory calculations, it was suggested that a challenging selective 1,4-dehydration path can be achieved, thanks to the inhibition of a bulkier 2,5-dehydation transition state within the zeolite micropores (Scheme 7). The catalyst could be reused with a slight activity decrease (*ca.* 10%) over four cycles. The synthesis of isomannide in 92% yield was also reported in the homogeneous phase, using the basic catalyst 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and dimethyl carbonate (DMC), *via* a mechanism analogous to that described

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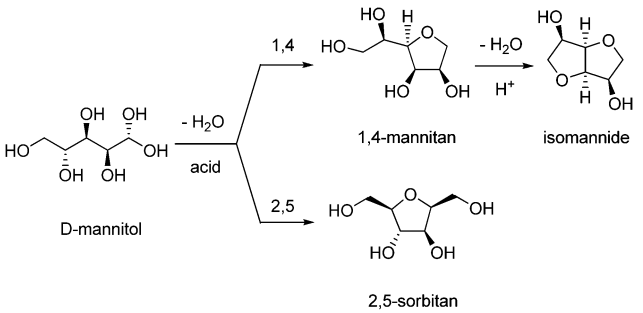

Scheme 7 Pathways of acid-catalyzed dehydration of mannitol to isomannide.

below for isosorbide (Scheme 10).[220] Isomannide could be isolated after evaporation of the excess of DMC and methanol solvent, without a chance of catalyst reuse, however.

The most efficient strategy for the synthesis of isoidide is the catalytic epimerization of the other isohexides. After the first approaches of Fletcher and Wright,[221,222] a detailed study was reported in 2013 by Le Nôtre, wherein the process was achieved in water over heterogeneous Ru@C catalysts and in the presence of H_2 (40 bar, 220 °C).[223,224] It was demonstrated that epimerization occurs through a dehydrogenation–hydrogenation path (Scheme 6). The catalyst could be reused once with a moderate loss of activity (20%), whereas >99% pure starting isosorbide was required. More recently, epimerization of an "impure isosorbide" feed (*i.e.* an isosorbide-rich mixture containing up to 10% of sorbitans) was conveniently achieved over Ni RANEY® catalysts at 230 °C, using various hydrogen flows.[225] 99% pure isoidide was obtained after chromatographic separation and crystallization. The advantages of the methods are the reduction of costs and isosorbide loss, usually caused by prior heat-sensitive isosorbide distillation.

Due to the large availability of bio-based precursors (sorbitol, glucose or cellulose), isosorbide is by far the most important of isohexides. The synthesis[182,212] and applications[183,215] of isosorbide have been reviewed up to 2016. Hence, only the most recent achievements in catalytic synthesis will be described herein. Table 1 summarises the most significant reaction parameters (solvent, temperature, H_2 pressure) for the catalytic processes described in the present review which lead to isohexides from biomass-derived sources. Catalyst productivity to the products specified, as $mmol_{prod}\ g_{cat}^{-1}\ h^{-1}$, is also reported aimed at providing a significant and quantitative estimate of catalyst efficiency.

4.1.1. Sorbitol dehydration. Isosorbide is a monomer for several bioplastics, including poly-(ethylene-*co*-isosorbide) terephthalate (PEIT), poly(isosorbide carbonate) (PIC) and poly(isosorbide oxalate). The isosorbide volume demand for

Table 1 Summary of recent catalytic systems for proposed BPA monomeric replacements from isohexides[a]

Catalyst	Biomass-derived substrate	Product	Reaction conditions			Conv.[c] (%)	Sel.[d] (%)	Prod.[e] ($mmol_{prod}\ g_{cat}^{-1}\ h^{-1}$)	Ref.
			Solvent[b] (M)	T (°C)	H_2 (bar)				
Hβ-75	Mannitol	Isomannide	Free	140	—	99	65	4.3	219
DBU	Mannitol	Isomannide	Methanol (2.7)	Reflux	—	100	92	5.1	220
DBU	Mannitol	Isosorbide	Methanol (2.5)	Reflux	—	100	98	2.5	220
Ru@C	Isosorbide	Isoidide	H_2O (6.9)	220	—	100	51	22.3	224
Amberlyst-36	Sorbitol	Isosorbide	H_2O (13.5)	150	—	100	69	12.7	232
Hβ-75	Sorbitol	Isosorbide	H_2O (0.5)	200	—	100	77	n.a.	235
Hβ-75	Sorbitol	Isosorbide	Free	127	—	100	76	7.6	236
Glu-Fe_3O_4-SO_3H	Sorbitol	Isosorbide	Free	140	—	100	94	25.8	237
SAC-13[f]	Sorbitol	Isosorbide	Free	130	—	100	83	0.6	239
Dowex-50WX2	Sorbitol	Isosorbide	Free	130	—	100	78	1.5	239
Amberlyst-15	Sorbitol	Isosorbide	Free	130	—	100	67	1.3	239
Deloxan	Sorbitol	Isosorbide	Free	130	—	100	68	2.3	239
SHTC	Sorbitol	Isosorbide	Free	130	—	100	80	2.7	239
SiO_2-SO_3H	Sorbitol	Isosorbide	Free	120	—	100	84	23.1	241
SBA15-$PrSO_3H$	Sorbitol	Isosorbide	Free	150	—	90	78	3.2	242
SBA15-$ArSO_3H$	Sorbitol	Isosorbide	Free	170	—	100	71	46.7	245
B phosphate	Sorbitol	Isosorbide	H_2O[g]	250	—	99	80	n.a.	248
Zr phosphate	Sorbitol	Isosorbide	Free	210	—	100	73	20.0	249
MST-450	Sorbitol	Isosorbide	Free	180	—	100	70	96.1	250
BIL-5	Sorbitol	Isosorbide	Free	130	—	99	85	95.6	251
$Bi(OTs)_3$	Sorbitol	Isosorbide	Free	145	—	100	67	23.1	257
Hβ-20	Sorbitol	Isosorbide	MIBK (0.4)	170	—	100	93	25.1	258
CH_3ONa	Sorbitol	Isosorbide	Methanol	Reflux	—	100	98	0.6	260
Ru@Dowex	Glucose	Isosorbide	H_2O (0.1)	190	30	100	85	0.1	261
RuO_x@C-SO_3H	Cellulose MCC	Isosorbide	H_2O (0.04)	170 + 200[h]	40	100	56	2.1	266
Ru@C + Amberlyst-70[i]	Milled cellulose	Isosorbide	H_2O (0.05)	190	50	78	72	0.35[j]	267
Ru@C + Amberlyst-70[i]	Cellulose	Isosorbide	H_2O (0.002)	190	50	38	67	0.01[j]	268
Ru/Fe_3O_4@PMO-SO_3H	Cellulose	Isosorbide	H_2O (0.12)	220	60	98	59	17.9	269
Ru@mNbPO	Cellulose	Isosorbide	H_2O (0.12)	220	60	100	40	24.7	270

[a] See Section 4.1 for labelling and abbreviations. [b] Reaction solvent, substrate concentration (M) in brackets. [c] Substrate conversion. [d] Selectivity to the product indicated. [e] Catalyst productivity to the product indicated. [f] Nafion–silica composite. [g] Sorbitol 70 wt%. [h] Two-stage process. [i] Mechanical mixture. [j] Calculated with respect to Ru@C.

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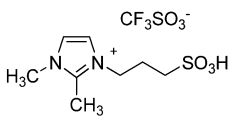
PEIT production was around 3 ktons in 2012, while the global isosorbide market is expected to reach 300 million Euros by 2023.[226] The conventional route to isosorbide synthesis involves a sequence of metal-catalysed hydrogenation of glucose to sorbitol, followed by twofold acid-catalysed dehydration of sorbitol through 1,4-sorbitan (Scheme 5). The latter steps are slowed down in the presence of water, thus requiring much higher reaction temperatures.[227] On an industrial scale, isosorbide is currently produced in high purity *via* a three-stage process, comprising enzymatic depolymerisation of starch, hydrogenation over Ni catalyst and H_2SO_4-catalysed dehydration,[228,229] however after a complex purification procedure.[230,231] The world's largest manufacturer of isosorbide, the French company Roquette with a production capacity of 20 000 tons $year^{-1}$, has recently patented an isosorbide process based on acidic ion-exchange resin dehydration under vacuum, whose yield based on sorbitol is around 94%.[232] On the other hand, sorbitol itself is largely used in the food and pharmaceutical industries due to its low-calorie sweetener, laxative and humectant properties, as well as in the preparation of several other chemicals, including vitamin C, besides isosorbide.[201,233] As a matter of fact, sorbitol has the biggest market share among the sugar alcohols.[234]

As mentioned above for the synthesis of isomannide, several zeolites were used in the solid acid-catalyzed dehydration of sorbitol and, among them, Hβ-75 showed the highest activity, which was attributed to its appropriate Brønsted/Lewis acidic site ratio, hydrophobicity and three-dimensional porous structure, favorable for the diffusion of sorbitol. A constant 87% isosorbide yield was observed in water at 200 °C over Hβ-75, wherein the catalyst could be reused three times, with no significant efficiency decay, after calcination at 550 °C.[235] Solvent-free conditions resulted in 76% yield at 127 °C.[236]

Sulfonic acid heterogeneous catalysts, inorganic, silica-based or polymeric, have also been successfully used in sorbitol dehydration reaction. Excellent isosorbide yields (94%) were obtained at 140 °C, using a large amount (20 wt%) of magnetically-recoverable Glu–Fe_3O_4–SO_3H catalysts under neat conditions.[237,238] The Nafion–silica composite SAC-13 showed up to 83% isosorbide yield under solvent-free conditions, 130 °C and high vacuum, better than those obtained using the comparable catalysts Amberlyst-15 (67%), Deloxan (68%), Dowex 50WX2 (78%), Purolite CT269 (75%) or Sulfonated Hydrothermal Carbon (SHTC, 80%).[239,240] This finding was tentatively attributed to the better site-accessibility of silica under catalytic conditions, compared to polymeric support materials, and to the higher acidic strength of the perfluorosulfonic groups. Indeed, similar catalytic performances were observed using sulfonic acid-functionalized silica catalysts. For instance, an 84% isosorbide yield was obtained over microbead silica catalysts, having different acid densities (120 °C, solvent-free), and obtained by reacting silica with variable amounts of (3-mercaptopropyl)trimethoxysilane (MPTS).[241] The yield of isosorbide increased by increasing the acid density (up to 60% MPTS loading). The catalyst was reused ten times, showing no activity loss, but significant selectivity decrease (*ca.* 10%). The excellent catalytic performance was attributed to the appropriate combination of acidity, pore size (*ca.* 8 nm) and high surface hydrophilicity of the silica support, favoring the adsorption of feed, in that case. The effect of acid density/hydrophilicity balance on the catalytic efficiency of sorbitol dehydration was studied over mesostructured SBA-15 silica, functionalized with different amounts of hydrophilic propyl sulfonic acid groups and hydrophobic silyl moieties.[242] The results indicated that an increase in the acid content slowed down the sorbitol to sorbitan step, but increased the rate of the sorbitan to isosorbide dehydration. On the other hand, an increase in surface hydrophobicity reduced the affinity of sorbitol for the catalyst, but increased the accessibility of sulfonic groups, thus slowing down the first step, but enhancing the second one. The best compromised results (70% yield at 150 °C) were obtained over 10% propyl sulfonic silica catalysts bearing trimethylsilane substituents. The catalyst lost most of its activity after the first run, which was ascribed to (by)-product adsorption, although decomposition of silica-bound propyl sulfonic groups cannot be ruled out.[243,244] Comparable results (71% isosorbide yield at 170 °C) were obtained using an arenesulfonic acid-functionalized SBA-15 catalyst.[245]

Metal phosphates have been shown to be convenient dehydration catalysts, due to their nontoxicity, thermal stability and strong acidity.[246,247] A series of phosphates were tested in the dehydration of 70 wt% aqueous sorbitol and their activity was found to increase in the order Al < Zr < Fe < La < Ce < B.[248] At 250 °C a yield of 79.9 mol% of isosorbide was achieved using boron-phosphate. Quantitative sorbitol conversion, with 73% isosorbide selectivity, was obtained over porous zirconium phosphate (ZrP) at 210 °C without solvents.[249] ZrP reusability was examined, showing quantitative sorbitol conversion up to the fifth run, with only a slight selectivity decrease (5%). A similar performance, though at a lower reaction temperature (180 °C), was observed using a mesoporous sulfated titania catalyst calcined at 450 °C (MST-450).[250]

Brønsted acidic ionic liquids (BILs) were recently explored as catalysts, due to their inherent advantages, compared to conventional mineral acids, in terms of reduced volatility and corrosivity.[251] A series of ionic liquids bearing diverse acidic substituents and counterions was synthesized, and their efficiency rationalized in terms of the Gutmann acceptor number,[252] rather than inherent acidity. Kinetic studies indicated that the ionic liquids have diverse abilities in forming adducts with sorbitol and the intermediate 1,4-sorbitan. The best results were achieved using BIL-5 catalyst (Scheme 8), which resulted in 85% isosorbide yield at 130 °C. The catalytic efficiency compared favourably with that of the homogeneous catalysts H_2SO_4 and



BIL-5

Scheme 8 BIL-4 Brønsted acidic ionic liquid catalyst for sorbitol dehydration.

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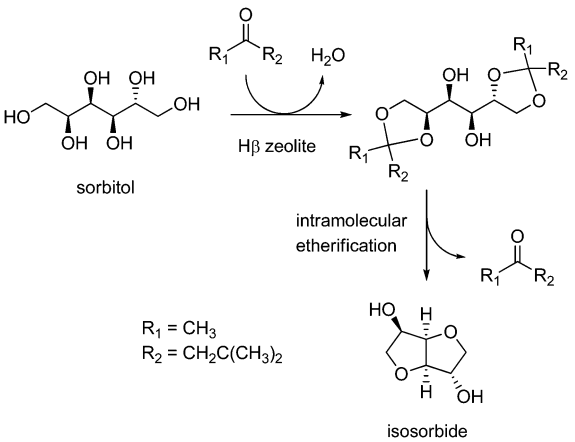
CF_3SO_3H under the same reaction conditions. Despite the increasing interest and use of BILs in catalysis, some questions still remain to be addressed, particularly in relation to toxicity,[253,254] reaction kinetics,[255] and reusability.[256] In the cited work, catalyst recycling experiments were performed by vacuum distillation of the product at 170 °C, well below the TGA decomposition temperature of *ca.* 300 °C, followed by addition of a fresh amount of substrate, showing pretty constant catalytic efficiency over five consecutive runs.

Metal tosylate salts were also explored as homogeneous-phase acidic catalysts. Thus, use of $Bi(OTs)_3$ resulted in full conversion and 67% isosorbide yield, under solvent-free conditions, 145 °C and vacuum (40 mbar).[257] Heterogenization onto Amberlyst 70 resin, although enabling effective removal of catalyst, resulted in their substantial deactivation.

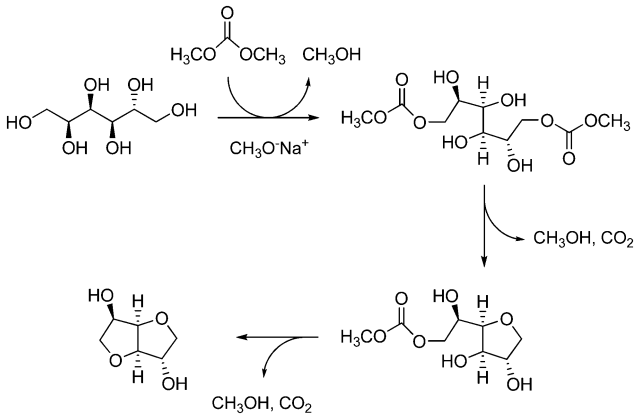
Recently, a 93% isosorbide yield was achieved under mild conditions (170 °C, solvent-free), thanks to a new strategy based on sorbitol ketalization by methyl isobutyl ketone (MIBK), followed by double intramolecular etherification over Hβ-20 zeolite catalysts (Scheme 9).[258] The approach allowed reducing the number of etherification active sites, thus controlling cyclisation selectivity and minimizing byproduct formation (humins, 2,5-sorbitan). Intramolecular etherification was facilitated by the ketone, as a better leaving group than water. After regeneration at 550 °C, the solid catalyst could be used three times without loss of activity.

Although sorbitol dehydration to isosorbide mostly occurs by acid catalysis, in a few cases it was achieved in the presence of strong (*i.e.* sodium methoxide)[259,260] or nitrogen bicyclic (*i.e.* DBU) bases.[220] Thus, using dimethyl carbonate as both a carboxymethylating agent and a leaving group, the double intramolecular cyclization of sorbitol yielded isosorbide almost quantitatively (98%) (Scheme 10). However, the reaction was performed in the homogeneous phase and details on the fate of soluble catalysts were not provided. Carboxymethyl derivatives of isosorbide may be observed as by-products.

4.1.2. Glucose conversion. The one-pot, one-stage synthesis of isosorbide, directly from glucose and in water, was recently reported using a bifunctional (hydrogenation/acid) heterogeneous



Scheme 9 One-pot synthesis of isosorbide *via* sorbitol ketalization.



Scheme 10 Mechanism of sorbitol dehydration in dimethyl carbonate under basic conditions. Adapted with permission from ref. 260 (F. Aricò, P. Tundo, *Beilstein J. Org. Chem.*, 2016, **12**, 2256–2266). Copyright 2016, Aricò and Tundo, Open Access article under the terms of Creative Commons Attribution License. (https://creativecommons.org/licenses/by/4.0/deed.it) license Beilstein-Institut.

catalyst comprising Ru nanoparticles (1.3 nm) immobilized onto commercial sulfonic-acid ion-exchange resin Dowex 50WX2 (Ru@Dowex-H).[261] Selection of the appropriate reaction conditions (190 °C, 30 bar H_2, 48 h) allowed obtaining isosorbide in a remarkable 85% yield (based on glucose) at full substrate conversion, with the only significant by-product being 1,4-sorbitan. Interestingly, the process outcomes could be selectivity tuned to the intermediate sorbitol (>99% yield), by a simple modulation of the reaction conditions (*i.e.* 120 °C, 30 bar H_2, 7 h). The effect of the reaction temperature on the reaction products, at fixed time and H_2 pressure, is reported in Fig. 3. The high selectivity of the catalyst was attributed to the combination of appropriate swelling of the gel-type resin support in water and to the balanced loading of Ru-hydrogenation and Brønsted acid-dehydration sites (rate-determining).[262,263]

4.1.3. Cellulose conversion. Methods for the direct, catalytic conversion of aqueous lignocellulosic biomass to isosorbide (Scheme 5) are receiving increasing attention, though only a few articles describe real improvements in terms of yields and catalyst reusability. Selectivity in such processes is an usual drawback, as several (poisoning) by-products may form and the

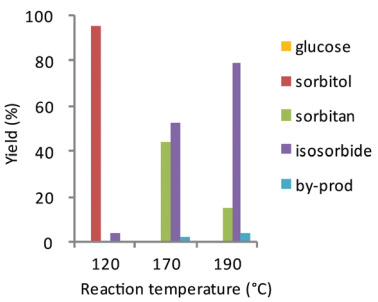


Fig. 3 Effect of reaction temperature at 24 h reaction time on the direct, catalytic conversion of glucose over bifunctional Ru@Dowex-H (0.2% w/w Ru, water, 30 bar H_2). Adapted with permission from ref. 261. Copyright 2016, Royal Society of Chemistry.

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carbon balance of the final products is often moderate.[264,265] A new efficient catalyst, based on Ru oxide on sulfonated carbon, showed high catalytic activity in an optimized two-stage isosorbide synthesis from lignocellulosic substrates, whether containing lignin (bagasse pulp, yield 49 wt%) or not (microcrystalline cellulose, yield 56 wt%).[266] The first stage involved the hydrolysis of cellulose to glucose and hydrogenation of glucose into sorbitol (170 °C), whereas the acid-catalysed dehydration to isosorbide was accomplished in the second stage (200 °C). A carbon balance in the range 85–92% was observed, wherein the only products detected, besides isosorbide, were unreacted intermediate glucose, sorbitol and 1,4-sorbitan, and the partial dehydration isomers 1,5- and 2,5-sorbitan. A reasonable selectivity of 56% to isosorbide was measured. Compared to conventional Ru@C/H_2SO_4 catalytic mixtures, the system showed constant activity over four consecutive runs (although with slight changes in the distribution of products) and superior recyclability, even for lignin-containing substrates. This was ascribed to the oxidative treatment of the catalyst, which increased the amount of carboxylic acid groups on the carbon support and reduced the adsorption of oligomer by-products (*e.g.* glucose) on the catalyst surface.

The one-pot, single-stage conversion of milled cellulose in water was performed using a mechanical mixture of commercial Ru@C and sulfonated resin Amberlyst-70 catalyst at 190 °C.[267] A 56% isosorbide yield was observed in the first run, which decreased to 11% in the second run, due to the adsorption of by-products on the ruthenium surface (including 1,4-sorbitan, isomannide and various amounts of unidentified soluble materials). The same catalyst was used, under the same conditions, to convert lignocellulosic biomass from Japanese cedar (*ca.* 40 wt% cellulose content). However, the isosorbide yield was less than 30%.[268]

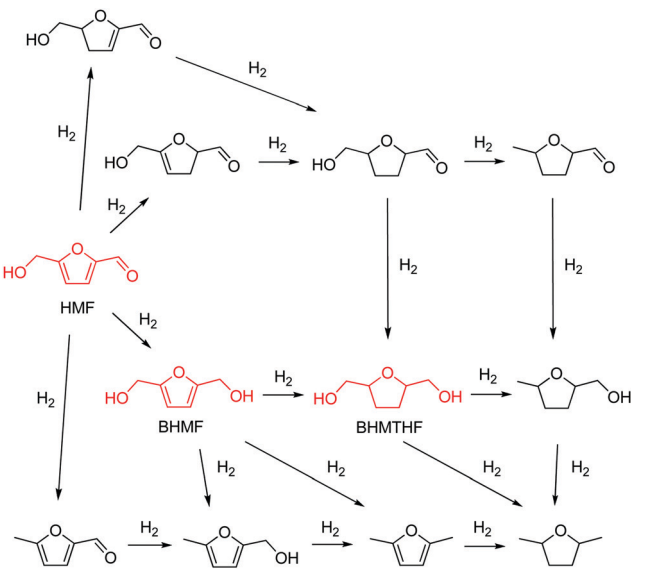
A sophisticated bifunctional catalyst featuring a core@void@shell structure (Ru/Fe_3O_4@void@PMO-SO_3H) was recently developed and used in the direct conversion of cellulose to isosorbide, for the first time.[269] By tailoring the size of Ru nanoparticles (2.2 nm), on a yolk–shell nanostructure containing an Fe_3O_4 core and a sulfonated periodic mesoporous organosilica (PMO) shell, an almost complete conversion of cellulose (98 wt%) was achieved at 220 °C, with a carbon efficiency of around 80%. A selectivity to isosorbide of 59% was observed, due to the significant formation of a variety of by-products, including sorbitol, mannitol, xylitol, erythritol and ethylene glycol originating from several side-reactions. The isosorbide productivity was 2.19 $mol_{isosorb}$ h^{-1} g_{Ru}^{-1}, higher than that obtained using previously reported ruthenium-based bifunctional catalysts, *e.g.* Ru@mNbPO.[270] No significant decrease in the yield and conversion after four runs was observed.

4.2. Furanic diols

5-Hydroxymethylfurfural (HMF) is an important platform molecule obtainable from cellulose depolymerisation, *via* three-fold acid-catalyzed dehydration reaction of glucose (or fructose).[271,272] HMF is usable to produce several value-added chemicals, including monomers for polymers (Scheme 5).[273,274] Reduction of HMF provides a "family" of rigid cyclic diols, namely 2,5-bis(hydroxymethyl)furan (BHMF) and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF), that have been proposed as BPA replacements. The topic has been partially covered by previous reviews.[275,276] Actually, given the double functionality susceptible of reduction within HMF (C–O and C=C), its reduction is prone to significant selectivity issues, due to the complex network of potential reduction products that can be generated (Scheme 11),[277,278] in addition to those usually observed in the processing of sugar-derived compounds (oligomers, humins, levulinates).[279,280] As for any other partial reduction process, the challenge in BHMF and BHMTHF synthesis is to achieve the reduction of one specific group at full substrate conversion, which strongly depends on a subtle combination of metal catalyst, reaction conditions and, in the case of heterogeneous systems, properties of the support material.[281,282] Continuous flow catalysis can be particularly useful in this regard, as it allows the fine tuning of reaction conditions and contact times, while enabling fast removal of intermediate products before further reduction.[283,284] Table 2 summarises the main features of the catalytic processes hereinafter described leading to furanic diols from biomass-derived sources.

The hydrogenation of HMF has been recently reported by Hashmi *et al.* using homogeneous-phase catalysts in toluene solution.[285,286] A screening study was performed through a variety of ligands and metals, wherein the best BHMF (98%) and BHMTHF (79%) yields were obtained at full HMF conversion with Ru bispyridine and DTBM–SEGPHOS complexes, respectively, at 120 °C and 10 bar H_2 (Scheme 12). However, despite its fundamental interest and good yields, the system suffers from limitations that hamper its use for real applications: high catalyst loading, cost of chiral ligands, non-reusability of catalysts, and toxic toluene solvent.

Several heterogeneous catalysts have been reported in recent years for the hydrogenation of HMF. Use of commercial Ru@C



Scheme 11 Simplified network of hydrogenation products originating from HMF.

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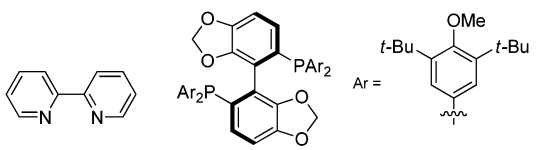
Table 2 Summary of recent catalytic systems for proposed BPA monomeric replacements from furanic diols[a]

Catalyst	Biomass-derived substrate	Product	Reaction conditions			Conv.[c] (%)	Sel.[d] (%)	Prod.[e] ($mmol_{prod}\ g_{cat}^{-1}\ h^{-1}$)	Ref.
			Solvent[b] (M)	T (°C)	H_2 (bar)				
Ru complex[f]	HMF	BHMTHF	Toluene (0.08)	120	10	100	79	10.8[g]	285
Ru complex[f]	HMF	BHMF	Toluene (0.08)	120	10	100	98	30.1[g]	285
Ru@C	HMF	BHMTHF	H_2O (0.25)	100	50	100	95	9.5	287
Ru@C	HMF	BHMF	H_2O (0.25)	50	30	100	93	9.2	287
Ru@C	HMF	BHMF	H_2O (0.25)	100	50	100	73	7.2	287
Ru@CNF	HMF	BHMF	2-Butanol (0.08)	150	20	86	95	810.4[g]	288
$Ru(OH)_x@ZrO_2$	HMF	BHMF	1-Butanol (0.329)	120	15	100	99	10.7	289
Pd@MIL-101(Al)-NH_2	HMF	BHMTHF	H_2O (0.13)	30	10	100	96	4.0	293
Pd@mpg-C_3N_4	HMF	BHMTHF	H_2O (0.17)	60	10	100	96	4.0	294
Cu–ZnO	HMF	BHMF	1,4-Dioxane (0.34)	100	15	100	99	11.8	295
Cu–Zn nanoalloy	HMF	BHMF	Ethanol (0.2)	120	70	100	95	12.5	296
Ni–Al@LDH	HMF	BHMTHF	H_2O (0.04)	80	20	100	99	4.8	297
Ni-Fe@CNT	HMF	BHMF	1-Butanol (0.2)	110	30	100	96	4.3	298
Ni–Al_2O_3	HMF	BHMTHF	1,4-Dioxane (0.34)	60	60	100	96	9.5	299
RANEY® Cu[h]	HMF	BHMF	H_2O (0.08)	90	90	94	92	1.48[i]	300
Pd@SiO_2 + Ir-ReO_x@SiO_2[h,j]	HMF	BHMTHF	H_2O/THF (0.08)	100	30	100	77	0.37[k]	301
K-Cu@Al_2O_3[h]	HMF	BHMF	Ethanol (0.24)	120	20	99	99	0.30	302
Ru@SiO_2 + Nb_2O_5–PO_4[h,j]	Fructose	BHMTHF	Cyclohexane (0.17)	160	40	98	41	3.3[l]	304
Ru@SiO_2 + Nb_2O_5–PO_4[h,j]	Glucose	BHMTHF	Cyclohexane (0.17)	160	40	32	63	1.68[l]	304
Ru@SiO_2 + Nb_2O_5–PO_4[h,j]	Inulin	BHMTHF	Cyclohexane (0.17)	160	40	96	33	2.6[l]	304
Cu–SiO_2	HMF	BHMTHF	1-Butanol (0.79)	100	15	95	98	20.2	307
HY + HT-Cu@ZnO@Al_2O_3[h,j]	HMF	BHMF	GBL/H_2O (0.19)	140	10	n.a.	48	0.002[m]	308
NiO	HMF	BHMF	2-Propanol (0.1)	150	—[n]	77.9	94	3.1	311
Ru@Co_3O_4	HMF	BHMF	2-Propanol (0.03)	170	—[n]	94	85	0.19	312
Zr-Ba oxide	HMF	BHMF	2-Propanol (0.06)	150	—[n]	98	92	2.9	313
Al_7Zr_3@Fe_3O_4	HMF	BHMF	2-Propanol (0.2)	180	—[n]	83	86	4.4	315
Hf-TPA	HMF	BHMF	2-Butanol (0.13)	130	—[n]	99	98	3.8	316
K_2CO_3	HMF	BHMF	2-MeTHF (0.25)	25	—[o]	100	94	17.7	317
KF	HMF	BHMF	DMSO (0.25)	25	—[o]	99	99	5.4	318
Amberlyst-15 + KF[j]	Fructose	BHMF	DMSO (0.25)	25	—[o]	99	89	7.3[p]	318

[a] See Section 4.2 for labelling and abbreviations. [b] Reaction solvent, substrate concentration (M) in brackets. [c] Substrate conversion. [d] Selectivity to the product indicated. [e] Catalyst productivity to the product indicated. [f] Homogeneous-phase catalysts. [g] Calculated with respect to the amount of Ru. [h] Under continuous flow conditions. [i] First of a two-step process. [j] Mechanical mixture. [k] Calculated with respect to the Ir catalysts. [l] Calculated with respect to the amount of Ru@SiO_2 catalyst. [m] Calculated with respect to the amount of HT-Cu@ZnO@Al_2O_3 catalyst. [n] Catalytic transfer hydrogenation. [o] Reduction by silanes. [p] Calculated with respect to the amount of KF.



Bispyridine DTBM-SEGPHOS

Scheme 12 Structures of bipyridine and DTBM–SEGPHOS ligands.

gave BHMF and BHMTHF from aqueous HMF in 93% and 95.3% yield, respectively, by a simple change in the reaction temperature (from 50 °C to 100 °C) and hydrogen pressure (from 30 bar to 50 bar).[287] The same catalyst gave BHMF in 73% (100 °C and 50 bar H_2) using a crude HMF-rich hydrolyzate mixture from fructose dehydration as a substrate. Ru nanoparticles immobilized onto carbon nanofibers (CNF) were used in the hydrogenation of HMF in 2-butanol.[288] BHMF was obtained in 82% yield at 86% HMF conversion at 150 °C and 20 bar H_2. On the other hand, $Ru(OH)_x@ZrO_2$ in 1-butanol gave BHMF in 99% yield at full HMF conversion at 120 °C and 15 bar H_2.[289] A turnover frequency (TOF) of 304 h^{-1} was calculated, in that case. The catalyst could be recovered and reused five times with no significant loss of activity, after acetone/NaOH washings. Heterogeneous catalysts based on noble metals other than Ru (Pd, Pt) were reported for the synthesis of BHMTHF with high selectivity.[290] This approach can be rationalized in terms of the different affinities toward C–O (Pt, Ru), rather than C=C bond hydrogenation (Pd, Rh).[291,292] In a recent study, a palladium catalyst immobilized onto amine-functionalized metal–organic frameworks [Pd@MIL-101(Al)-NH_2] was used to obtain a 96% yield of BHMTHF, at full conversion of aqueous HMF, under mild reaction conditions (30 °C, 10 bar H_2). The choice of metal–organic framework supports was motivated by their tunable physicochemical properties. In that case, amine group functionalization resulted in the modification of the nanoparticle dispersion and acidity/basicity of the catalyst, hence in its selectivity, due to the stronger hydrogen bonding interaction between MIL-101(Al)-NH_2 and the intermediate BHMF, instead of HMF (Scheme 13).[293] Comparable results in terms of conversion (>99%) and BHMTHF selectivity (96%) were obtained using Pd catalysts immobilized onto mesoporous graphitic carbon nitride (Pd@mpg-C_3N_4) under similar reaction conditions (water, 60 °C, 10 bar H_2).[294]

Use of non-noble catalysts (Cu, Ni) was investigated due to their low cost and higher hydrogenation activity toward C–O than C=C bonds. Thus, mineral-derived Cu/ZnO catalysts

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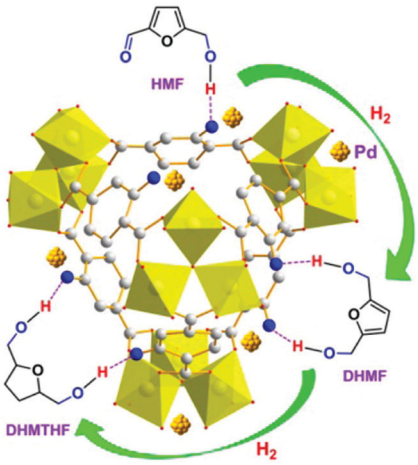

Scheme 13 Molecular interactions in the hydrogenation of HMF over Pd/MIL-101(Al)-NH_2. Gray and blue balls represent carbon and nitrogen atoms, respectively. The palladium nanoparticles are golden in color. Reprinted with permission from ref. 293. Copyright (2015) American Chemical Society.

(malachite, rosasite and aurichalcite) provided BHMF in 99% yield from HMF at 100 °C, whereas an increase in the reaction temperature to 220 °C afforded the fully C–O hydrogenated product 2,5-dimethylfuran.[295] A sharp decrease of the catalytic efficiency was observed after the first run, which was attributed to the deposition of the carbonaceous material on the catalyst surface. Cu/Zn nanoalloys with particle sizes <150 nm were employed to synthesize BHMF from HMF with an excellent yield (95%), at 120 °C and a high hydrogen pressure of H_2 (70 bar).[296]

A Ni–Al layered double hydroxide (LDH) bearing supported Ni nanoparticles (8–10 nm) was tested in the liquid-phase hydrogenation of HMF in water (0.4 M) at 80 °C and 20 bar H_2.[297] Complete conversion (96%) was achieved after 6 h, yielding a mixture of BHMF (25%) and BHMTHF (71%), however. Higher BHMTHF yields (>99%) were obtained upon increasing the reaction time to 12 h, whereas an increase of the reaction temperature promoted the formation of by-products *via* ring opening-cyclization (to 3-hydroxymethylcyclopentanone) and cross-polymerisation. Better BHMF yields (96%) were achieved using a carbon-nanotube (CNT)-supported bimetallic Ni–Fe catalyst at 110 °C, wherein 2,5-dimethylfuran formed preferentially at 200 °C (91% yield).[298] Hydrotalcite-derived Ni–Al_2O_3 catalysts were scrutinized in the hydrogenation of HMF to 2,5-dimethylfuran, BHMF and BHMTHF. Selectivity was found to be dependent on the calcination temperature, which was ascribed to the different dispersion of the surface metallic sites. The best results were obtained for BHMTHF (96% selectivity at full conversion) using catalysts calcined at 450 °C, 60 °C reaction temperature and 60 bar H_2.[299]

In a few studies, the catalytic hydrogenation of HMF was examined using continuous flow setups. A BHMTHF yield of 98% was obtained in two-stages, wherein two different catalysts were used sequentially, under the same reaction conditions: RANEY® Cu for the hydrogenation of HMF to BHMF, and RANEY® Ni for further hydrogenation to BHMTHF (90 °C, 90 bar H_2, water solution rate 0.05 mL min^{-1}).[300] The calculated productivity of BHMTHF was 1.45 mmol $g_{catalyst}^{-1}$ h^{-1} (based on BHMF, yield 98%). The intermediate BHMF stream showed an average 94% HMF conversion and 92% selectivity. Unfortunately, the catalytic activity decreased significantly after 32 h time-on-stream, due to RANEY® Ni deactivation. Lower BHMTHF yields (77%) were previously reported using double layered catalyst Pd@SiO_2/Ir-ReO_x@SiO_2, 100 °C, 50 bar H_2 and THF solvent.[301] HMF in ethanol (0.24 M) was also hydrogenated by flowing through a potassium-doped Cu@Al_2O_3 catalyst at 120 °C, using a concurrent stream of H_2 (20 bar, 50 mL min^{-1}), to give BHMF in 98.9% yield.[302] The high efficiency was tentatively attributed to the fact that the addition of appropriate amounts of potassium improved the dispersion of copper and reduced the acidity of the catalyst, thus enhancing the catalytic activity, while suppressing unwanted side reactions. A totally selective hydrogenation of HMF to BHMF was achieved in the gas phase over Au-Cu@CeO_2 catalyst, using *in situ* generated hydrogen by dehydrogenation of 2-butanol.[303]

The synthesis of furanic diols was also sought by direct conversion of carbohydrates. Thus, a heterogeneous catalyst based on the combination of acid-treated Nb_2O_5 (HF and H_3PO_4) and hydrophobic Ru@SiO_2 catalyst (treated with trimethylchlorosilane) was used for the one-pot dehydration–hydrogenation reaction of diverse carbohydrates (mono-, di- and polysaccharides) (Scheme 5).[304] Niobic acid and its derivatives are well-known strong solid acids, featuring high tolerance to water and catalytic activity.[305,306] The best results in terms of conversion (98%) and selectivity to BHMTHF (41%) were obtained using fructose as a substrate (160 °C, 40 bar H_2, in cyclohexane.) Under the same conditions, the selectivity for glucose was 63%, at 32% conversion, however. Conversions and selectivities around 30–40% were achieved using disaccharides (sucrose, maltose, cellobiose). A high conversion value (96%), but lower selectivity (33%), was obtained using inulin polysaccharides. In order to foster the production of BHMF directly from fructose, an integrated batch process, consisting of dehydration over Amberlyst-15 and a further hydrogenation over a Cu–SiO_2 nanocomposite in 1-butanol, was developed.[307] Highly concentrated fructose (15 wt%) gave HMF in 95% yield at 100 °C. The HMF feed obtained after extraction was hydrogenated with Cu–SiO_2 (50% Cu), to give BHMF in 88% yield. A continuous process for the direct conversion of fructose to BHMF was recently engineered, combining two catalysts in the same reactor: HY zeolite for the conversion of fructose to HMF, and hydrotalcite HT-Cu@ZnO@Al_2O_3 for the hydrogenation of HMF to BHMF.[308] The tandem dehydration–hydrogenation of fructose was achieved by pumping a fructose solution (3 wt%) in γ-butyrolactone/water, together with a H_2 stream. The effects of the water content, the reaction temperature and the fructose weight-hourly-space-velocity (WHSV) were examined, to give 48.2% yield of BHMF under optimized conditions (15 wt% water, 140 °C, 15 mL min^{-1} H_2 flow and of 0.02 h^{-1} WHSV).

Other approaches than H_2 hydrogenation were used to reduce HMF to BHMF or BHMTHF. For instance, catalytic transfer

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hydrogenation (CTH) is a conventional method previously applied to diverse biomass-derived substrates.[309,310] The strategy proved to be particularly useful in the selective synthesis of BHMF. The most successful heterogeneous systems recently reported include 3D-nanostructured NiO catalysts with a sea urchin-like morphology, yielding 74% BHMF at 150 °C,[311] and Ru@Co_3O_4, yielding 80% BHMF at 170 °C,[312] both using 2-propanol as a hydrogen source. Better BHMF yields (91%) were obtained in 2-propanol at 150 °C using a mixed Zr-Ba oxide catalyst supported on SBA-15 mesoporous silica.[313] The efficiency of the mixed catalyst was attributed to the negligible amount of Brønsted acidic sites, usually favoring etherification side-reactions, and to the content of Lewis acidic sites, promoting the reduction of HMF *via* a Meerwein–Ponndorf–Verley mechanism.[314] Despite its moderate BHMF yield (71%), the magnetically recoverable catalyst Al_7Zr_3@Fe_3O_4 was particularly interesting in terms of ease of separation from the reaction mixture and reuse.[315] Recently, an excellent (96.8%) yield of BHMF was achieved in 2-propanol at 130 °C, using a large amount of Hf-TPA catalyst (50 wt%) prepared from hafnium tetrachloride and diethylene triamine penta(methylene)phosphonic acid (TPA).[316] The high catalytic efficiency was attributed to the synergistic effect of Hf^{4+} Lewis acidic sites and O^{2-} Lewis basic sites, in that case. The catalyst could be easily recovered and reused for five successive recycles, without activity drops.

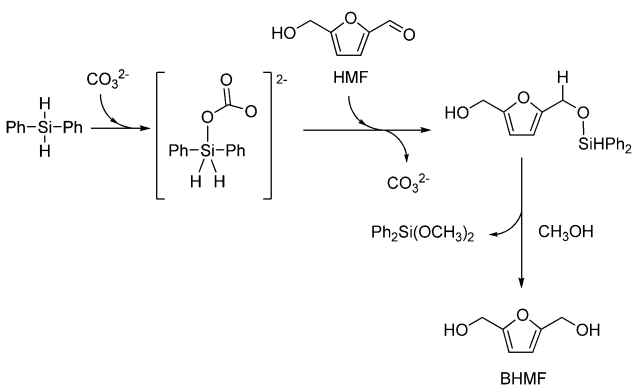
Silanes were used as cheap and easy-to-handle reducing agents. A K_2CO_3-catalyzed conversion of HMF to BHMF in 94% yield was reported at room temperature, using diphenyl silane as reagent and bio-based 2-methyltetrahydrofurane as solvent.[317] Although an irritant and a high-boiling point liquid, Ph_2SiH_2 avoids usual noble metal-based hydrogenation catalysts and high H_2 pressures. A mechanism was speculated in which a carbonate-promoted hydride transfer from silane to the aldehyde group occurs, to afford a siloxane intermediate that gives BHMF after reaction quenching with methanol (Scheme 14). Use of potassium fluoride as a catalyst and polymethylhydrosiloxane (PMHS) as a hydrogen donor was described, providing BHMF in 95% yield with a TOF of 4.2 h^{-1} at room temperature.[318] The catalyst could be reused over five runs, without activity loss. An increase of the reaction temperature to 80 °C resulted in 98% yield. A two-step, one-pot process for the direct conversion of fructose to BHMF in 88% yield was also achieved, combining Amberlyst-15 for the dehydration of the sugar to HMF at 120 °C, and KF/PMHS, for the hydrogenation step at room temperature.

4.3. Other compounds

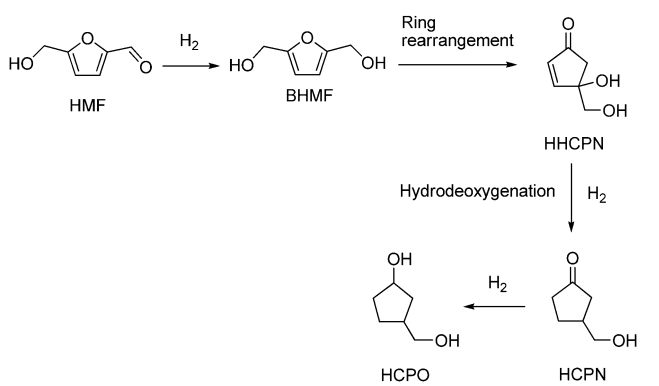
The synthesis of other alicyclic compounds, potential functional substitutes of BPA, such as 3-hydroxymethylcyclopentanol (HCPO) which is currently produced from petrochemicals,[319,320] has recently been reported using HMF as a substrate in water. Use of a catalyst composed of a mechanical mixture of Pt@$SiO_2$and Nd_2O_3 gave HCPO in 88% yield, through a multi-step, one-pot process based on Pt-catalyzed hydrogenation of HMF to BHMF, Lewis acid-catalyzed Piancatelli ring-rearrangement to 4-hydroxy-4-(hydroxymethyl)-cyclopenten-2-one (HHCPEN), and successive acid-catalyzed hydrodeoxygenation and hydrogenation to HCPO, at 140 °C and 30 bar H_2 (Scheme 15).[321] Similarly, HCPO was obtained in higher yield (94%) using Co@Al_2O_3 as a bifunctional catalyst at 140 °C and 20 bar H_2.[322]

In a different approach, homo- or cross-coupling of HMF with furfural (see Section 6) was catalyzed to give furoin-type difuranics, usable in the synthesis of polyurethanes and polyesters.[323,324] Thus, organocatalytic homocoupling of HMF using TPT-OMe (5-methoxy-1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazoline) gave the triol DHMF shown in Scheme 16 (95% yield), which could then be oxidized (MnO_2 or air, 95–86% yield)[325,326] or reduced ($NaBH_4$, 63% yield),[327] to give the diol BHF and the tetraol BHMH, respectively. Furfural–HMF cross-coupling, catalyzed by N-heterocyclic carbene (NHC) in the presence of a base, gave C11 furoins in around 60% yield.[328] The production of C10 and C12 furoins could be significantly improved to 97% yield by using an azolium catalyst grafted onto either silica or Merrifield resin.[329]

It must be mentioned that *p*,*p*′-diphenolic acid (DPA) was previously proposed as a BPA substitute from biomass. DPA can be produced from levulinic acid and phenol using mineral acids (HCl, H_2SO_4),[330] Brønsted acidic ionic liquids,[331] heteropolyacids[332] and sulfonated polymer[333] catalysts (Scheme 17). Levulinic acid and alkyl levulinates are obtainable from woody raw materials, particularly non-edible agricultural wastes, and from biorefinery side-streams.[334] Technologies are nowadays



Scheme 14 Proposed mechanism for carbonate-catalyzed reduction of HMF by Ph_2SiH_2.



Scheme 15 Catalytic synthesis of HCPO from HMF.

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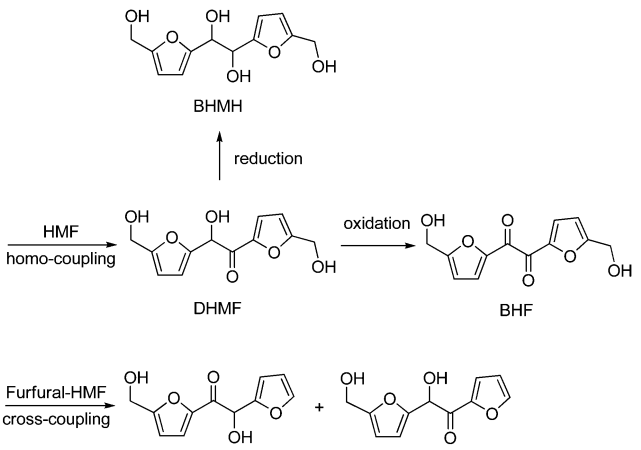
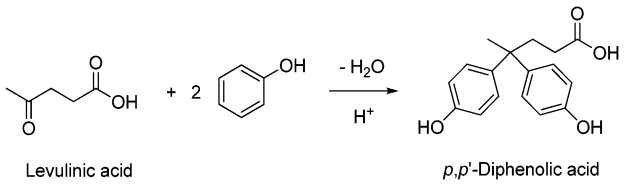


Scheme 16 Catalytic coupling syntheses of bis-furanic diols.



Scheme 17 Synthesis of DPA.

available for the production of levulinic acid on a tons per day scale by acid-catalysed dehydration of cellulose sugars.[335,336] Polyether ketones containing DPA units,[337] as well as polyethers bearing DPA pendant groups,[338] have been synthesized.

Table 3 summarises the main features of the catalytic processes detailed in the present review which lead to proposed BPA substitutes from other cellulose-derived sources.

5. Substitutes from the lignin depolymerisation chain

Lignin is extracted from biomass using different processes that greatly influence its structure and composition.[339,340] Methods have then been developed to depolymerise and fragment lignin into a huge variety of smaller aromatic molecules, usually referred to as lignin-derived platforms, whose nature depends on the native biomass and the deconstruction method used.[341,342] Selected examples are shown in Scheme 18. These lignin platforms may be categorised according to the monolignol G, H and S units from which, at least formally, they are derived (Scheme 4).[343,344] A detailed description of the several strategies, techniques and processes to extract, fraction (particularly *via* reductive catalysis)[345,346] and depolymerise lignin is outside the scope of the present review and can be found elsewhere.[347,348] As lignin is by far the most abundant renewable source of aromatic platforms,[349,350] exploding interest has been recorded in recent years toward lignin valorisation.[351,352] The lignin biorefinery concept has equally become of increasing importance.[353,354]

Several possibilities exist to convert lignin platforms into building blocks for polymers, taking advantage of the multiple functionalities that they feature: phenolic, aromatic and side-chain.[355,356] Catalytic methods for the synthesis of diol building blocks will be considered in the present review. Other compounds (*e.g.* epoxies, esters, ethers) can then be obtained by further functionalisation.[357,358] It must be underlined, however, that most proposed BPA substitutes from lignin are based on bis-phenolic moieties that, with few notable exceptions, are still obtained by means of classical organic processes using noxious reagents and/or solvents, *e.g.* coupling reactions by carcinogenic formaldehyde. The development of innovative scaffolds and synthetic strategies is thus strongly desirable, including improved heterogeneous catalysts.

5.1. Substitutes from coniferyl-derived compounds

5.1.1. Vanillin-derived substitutes. One of the most important lignin-derived platforms is vanillin and its direct derivatives (vanillic acid, vanillyl alcohol, 2-methoxyhydroquinone, creosol), together referred to as "vanillin platforms".[359]

A reason for that lies in the usual difficulty of separating and recovering aromatic compounds, with purities and yields attractive for commercial applications, from lignin-depolymerisation streams.[360] Indeed, vanillin is the highest volume, and one of the few, aromatic molecules currently produced on an industrial scale from lignin. To date, the vanillin obtained from lignosulfonates has accounted for around 15% of the total vanillin market (*ca.* 20 000 tons year^{-1}).[361,362] The remaining amount is still produced from oil, through the catechol–guaiacol process.[363,364]

Table 3 Summary of recent catalytic systems for proposed BPA monomeric replacements from other cellulose-derived sources[a]

Catalyst	Biomass-derived substrate	Product	Reaction conditions: Solvent[b] (M)	T (°C)	H_2 (bar)	Conv.[c] (%)	Sel.[d] (%)	Prod.[e] ($mmol_{prod}$ g_{cat}^{-1} h^{-1})	Ref.
$Pt@SiO_2$ + Nd_2O_3[f]	HMF	HCPO	H_2O (0.07)	140	30	100	88	0.6[g]	321
$Co@Al_2O_3$	HMF	HCPO	H_2O (0.04)	140	20	100	94	1.8	322
TPT-OMe	HMF	DHMF	CH_2Cl_2 (3.2)	40	—	100	95	573.6	327
MnO_2	DHMF	BHF	THF (0.1)	r.t.	—	100	95	0.27	327
DBU	DHMF	BHF	THF (0.1)	60	—	100	86	4.7	327
NHC + NEt_3	Furfural-HMF	C11 furoin	Free	80	—	95.2	34	2.6[h]	328

[a] See Section 4.3 for labelling and abbreviations. [b] Reaction solvent, substrate concentration (M) in brackets. [c] Substrate conversion. [d] Selectivity to the product indicated. [e] Catalyst productivity to the product indicated. [f] Mechanical mixture. [g] Calculated with respect to the Pt catalyst. [h] Calculated with respect to NEt_3.

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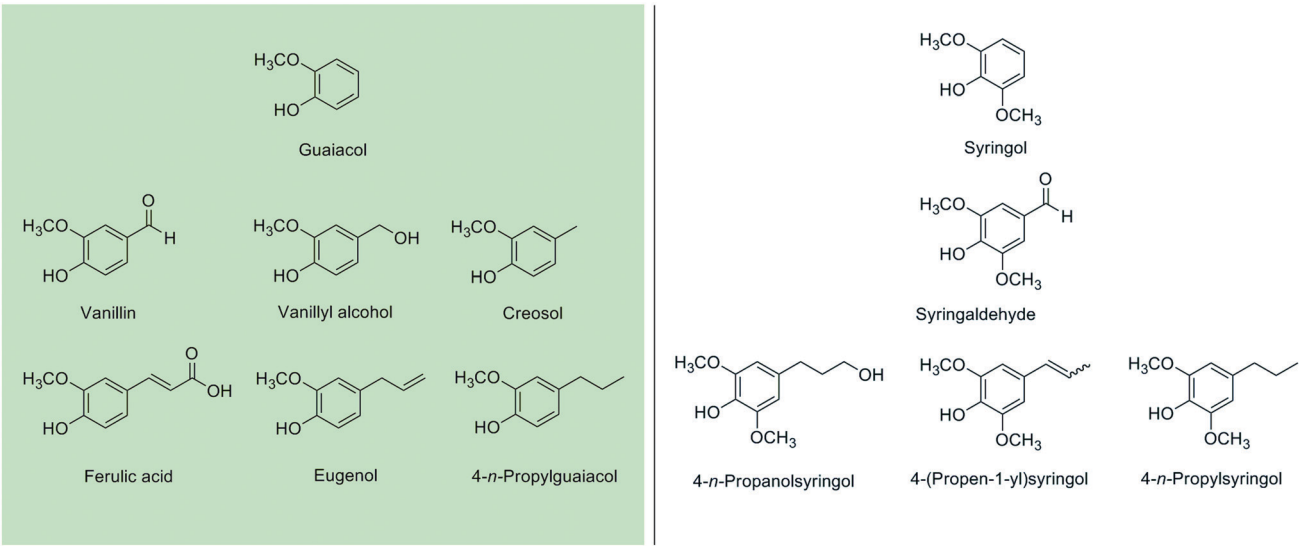

Scheme 18 Some aromatic molecules obtained from lignin deconstruction processes and used in the production of monomeric substitutes of BPA.

Lignin-to-vanillin processes have been detailed in a recent account.[365]

The building blocks prepared from vanillin platforms, and the bio-polymers thereof, have been exhaustively reviewed up to 2017.[366,367] These building blocks include divanillin (by enzymatic catalysis)[368,369] and the corresponding methylated diol,[370] *meso*-hydrovanilloin,[371] vanillin acetals (**1** and **2**),[372,373] polyaromatic Schiff-bases[374,375] and C1-bridged[376,377] and C2-bridged diphenols (**4** and **5**)[378] shown in Scheme 19. Catalytic steps in the syntheses of these compounds from platform molecules were limited to C=C side-chain hydrogenation, over conventional PtO_2 catalysts,[377] and acid-catalysed acetalisations (by *p*-toluenesulfonic acid). The various coupling methods leading to these building blocks have been described in a recent survey.[379] It is worth mentioning, however, that the synthesis of bisguaiacol F (BGF) isomers has recently been reported *via* the acid-catalysed condensation of vanillyl alcohol with guaiacol, as safer alternatives to formaldehyde, with the preferential formation of the *p*,*p*′-BGF isomer (70% yield, 82% purity, Scheme 20). Use of the solid acid resin catalyst Dowex DR2030 adds significant benefits to the method.[380] A later study showed that the estrogenic activity of these BGF isomers was lower than that of BPA, thus suggesting their potential as viable alternatives to BPA.[381,382] A number of vanillin-based bis-epoxides,[383,384] polycarbonates and polyesters[385,386] have been made available from the above mentioned scaffolds.

More recently, a diol with a spirocyclic acetal structure (**3**) was obtained by alkali treatment of **2** with ethylene carbonate.[387] Therein, the greenhouse gas emissions generated by the production of **3** were evaluated to be around one-half of those related to BPA. Copolymerization of **3** with 1,6-hexanediol and dimethyl terephthalate resulted in copolyesters showing improved glass transition temperature and thermal stability, upon incorporation of the spiroacetal unit. The synthesis of the bisphenol carbonate BHMC shown in Scheme 21 was also reported, however using an un-catalysed reaction sequence, chlorinated and THF solvents and toxic phosgene reagent.[388]

5.1.2. Substitutes from ferulic acid. Ferulic acid is the second monophenolic compound produced from lignin by volume.[389,390] It is highly abundant (predominantly the *trans* isomer) in the cell walls of flowering plants, as well as in sugar beet and sugar cane.[391,392]

Ferulic acid was previously reported as a substrate in the synthesis of homopolymers mimicking the thermal properties of polyethylene terephthalate (PET), *i.e.* poly(dihydroferulic acid), *via* Pd@C hydrogenation, followed by $Zn(OAc)_2$ polymerisation (Scheme 22).[393] More recently, a ferulic acid-derived bisphenol containing an isosorbide core (Section 4.1), namely bis-*o*-dihydroferuloyl isosorbide (IDF), was reported *via* two-step acid-catalysed esterification and Pd@C-catalysed hydrogenation of ferulic acid in ethanol, followed by lipase-mediated transesterification with isosorbide (Scheme 23).[394] The as-prepared macromonomer was used in the synthesis of polyesters.[197]

5.1.3. 4-*n*-Propylguaiacol. A valuable product of softwood lignin catalytic depolymerisation is 4-*n*-propylguaiacol.[395] Brønsted acid-catalysed condensation of 4-*n*-propylguaiacol with formaldehyde, by either homogeneous HCl[396] or heterogeneous zeolites (FAU-40),[397] afforded the bisguaiacol 5,5′-methylenebis-(4-*n*-propylguaiacol) (*m*,*m*′-BGF-4P) represented in Scheme 24, in moderate yield and high purity (minor amounts of *o*,*m*′ and *o*,*o*′ regioisomers were detected). As for other condensation or dehydration processes (Section 4.1.1), the rationale for the use of acidic zeolite catalysts is to avoid unrecoverable mineral acids (*e.g.* HCl, H_2SO_4) or thermolabile sulfonated resins (*e.g.* Dowex, Amberlyst) often used to this aim. The benefits of zeolites include their thermal stability, high Brønsted acidic-site density and ease of recovery. Indeed, the zeolite catalyst could be easily separated and reused, unfortunately showing a significant loss of activity, which can be regenerated by coke burn-off. Common shortcomings of zeolites are the limited site accessibility and mass transfer of large substrates, due to their intrinsic microporous structure, that can be partially circumvented by the introduction of additional mesoporosity. Noteworthily, *m*,*m*′-BGF-4P showed

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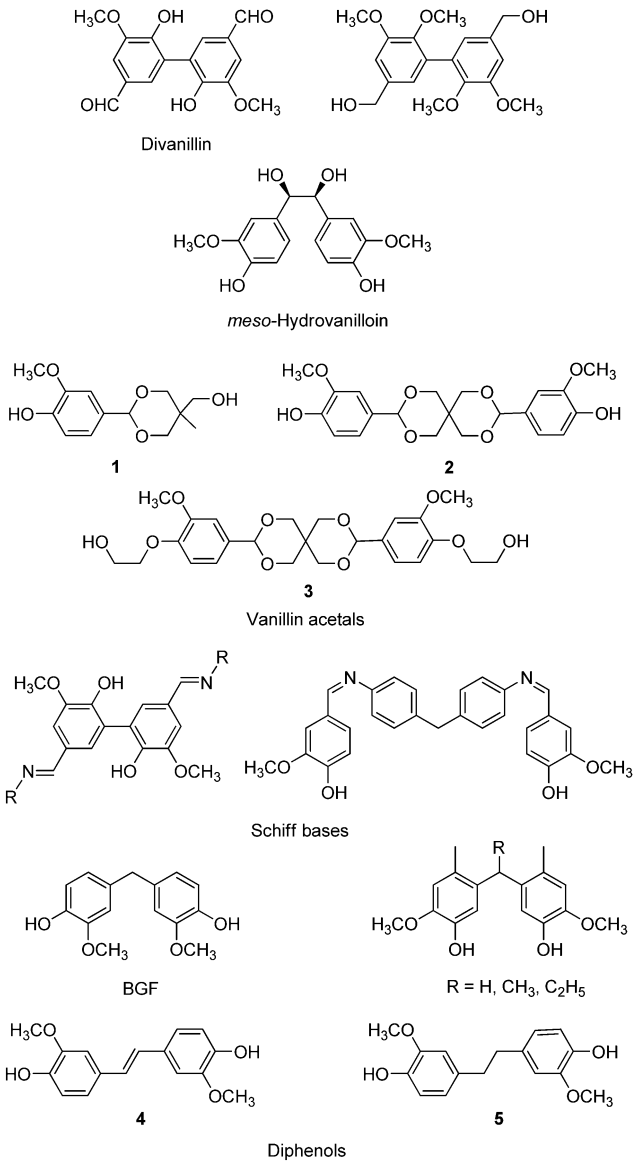
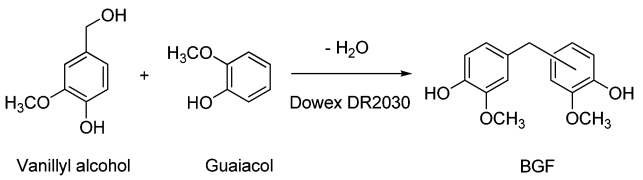
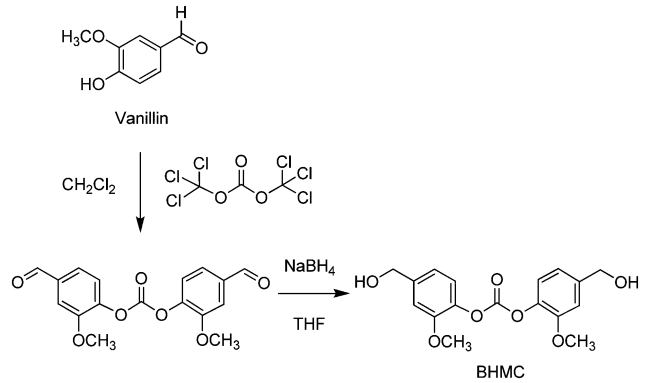


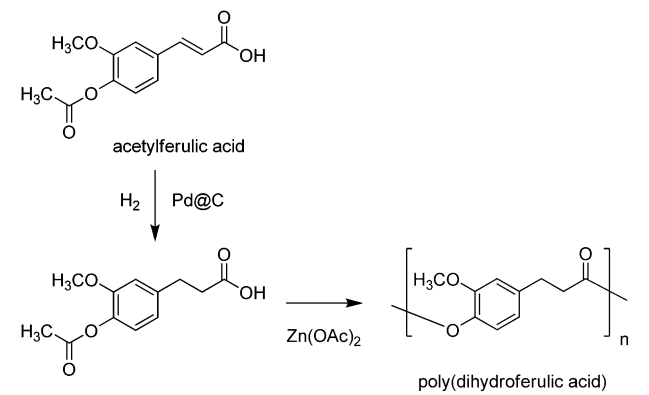
Scheme 19 Some diol building blocks prepared from vanillin platforms.



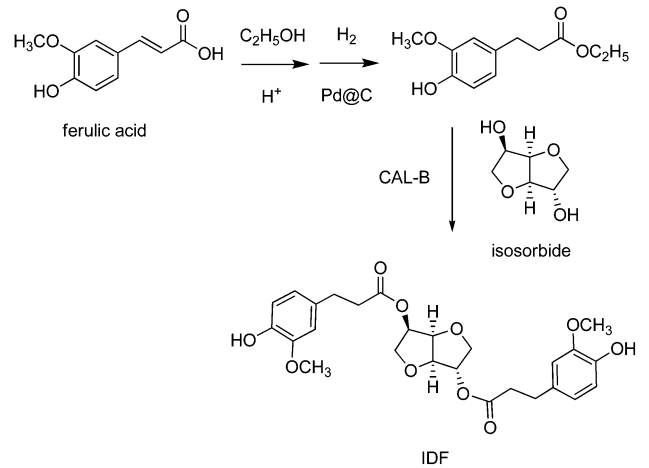
Scheme 20 Synthesis of BGF isomers from vanillyl alcohol and guaiacol.



Scheme 21 Synthesis of BHMC from vanillin.



Scheme 22 Synthetic pathway to poly(dihydroferulic) acid.



Scheme 23 Synthetic pathway to IDF from ferulic acid.

reduced estrogenic receptor activity compared to BPA. This finding, together with the similar one previously reported for BGF, suggests that the presence of methoxy groups in the *ortho* position strongly decreases the ability to bind and/or activate estrogen receptors in alkylphenols, which was attributed to steric hindrance.[398,399] Polycarbonates (T_g 99 °C), cyanate ester (T_g 193 °C)[396] and a variety of epoxy resins were prepared from *m*,*m*′-BGF-4P.[400,401] The increase of the length of the phenolic side-chain did not affect significantly the yield of polycarbonates (around 60% for the *n*-propyl, ethyl and methyl monomers), whereas it lowered their tendency to crystallize and their glass transition temperature and improved their solubility in common organic solvents.

5.1.4. Eugenol. Eugenol (and iso-eugenol) can be isolated from lignin and, in higher amounts, from the essential oils of several plants.[402,403] About 2000 tons of eugenol are produced

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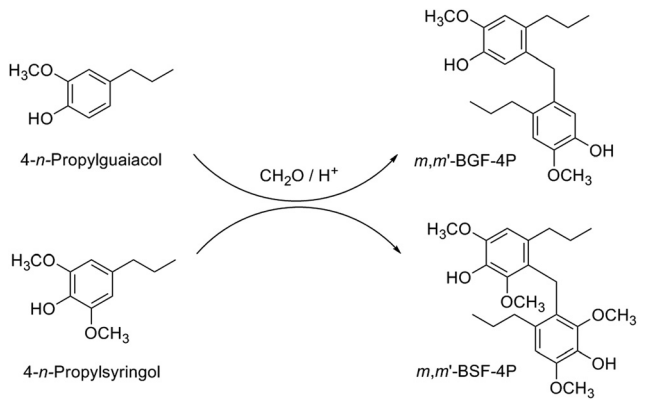
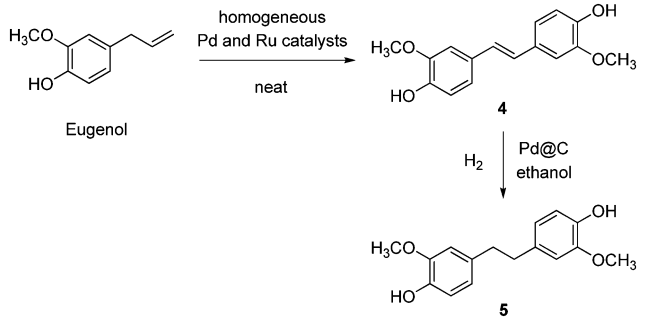


Scheme 24 Synthesis of C1-bridged diphenols from propylguaiacol and propylsyringol.



Scheme 25 Catalytic metathesis-hydrogenation pathway to C2-bridged diphenols.

yearly from clove oil.[404] These molecules may be used in the synthesis of polymer building blocks.[405]

Thus, the dihydroxystilbene **4** and its di(hydroxyphenyl)-ethane **5** analogue were prepared from eugenol, *via* a catalytic process involving isomerising metathesis and C=C bond hydrogenation, respectively (Scheme 25).[406] A combination of Pd isomerisation ($[Pd(\mu\text{-}Br)(t\text{-}Bu_3P)]_2$) and Ru metathesis (Hoveyda–Grubbs type) homogeneous catalysts was required for the first step, whereas the second step was accomplished over conventional Pd@C. Compared to the previously reported synthesis from vanillin,[378] the benefits of the approach are use of safer solvents (ethanol), a simpler purification procedure, an entirely catalytic protocol, potential for a one-pot process, and use of a less expensive hydrogenation catalyst (Pd *vs.* Pt). As for most homogeneous-phase catalysts, the drawbacks include the non-reusability of expensive metal complexes. Both **4** and **5** were found to be non-estrogenic. Polycarbonate and thiol–ene polymers were prepared from these monomers. Polycarbonates were obtained in *ca.* 80% yield by reacting the monomers with diphenyl carbonate and catalytic LiOH at 180 °C, showing lower molecular weights compared to the BPA analogue and T_g 127 °C and 81 °C, respectively.

Table 4 summarises the main features of the catalytic processes described in the present review leading to proposed BPA substitutes from coniferyl-derived compounds.

5.2. Substitutes from sinapyl-derived compounds

Various sinapyl-derived molecules (including syringaldehyde, 4-*n*-propylsyringol, 4-*n*-propanolsyringol, and 4-propenylsyringol) can be obtained with remarkable selectivity by lignin depolymerisation through catalytic oxidation or reduction processes,[407,408] particularly hydrogen-free fractionation of woody biomass over Pd@C catalysts[409] and lignin-first strategies.[410,411]

Enzymatic oxidative dimerization of sinapyl alcohol, either from lignin degradation or by chemical reduction of sinapic acid, affords syringaresinol (SYR) in very high yield.[412] SYR is a naturally occurring phenol that can be found is small quantities in some flowering plants.[413,414] It can also be obtained by chemical methods from sinapyl alcohol *via* multistep reaction processes and using stoichiometric amounts of peracids or potassium ferricyanide, however.[415,416] The structure of SYR consists of a rigid *cis*-fused bis-tetrahydrofuranic ring and two pendant syringol units (Scheme 26). Its rigid core makes it a good functional substituent candidate for BPA. Compared to IDF, featuring a similar bisfuran core (Scheme 23), SYR lacks the flexibility of the aliphatic ester side-chain. Indeed, poly(hydroxy)urethanes[417] and epoxy-amine resins were synthesized based on the epoxy derivative SYR-EPO, showing better thermal properties compared to parent IDF-based resins.[418] Syringaresinol showed no endocrine disruption activity.

5.2.1. Syringaldehyde. Bisphenols having structures with diverse flexibilities were synthesized from syringaldehyde, *via* a two-step process comprising uncatalysed Wittig olefination (step 1), followed by either HCl treatment or acid-catalysed (*p*-TsOH) addition of di(trimethylolpropane) (DTMP) (step 2), to

Table 4 Summary of recent catalytic systems for proposed BPA monomeric replacements from coniferyl-derived compounds[a]

Catalyst	Biomass-derived substrate	Product	Reaction conditions: Solvent[b] (M)	T (°C)	H_2 (bar)	Conv.[c] (%)	Sel.[d] (%)	Prod.[e] ($mmol_{prod}\ g_{cat}^{-1}\ h^{-1}$)	Ref.
Dowex DR2030	Vanillyl alcohol	*p*,*p*′-BGF	Free	60	—	70	82	0.5	380
K_2CO_3	Vanillin acetal **2**	**3**	DMF (0.4)	160	—	100	90	9.1	387
Pd@C + CAL-B	Ferulic acid	IDF	Ethanol (1.4)	r.t. + 75	1	100	72	n.a.	197
FAU-40	4-*n*-Propylguaiacol	*m*,*m*′-BGF-4P	Toluene (0.5)	100	—	40	80	4.3	397
Pd + Ru complexes[f]	Eugenol	**4**	Ethanol (0.3)	70	—	100	81	n.a.	406
Pd@C	**4**	**5**	Ethanol (0.3)	50	7	100	95	19.1	406

[a] See Section 5.1 for substrate and product numbering and labelling. [b] Reaction solvent, substrate concentration (M) in brackets. [c] Substrate conversion. [d] Selectivity to the product indicated. [e] Catalyst productivity to the product indicated. [f] Homogeneous-phase catalysts.

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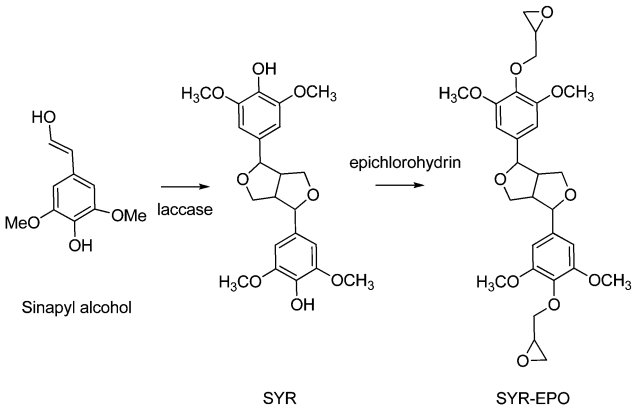
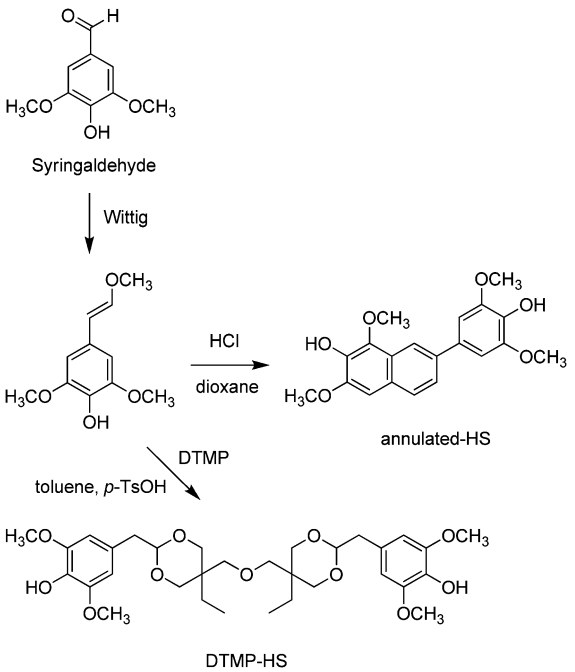


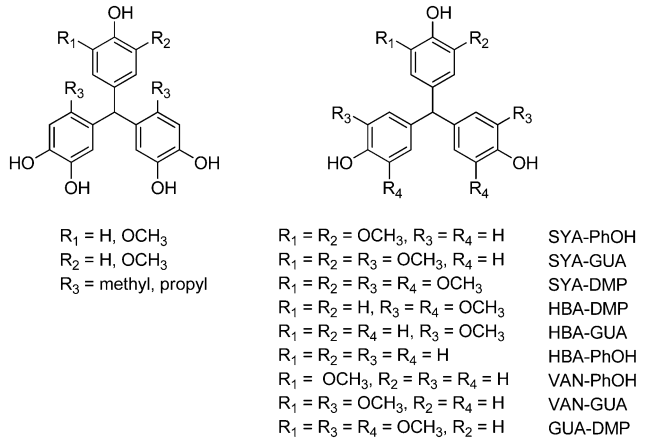
Scheme 26 Catalytic synthesis of SYR and the structure of the epoxy derivative SYR-EPO.



Scheme 27 Two-step synthesis of bisphenols from syringaldehyde.

give the annulated-HS and the bis-acetal DTMP-HS products shown in Scheme 27, respectively.[419] These compounds could also be obtained directly from lignin after selective degradation in methanolic H_2SO_4, in much lower yields, however. The corresponding bis-epoxy based resins were also synthesized, showing glass transition temperatures of 130 °C and 67 °C, respectively.

A series of highly rigid triphenylmethane polyphenols (TPs), bearing a various number of methoxy and alkyl substituents, were prepared by conventional acid-catalysed condensation of lignin-derived aldehydes (including syringaldehyde and vanillin) and bio-based phenols (guaiacol, syringol, catechols).[420,421] Their structures are reported in Scheme 28. The benefits of the method include the use of aromatic aldehydes as bridging reagents, thus avoiding toxic formaldehyde usually employed for this purpose. However, an excess of concentrated H_2SO_4 (*ca.* 3 : 1) was required



Scheme 28 Structures of triphenol TPs.

to achieve yields in the range 5–69%, which decreased upon increasing the number of methoxy substituents. This clearly reduces the feasibility of bulkier TPs as precursors for polymers. Indeed, epoxy thermosets were prepared using TPs with up to four methoxy groups, which exhibited excellent glassy moduli and glass transition temperatures, which was attributed to the rigidity of the TP scaffold. An increase in the number of methoxy groups decreased the T_g value (132–118 °C) and the glassy modulus (2.7–2.2 GPa), in this case.

5.2.2. 4-*n*-Propylsyringol. Similar to that described above for 4-*n*-propylguaiacol, the bissyringol 5,5′-methylenebis(4-*n*-propylsyringol) (*m*,*m*′-BSF-4P) was isolated in 60% yield and 99% purity, by condensation of 4-*n*-propylsyringol (obtained by catalytic hydrogenolysis of hardwood lignin over Ru@C; a detailed study was provided) with formaldehyde using HCl as a catalyst (Scheme 24).[422] Compared to BPA, the bissyringyl scaffold showed lower potency and efficacy toward human estrogen receptor α. The presence of the bulky methoxy substituents in the 2,6-positions and the *para*-propyl side chain had two significant consequences: reduced tendency to form oligomers and high thermal resistance of the resulting polymers, which may be tentatively attributed to the hindered rotation. Indeed, *m*,*m*′-BSF-4P-based aromatic polyesters were synthesized in >90 wt% yield, showing glass-transition (157 °C) and degradation temperature ($T_{d,5\%}$ 345 °C) values among the highest reported for lignin-based thermoplastics.

Table 5 summarises the main features of the catalytic processes detailed in the present review which lead to proposed BPA substitutes from sinapyl-derived compounds.

6. Substitutes from the hemicellulose depolymerisation chain

Hemicellulose is a group of branched heteropolysaccharides containing mainly pentose (xylose, arabinose), as well as hexose units (galactose, glucose, mannose).[423,424] Hemicellulose is an amorphous polymer, hence more easily solubilised and attacked than cellulose. It represents a natural source of C5

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Table 5 Summary of recent catalytic systems for proposed BPA monomeric replacements from sinapyl-derived compounds[a]

Catalyst	Biomass-derived substrate	Product	Reaction conditions		Conv.[c] (%)	Sel.[d] (%)	Prod.[e] ($mmol_{prod}\ g_{cat}^{-1}\ h^{-1}$)	Ref.
			Solvent[b] (M)	T (°C)				
Laccase	Sinapyl alcohol	Syringaresinol	CH_3CN/H_2O[f]	50	100	93	30.4	412
p-TSA[g]	Syringaldehyde	DTMP-HS	Toluene/methanol (n.a.)	70	100	58	n.a.	419
H_2SO_4	Syringaldehyde	SYA-PhOH	Ethanol (0.6)	65	100	64	0.05	421
H_2SO_4	Syringaldehyde	SYA-GUA	Ethanol (0.6)	65	100	46	0.03	421
H_2SO_4	Syringaldehyde	SYA-DMP	Ethanol (0.6)	65		5[h]	n.a.	421
HCl	4-*n*-Propylsyringol	*m*,*m*′-BSF-4P	H_2O	100	100	60	n.a.	422

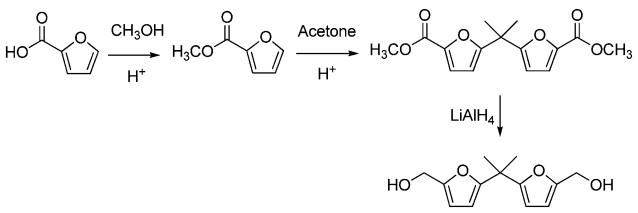
[a] See Section 5.2 for substrate and product numbering and labelling. [b] Reaction solvent, substrate concentration (M) in brackets. [c] Substrate conversion. [d] Selectivity to the product indicated. [e] Catalyst productivity to the product indicated. [f] Buffer. [g] Two-step reaction sequence, the first is an uncatalysed Wittig olefination. [h] Yield (%).

carbohydrate platform molecules (xylose, xylitol, furfural), which are accessible by hydrolytic depolymerisation,[425,426] followed by acid-catalysed dehydration or metal-catalysed reduction.[427,428] In particular, furfural is obtainable from hemicellulose-derived xylose *via* challenging threefold acid-catalyzed dehydration, at high temperatures.[429,430] Current production methods rely on aqueous phase mineral acid (H_2SO_4) treatment.[431,432] Several key industrial intermediates and consumer chemicals are then available through further furfural processing.[433,434]

Thus, a bis-furanic diol was reported earlier, having a structure resembling that of BPA, and obtained by classical organic reaction from furoic acid and acetone, *via* mineral acid-mediated coupling and unviable $LiAlH_4$ reduction (Scheme 29).[435] The parent epoxy derivatives were synthesized.

7. Substitutes from other biomass-derived sources

The catalytic synthesis of rigid diols has been described from naturally occurring, renewable raw materials other than lignocellulosic biomass. Table 6 summarises the main features of the catalytic processes hereinafter described leading to proposed BPA replacements from other biomass-derived sources.



Scheme 29 Synthesis of diols from furoic acid.

Cyclic terpenes and terpenoids are other important sources of non-petrochemical phenols. They are obtained on a thousands of tons per year scale from trees, from essential oils or as by-products of the food and paper industries.[436] Besides being extracted from plants, terpenoids may also be produced *via* chemical synthesis from terpenes. In particular, carvacrol is obtained from the essential oils of thyme and origanum,[437,438] and synthetically from bio-sourced limonene (found in citrus fruit oils).[439] The *p*,*p*′-isomer of the methylene-bridged bisphenol **6** shown in Scheme 30 was synthesized in high yields, by the HCl-catalyzed coupling of carvacrol with 1,3,5-trioxane.[440] The bisphenol was used as building block for polycarbonates, cyanate ester and epoxy resins[441] whose thermomechanical properties were evaluated, showing T_g values around 120 °C.

Cashew nut shell liquid (CNSL) is a non-edible waste product of the cashew nut industry, whose yearly production is around 450 ktons.[442,443] Crude CNSL consists of a mixture of phenol, resorcinol, 2,6-xylenol and salicylic acid derivatives having C-15 aliphatic side chains, with different unsaturation degrees.[444,445] The main component of refined CNSL is cardanol.[446] Several polymer and surfactant building blocks were prepared from cardanol. The topic has been reviewed in detail up to 2018.[447,448]

Lately, the cardanol-derived bisphenol 7 was prepared by conventional formaldehyde condensation using oxalic acid as a catalyst (Scheme 31).[449] This was used in the synthesis of thermosetting epoxy resins that showed higher tensile strength and impact strength compared to the BPA-based congener.

Table 6 Summary of recent catalytic systems for proposed BPA monomeric replacements from other biomass-derived sources[a]

Catalyst	Biomass-derived substrate	Product	Reaction conditions			Conv.[c] (%)	Sel.[d] (%)	Prod.[e] ($mmol_{prod}\ g_{cat}^{-1}\ h^{-1}$)	Ref.
			Solvent[b] (M)	T (°C)	H_2 (bar)				
HCl	Carvacrol	**6**	H_2O (0.9)	80	—	100	55	0.9	440
Oxalic acid	Cardanol	**7**	Free	100	—	n.a.	n.a.	n.a.	449
Pd@C	*trans*-Resveratrol	Dihydroresveratrol	THF	r.t.	0.5	100	98	n.a.	450
Cu/Zn/Al	4-Formylcyclohex-3-enecarboxylate	CHDM	Ethanol (0.6)	240	40	100	76	2.3	460

[a] See Section 7 for substrate and product numbering and labelling. [b] Reaction solvent, substrate concentration (M) in brackets. [c] Substrate conversion. [d] Selectivity to the product indicated. [e] Catalyst productivity to the product indicated.

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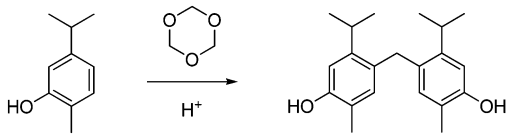
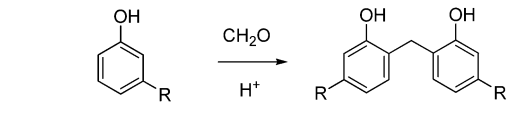
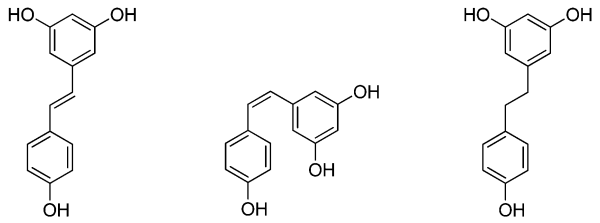


Scheme 30 Synthesis of carvacrol-derived bisphenol **6**.



Scheme 31 Synthesis of **7** from cardanol.

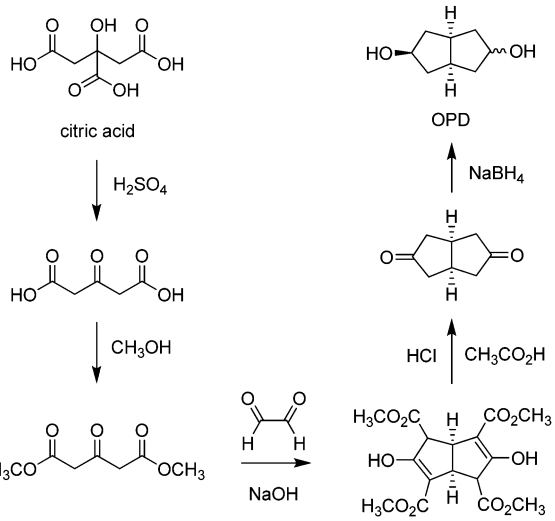


Scheme 32 Structures of resveratrols.

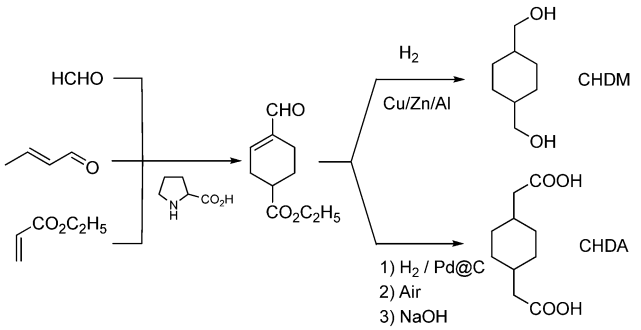
trans-Resveratrol, as well as its congeners *cis*-resveratrol and dihydroresveratrol, was used as a basis for cyanate ester thermosettings, showing very high T_g (>350 °C) and decomposition temperature (>400 °C), which are significantly higher than those of the BPA and BPE parents.[450] *trans*-Resveratrol is found in remarkable amounts in the skin of grapes, peanuts and Japanese knotweed.[451,452] The structure of *trans*-resveratrol, shown in Scheme 32, consists of a stilbene scaffold bearing three hydroxyl groups, from which the *cis* isomer and the dihydro-derivative can be obtained by UV irradiation[453] and usual Pd@C hydrogenation,[454] respectively.

Recently, several homo- and co-polymers were described containing the octahydro-2,5-pentalenediol (OPD) unit, which features a rigid bicyclic skeleton of fused cyclopentane rings (Scheme 33).[455,456] This scaffold was aimed at increasing the thermal stability of the isosorbide core (Section 4.1), while retaining a similar rigidity. OPD can be prepared from naturally occurring citric acid, *via* dimethyl-1,3-acetonedicarboxylate and glyoxal, through a multiple reaction sequence of classical, un-catalysed organic reactions.[457,458] Co-polycarbonates containing OPD, CHDM (see below) and diphenyl carbonate were synthesized, showing an increase in tensile modulus and glass transition temperature upon increasing the OPD content.[459]

It is worth mentioning that cyclohexane oxygenates, such as 1,4-cyclohexanedimethanol (CHDM) and 1,4-cyclohexanedicarboxylic acid (CHDA), were obtained from biomass-derived raw materials and used in the synthesis of copolyesters.[460] These



Scheme 33 Synthesis of OPD from citric acid.



Scheme 34 Biomass-derived synthesis of CHDM.

monomers are usually prepared by hydrogenation of oil-based phthalic acids under harsh reaction conditions. A mild two-step procedure using crotonaldehyde, formaldehyde and ethyl acrylate, from biomass fermentation/gasification processes, afforded CHDM in 76% yield, as sketched in Scheme 34. In the first step, a one-pot proline-catalyzed [3+1+2] cycloaddition gave 4-formyl-cyclohex-3-enecarboxylate, which was then hydrogenated over commercial Cu/Zn/Al catalysts (240 °C, 4.0 MPa H_2). An alternative hydrogenation, oxidation, and hydrolysis reaction sequence yielded 78% CHDA.

Although outside the timespan covered by the present review, it must be mentioned that BPA substitutes were also proposed from bio-sourced gallic acid (from hydrolyzable tannins found in several flowering plants),[461] hydroxytyrosol (from oleuropein found in argan oil, olive oil and olive leaves),[462] anethole and other substrates.

Anethole, predominantly in the *trans* form, is a flavouring aromatic compound found in the essential oils of several plants, including anise, fennel liquorice and star anise. The latter oil contains more than 90% anethole and it is produced on a hundreds of tons per year scale.[463] A peculiar rigid monomer has been reported based on a *cis*-fused ring diphenol (**8**) obtained from anethole in two steps: strong acid treatment,

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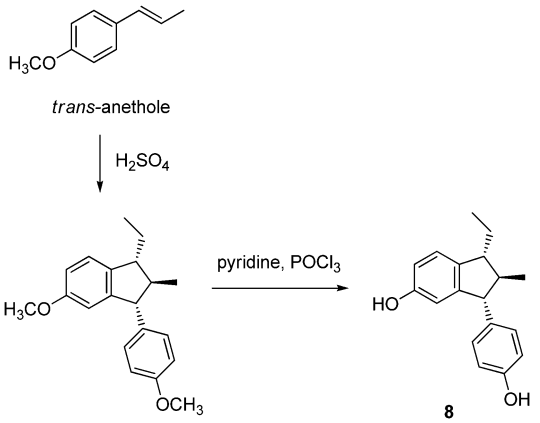
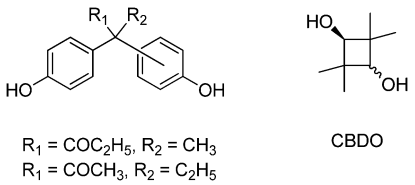


Scheme 35 Synthesis of diphenol **8**.



Scheme 36 Structures of 2,3-pentanedione-derived bisphenols and CBDO.

followed by demethylation (Scheme 35). Low overall yields were, however, observed, wherein stoichiometric use of dangerous reagents (H_2SO_4, pyridine, phosphorus oxychloride) was required.[464]

The bisphenols shown in Scheme 36 were obtained in good yields by the acid-catalysed condensation of phenol with lactic acid-derived 2,3-pentanedione.[465,466] In turn, lactic acid can be produced catalytically from bio-sourced polysaccharides.[467,468] Interestingly, homogeneous and heterogeneous sulfonic acid catalysts could be used for this purpose, wherein the reusability of insoluble ones (*e.g.* Nafion NR50) was demonstrated. The as-prepared bisphenols were coupled with PET to afford polyesters with improved thermal properties, compared to the BPA analogues.

2,2,4,4-Tetramethylcyclobutan-1,3-diol (CBDO, Scheme 36) and its derivatives have been recently used to replace BPA in commercial copolyesters, including Tritan™, PETF,[469] PPTF, PBTF[470] and PECTF.[471] The incorporation of these cyclic diols resulted in the improved thermal and mechanical properties of the polymers. However, CBDO is obtained from petroleum derived isobutyric anhydride.[472] In 2012 a synthesis of CBDO was proposed *via* Meldrum's acid, starting from bio-based malonic acid, through a complex eight-step procedure, wherein a catalytic C=C hydrogenation was achieved over Pd@C.[473]

Finally, it is worth mentioning that, while submitting the present review, at least two notable contributions appeared describing the selective hydrogenation of HMF to BHMF over a bimetallic Ni–Re@TiO_2[474] catalyst and the continuous flow hydrogenation of vanillin to vanillyl alcohol over Ni@porous nitrogen-doped carbon,[475] respectively. Further, the synthesis of the unconventional *m*,*p*′-BGF and *o*,*p*′-BGF isomers was achieved by condensation of guaiacol with bio-derived isovanillyl and *ortho*-vanillyl alcohol, respectively.[476] The oestrogenic activity of *p*,*p*′-BGF was also shown to be two orders of magnitude lower than that of the *p*,*p*′-BPF homologue, thus confirming the beneficial effect of *ortho*-methoxy substituents on the toxicity of bis-phenols. The readers may refer to the relevant literature for details.

8. Conclusions and future perspectives

Polymers are an important component of our society, contributing to the improvement of the quality of our life. Yet, they pose severe environmental issues.[477,478] Most commercial polymers are produced from fossil sources and disposed within relatively short periods, compared to the long time required for their biodegradation, if any. Still, they may contain or release components toxic to human health and the environment. An alternative and renewable supply of carbon feedstock is embedded in polysaccharides, lignin, terpenes, and other small molecules available from plants. From these matters it is possible to produce a large part of the chemicals currently manufactured form oil, including polymers. A clear industrial example is 2,5-furandicarboxylic acid, used to replace noxious terephthalic acid in plastic bottles, and obtained from biomass *via* glucose conversion.[479,480] Significant improvements are needed in the identification of abundant crops not competing with the food industry, including a better use of agricultural and forestry waste, and in the conversion of these crops into useful platforms through sustainable and safer processes.

Synthetic strategies for BPA replacements from biomass

A perusal of the literature highlights the great potential of catalysis, and the significant advancements achieved, in the synthesis of building blocks for polymers manufactured from biomass and its derivatives. A variety and a number of potential BPA substitutes have been made available through catalytic methods, using platform raw materials mostly originating from cellulose and lignin deconstruction processes. While cellulose is the source of furanic and alicyclic rigid diols, a spectrum of bis-phenols featuring hindered rotation is accessible from lignin. These bio-based diols have been demonstrated to be key building blocks in the design and synthesis of high-performance plastic materials, characterised by improved thermal and mechanical stabilities.

Since cellulose is a regular, monosaccharide-based polymer, a variety of catalysts and strategies have been developed allowing for the upgrade of cellulose-derived sugars to specific building blocks based on these units, each with its own advantages. Significant advancements were recently offered in the engineering of heterogeneous catalysts, often sophisticated, featuring high efficiency in the conversion of cellulose-derived platforms (sugar alcohols, HMF) to rigid diols, sometimes using concentrated aqueous solution feeds. Several catalytic systems have been

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demonstrated, enabling dehydration and hydrogenation steps. Still, by surveying the recent literature, a number of major challenges may be identified in this field. Challenge one: in order to be transferred from the bench to the industrial scale, catalysts should be available in appropriate amounts at competitive costs and, possibly, implemented into existing reactor plants. Therefore, a desirable achievement is the sustainable manufacture of heterogeneous catalysts based on non-critical support raw materials and non-noble metals.[481,482] Moreover, besides costs and efficiency, catalyst resistance is also considered as a crucial issue. Most reports claim catalyst recyclability; however, parameters such as selectivity drop, changes in reaction kinetics upon catalyst reuse, metal leaching, long-term productivity and the need for catalyst regeneration are not always evaluated quantitatively.[483,484] Challenge two: a major weakness of the above processes, particularly if intermediate conversion products are targeted, is selectivity under mild reaction conditions.[485] This is critical for industrial applications, wherein minimisation of energy inputs shall couple with reduced downstream processing (*i.e.* separation, purification). Use of organic solvents often used for this purpose,[486,487] as well as for the enhancement of substrate/product solubility, should also be avoided in favour of (concentrated) original water solutions. Great potential for selectivity improvement may be provided by catalysis under continuous flow conditions, because of the possibility for a careful control of reaction conditions, namely contact time with the catalyst and homogeneous heating.[488] Challenge three: design of novel catalysts enabling efficient multistep cascade processes in one-pot. This would open up the possibility for process intensification *via* direct conversion of cellulose to target chemicals, while avoiding intermediate conventional mineral acid depolymerisation protocols.[489] The engineering of truly heterogeneous bifunctional catalysts, wherein acidic and metal functionalities are comprised in a single catalytic body, will be both critical and intriguing to this aim. The efficiency of such catalysts is ruled by the fine tuning of diverse factors and their interplay: nature of metal, type and strength of acidic sites, balance of acid and metal loading, and site accessibility. Actually, examples have already been reported for the direct upgrade of cellulose without isolation of intermediate streams, for instance in the case of isosorbide synthesis (Section 4.1.3). However, these systems underperform with respect to carbon balance, mostly due to the significant formation of cellulose acidic depolymerisation by-products (humins, levulinates, oligomers) and dehydration isomers. This is partially due to the mixtures of supported metals and soluble acid catalysts often used to this aim.[490,491] Therefore, the development of innovative solid acid catalysts will be of utmost importance in the biorefinery industry,[492,493] provided that high acidic-site density and tolerance to water and to medium to high temperatures are ensured. Indeed, the conventional sulfonated resin catalysts used in the acid-catalysed depolymerisation steps suffer from limited thermal resistance. This may be circumvented, for example, using inorganic niobia or polymeric perfluorosulfonic acids.[494,495] Further, the engineering of single (continuous flow) processing lines, in which specialised molecules are directly obtained from upstream substrates, would be highly desirable, *e.g.* combining supported enzymatic catalysis (for depolymerisation) and inorganic catalysis (for the upgrade of the intermediate platforms).[496,497] Innovative solid support materials, with improved stability, mass transport properties and efficient processing, are thus required. This may be the case of unconventional, inorganic monoliths featuring interconnected dual porosities (meso, macro).[498,499] Finally, the existing gap in catalysis between the laboratory scale and the validation scale at the industrial readiness level shall be bridged in most cases.

By contrast, lignin is a very complex polymer which results in a variety of chemicals by deconstruction, depending on the biomass source and the method, and hardly reducible to single platform molecules. As a consequence, despite the huge amount of lignin available, its potential for chemical synthesis is still underutilised. Despite the recent remarkable advancements, *e.g.* reductive catalytic fractionation or catalytic oxidative depolymerization methods,[410,500] here the bottleneck is the immature technology for the selective depolymerisation of lignin and the conversion to the desired platforms.[501,502] The further step is the upgrade of lignin platforms to potential BPA substitutes, which at present is often available through unexceptional organic methods, however. Indeed, recent advancements, although significant, restrict to the adoption of zeolite or enzyme catalysts for the synthesis of diphenolic scaffolds from monolignol units.[397] Herein some challenges can be identified. Challenge one: development of improved technologies for the selective conversion of lignin to chemicals, economically and sustainably. These new solutions shall optimise the utilisation of heterogeneously composed raw materials, while enabling the large-scale production of bulk chemicals for the process industry. Challenge two: development of catalytic deconstruction technologies affording novel building blocks, other than monolignol-derived monomers, directly from lignin, *i.e.* bis-phenols as in the case of naturally occurring BPF,[503] SYR and lignans.[504,505] Challenge three: most proposed BPA replacements from lignin are based on bis-phenol moieties. However, with the few notable exceptions outlined above, they are usually synthesized *via* conventional, sometimes uncatalysed, organic reactions. Typical is the case of C1-bridged bis-phenols obtained by formaldehyde coupling, using soluble mineral acids (H_2SO_4 and HCl) and, often, noxious or unstable solvents (see Tables 4–6). Thus, inventive solutions are needed, which avoid use of toxic reagents and media and which comply with the principles of green and sustainable chemistry. Novel rigid scaffolds have to be designed, for instance mimicking natural molecules and built upon C0-linked phenols or fused rings.[504] Use of Brønsted acid solid catalysts would be, once again, highly beneficial in this case too.

As emerged from the literature, several other BPA replacements may be produced from the catalytic conversion of other biomass sources. Some specific challenges may be envisaged. Challenge one: to increase the scenario of available platforms and production of BPA replacements, featuring structure alternatives to monosaccharide or phenol-based ones. High-throughput

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screening methods are expected to be particularly useful to this aim. Herein, possibilities are plenty, provided that the amount of raw material is suitable for industrial use. From that, a second challenge is closely related: to improve the uptake of unconventional, non-edible biomass sources, such as algae, biorefinery side-streams and waste (food, agricultural). The role of catalysis will be crucial in developing flexible and sustainable conversion routes in this direction.

Properties of BPA monomer replacements and derived polymers

Although the present review does not explicitly cover the specific properties of monomers aiming at the manufacture of polymers with improved performances, rather the catalytic synthesis of the monomers themselves, some challenges may be inferred from the literature targeting a rational design of effective BPA replacements. They can be briefly summarised herein. Challenge one: are the proposed BPA replacements really safe? Before evaluating the potential for use in sustainable polymer synthesis, novel building blocks should undergo preliminary (endocrine) toxicity tests. This particularly concerns phenolic scaffolds, due to the known adverse health effects.[506,507] The absence of relevant data is not proof for safety. Hence, caution must be exercised whenever replacing chemicals of known toxicity, with others of unknown toxicity. We scrutinized the data available from ECHA for all BPA substitutes described in the present review. The Harmonised Classification and Labelling of Hazardous Substances reported at the time of publication are collected in the ESI,† Tables S1 and S2. With very few exceptions, a perusal of these tables shows that very little is known about the toxicity of most of the proposed BPA replacements. Indeed, no hazards have been classified in the REACH register only for isosorbide and isomannide. All other chemicals are not registered (mostly), pre-registered or registered in Annex III (*i.e.* substances predicted or suspected to meet hazard criteria). This means that most of the claimed BPA substitutes are actually "*potential*" substitutes, at least from a hazard point of view, and that this gap must be filled by further data.[508,509] On the other hand, additional issues shall be considered in this regard. In some cases, *e.g.* cashew nutshell phenols,[510,511] processable feedstock is toxic, which complicates their effective use on the industrial scale. Also, the endocrine activity of most replacement candidates was shown to be ruled by a combination of subtle factors. For instance, evidence indicates that the presence of *ortho* methoxy substituents in bis-phenols reduces their activity.[476] Further screenings are thus highly recommended, eventually extended to various receptors. Challenge two: are the suggested BPA replacements viable? As outlined in Section 3.1, once safety criteria are met, chemical substitution at large should be offered at competitive costs, compared to existing technologies. From a catalysis point of view, this includes evaluation of the cost of catalysts, the long term productivity and selectivity of catalysts, the cost of feedstock pre-treatment (if any) and downstream processing, and the availability of raw materials. This requires a techno-economic analysis which is seldom performed.[186,387] Other relevant parameters are the sustainability and environmental impact of production. Key enabling technologies, such as bifunctional or continuous flow catalysis, the use of concentrated water solutions and mild reaction conditions, would contribute substantially to this end, but still underutilised for the synthesis of monomers from biomass, see *e.g.* Tables 1–6. Challenge three: are the proposed replacements equally relevant to the synthesis of polymers? What is offered by the present overview is a panorama of suitable monomers for BPA substitutions. It is then the duty of polymer chemists to make a selection of appropriate scaffolds and strategies targeted at the obtainment of polymers with the desired properties. This will end up in the identification of novel industrially relevant chemical building blocks. However, this requires a more detailed molecular level understanding of structure–function relationships. For instance, in the case of BPA replacements, a "rigid structure" is a requirement that refers to a rather vague attribute, lacking detailed molecular descriptors. Computer-aided molecular simulations may help in addressing this point. Further, in most cases, the proposed substitutes indeed have been shown to result in polymers with the desired stability and thermoplastic properties, however with very different reactivities and processabilities, which sometimes hamper their effective use in the manufacture of polymers. This may be the case of triphenylmethane polyphenols.[420] Challenge four: once the toxicity, viability and effectiveness of proposed BPA substitutes are ascertained, it would be essential to perform degradation tests of the derived polymers. Deconstruction of polymers into low molecular weight, useful compounds or reusable monomers would help in addressing a circular economy of plastics, which is usually achieved (when possible) *via* enzymatic biocatalysis,[512,513] and, more recently, *via* organo[514,515] or metal-based catalysis.[516,517]

In conclusion, the results reported in the recent literature describing catalysts and approaches for the synthesis of monomers from biomass that are proposed as BPA replacements and that are collected in the present review provide a large choice of potential candidates for substitution. While quite advanced catalytic systems are available for the upgrade of cellulose-derived feeds, the conversion of platforms originating from lignin still needs significant improvements, mostly due to the inherent complexity of lignin materials. In addition, further studies should be performed aiming at a careful evaluation of compliance with the viability and effectiveness criteria of the proposed BPA replacements, whose extension to chemical substitution, in general, would contribute to a safer and more sustainable future.

List of acronyms

BGF	Bisguaiacol F
m,*m*′-BGF-4P	5,5′-Methylenebis(4-*n*-propylguaiacol)
BHMC	Bisphenol hydroxy methyl carbonate
BHMF	2,5-Bis(hydroxymethyl)furan
BHMTHF	2,5-Bis(hydroxymethyl)tetrahydrofuran
BPA	Bisphenol A
BPAF	2,2-Bis(4-hydroxyphenyl)hexafluoropropane

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BPF	4,4′-Methylenediphenol
BPS	Bis(4-hydroxyphenyl)sulfone
BILs	Brønsted acidic ionic liquids
m,*m*′-BSF-4P	5,5′-Methylenebis(4-*n*-propylsyringol)
CBDO	2,2,4,4-Tetramethylcyclobutan-1,3-diol
CHDA	1,4-Cyclohexanedicarboxylic acid
CHDM	1,4-Cyclohexanedimethanol
CNF	Carbon nanofibers
CNSL	Cashew nut shell liquid
CNT	Carbon-nanotubes
CTH	Catalytic transfer hydrogenation
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMC	Dimethyl carbonate
DMF	*N*,*N*-Dimethylformamide
DPA	*p*,*p*′-Diphenolic acid
DTMP	Di(trimethylolpropane)
ECHA	European Chemical Agency
GBL	γ-Butyrolactone
HCPO	3-Hydroxymethylcyclopentanol
HHCPEN	4-Hydroxy-4-(hydroxymethyl)-cyclopenten-2-one
HMF	5-Hydroxymethylfurfural
HT	Hydrotalcite
IDF	Bis-*o*-dihydroferuloyl isosorbide
LDH	Layered double hydroxide
MIBK	Methyl isobutyl ketone
MPTS	(3-Mercaptopropyl)trimethoxysilane
MST	Mesoporous sulfated titania
NHC	N-Heterocyclic carbene
OPD	Octahydro-2,5-pentalenediol
PET	Polyethylene terephthalate
PEIT	Poly-(ethylene-*co*-isosorbide)terephthalate
PIC	Poly(isosorbide carbonate)
PMHS	Polymethylhydrosiloxane
PMO	Periodic mesoporous organosilica
TGA	Thermogravimetric analysis
TOF	Turnover frequency
TPA	Diethylene triaminepenta(methylene)phosphonic acid
TPT-OMe	5-Methoxy-1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazoline
p-TsOH	*p*-Toluenesulphonic acid
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SDG	Sustainable development goals
SHTC	Sulfonated hydrothermal carbon
SVHCs	Substances of very high concern
SYR	Syringaresinol
SYR-EPO	Diepoxy syringaresinol
TPs	Triphenylmethane polyphenols
WHSV	Weight-hourly-space-velocity
ZrP	Zirconium phosphate

Conflicts of interest

There are no conflicts to declare.

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