Catalytic insights into the production of biomass-derived side products methyl levulinate, furfural and humins

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ABSTRACT

Biomass conversion into useful chemicals, materials and fuels emerged as a promising alternative toward replacing the current production of most of these commodities and specialty products from petroleum feedstocks. Interestingly, not only end products but also side-products from biomass valorization have a significant potential for future research and further conversion into novel families of useful derivatives. Based on such potential, the proposed contribution has been aimed to focus on catalytic insights into the production of three particular biomass-derived side products from the hemicellulosic fraction, namely methyl levulinate (MeL), Furfural and Humins using both homogeneous and heterogeneously catalyzed processes.

1. Introduction

Fossil-based resources currently used for energy and material production are not endless and will run out in due time. This ongoing depletion together with the detrimental augmentation of greenhouse effects have driven the worldwide scientific community to find economically valid, environmental-friendly, sustainable alternatives to current petroleum-based industry. Novel routes employing sustainable C-sources will need to be sought, especially in the case of materials and for some types of transportation fuels.

The development of high-output technologies in agronomics [1] has yielded a surplus of one of the most promising undepletable sources: vegetable biomass. In fact, plant-derived feedstocks have been proposed as the major renewable C-source alternative that can matches fossil resources in the chemicals and specific fuels production [2]. The variety of biological and/or chemocatalytic conversion strategies to *drop-in* fuels, high added value chemicals and novel materials make biomass an attractive and versatile resource [1–5]. In particular, the plentiful abundance of lignocellulosic biomass, along with its potential fast renewability, accommodate the need to find a cheap and readily available *green* resource.

Lignocellulose is the main structural constituent of all land-based plants [4], found in agricultural and forestry residues, herbaceous and woody crops alike. This makes lignocellulosic biomass a readily available non-fossil carbon source without being in competition with the food and feed industries [6]. A clear challenge in the conversion of lignocellulose into valuable-added chemicals relates to its structural complexity. In part, this is due to the nature of the three major components in biomass, namely: (i) lignin (15–30%) which confers structural rigidity to the plant, comprising a recalcitrant polyaromatic/phenolics polymer; (ii) cellulose (35–50%), an insoluble, crystalline, linear glucose polymer linked by β-1,4 glycosidic bonds whose crystallinity gives tensile strength to the plant cell walls; and (iii) hemicellulose (20–35%), a cross-linked fiberous amorphous polymer, mostly comprised of different pentoses with some hexoses and uronic acids sugar monomers often functionalized with methoxy and acetoxy groups. As a whole feedstock, lignocellulosic biomass can be directly converted into syngas and bio-oil by gasification and pyrolysis [7]. However, more promising routes seem to be the fractionation of lignocellulose into its individual constituents by the means of chemical and/or enzymatic hydrolysis [2,4].

Lignocellulosic biomass can be converted into a plethora of possible compounds, ranging from biofuels to fine chemicals and specialty materials, which include both commercial and unknown compounds [2]. In order to limit the research's targeted molecules, the 2004 US DOE report [8] listed the top biomass-derived chemical compounds (later revisited by Bozell and Petersen [9]), which comprised of the 10 most promising compounds that could achieve mass production with the current biorefinery tech-

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nologies. Several new industrial scale productions of biomass derivatives have already been achieved, for example with the two-step acid-catalyzed production of Levulinic Acid (LA) in the so-called *Biofine Process* [10], which recently has been revitalized by GFBiochemicals. Advancements of Avantium's *YXY technology* [11] have further plans for large scale production in Antwerp, Belgium for the sustainable conversion of plant-based feedstocks into 2,5-furandicarboxylic acid (FDCA), platform chemical for the complete substitution of polluting terephthalate plastics. It is, however, clear from the DoE report and exemplified by these processes that the preferred feedstock for selective chemical production are sugars from the (hemi-)cellulosic fraction of biomass.

Chemocatalytic sugar conversions often leads to numerous side-products which limit targeted product yields, increase separation costs and renders overall production uneconomical. Fine-tuning of the current processes with the aim to minimize waste has so far proven difficult, and thus, the valorization of side-products and waste streams has to be studied in depth.

The present contribution aims to provide a general overview of the production of three major products from acid catalyzed sugar conversion processes: Levulinic acid and its Methyl ester (LA, resp., MLA), Furfural (FF), and Humins (HUM). Exploring new ways of their utilization as a feedstock for novel process may lead to improved efficiencies in new biorefinery concepts.

2. Methyl levulinate

Levulinate esters are a promising class of biomass derivatives with low toxicity, high lubrification and moderate flow properties at low temperatures [12–15]. Due to their relative simple production, they possess wide application potential as fragrances [16], herbicides [17], cancer therapeutics [18], and as oxygenated additives for gasoline and diesel transportation fuels. In their production, humin formation via polymerization of formed furanic compounds upon hemicellulose dehydration is suppressed at high alcohol/water ratios, making alkyl levulinates a more attractive platform chemical as compared to its hydrolyzed counterpart, levulinic acid.

Methyl levulinate, in particular, is employed as a flavoring agent, and, more importantly, possesses great potential as platform molecule, due to its transformable keto and ester group. Alkyl levulinates may be produced by (i) alcohol esterification of levulinic acid [19], (ii) conversion of furfuryl alcohol and its ethers [20], (iii) alcohol reactive extraction [21–23], (iv) carbohydrates conversion in alcohol media [24], or (v) as a co-product by direct synthesis from biomass (Scheme 1).

For example, methyl levulinate is a side-product to Avantium's methanolic fructose dehydration to 5-methoxymethylfurfural (MMF) [11], as well as a by-product in the aromatic production from liquefaction and fractionation of lignocellulosic biomass under sub-critical methanol conditions [25].

2.1. Homogeneously catalyzed MeL production

Producing levulinic esters from levulinic acid has been attempted by esterification of levulinic acid, produced from an aqueous product mixture of homogeneously acid-catalyzed conversion of biomass [19] which comprises also furfural, formic acid and the mineral acid catalyst (the latter two catalyze the esterification as well). A summary of the different employed homogeneous catalytic systems for MeL production from various substrates is given in Table 1.

Homogeneous acid catalysts have been extensively used in the synthesis of methyl levulinate. Brønsted acids are known to catalyze fructose dehydration, while aldose isomerization, required

Table 1
Overall comparison of homogeneous catalysts employed in methyl levulinate production.

Catalyst	Substrate	$T (^\circ C)$	t (min)	Yield (%)	Refs.
HCl	Glucose	160	150	12	[31]
H_2SO_4	Glucose	160	150	13	[31]
H_2SO_4	Fructose	160	150	73	[31]
H_2SO_4	Cellulose	183	12	38	[32,33]
H_2SO_4	Cellulose	190	300	55	[34]
H_2SO_4	Glucose	200	120	49	[32]
$Al_2(SO_3)_4$	Glucose	160	150	64	[36]
$Al_2(SO_3)_4$	Glucose	200	120	54	[35]
PTSA	Cellulose	180	300	20	[42]
$In(OTf)_3$	Cellulose	180	300	52	[42]
$In(OTf)_3$ + PTSA	Cellulose	180	300	70	[42]
$In(OTf)_3$ + 2-NSA	Cellulose	180	300	75	[42]

when using glucose, is catalyzed by bases or Lewis acids [26–30]. For this reason, mineral acids such as H_2SO_4 and HCl yielded >70% methyl levulinate from fructose, but low yields (*ca.* 12%) were observed from glucose [31] (Table 1).

As for cellulose, yields of 46% [32,33] and 55% of methyl levulinate [34] were obtained in the presence of concentrated sulfuric acid at 179 °C and in near-critical conditions, respectively. Garves et al. [33] investigated the efficiency of extremely low acid (ELA) concentrations (up to 0.01 mol L^{-1}), obtaining 49% methyl levulinate from glucose after 2 h at 200 °C at the highest ELA. ELAs were also investigated in the methanolysis of cellulose, yielding 50% methyl levulinate at 210 °C using 0.01 mol L^{-1} sulfuric acid.

Homogeneous mixed acids, particularly $Al_2(SO_4)_3$, sparked scientific interest thanks to the co-presence of both Lewis and Brønsted acidity. Yields of 54% [35] and of 64% [36] from glucose were reported due to the metal cation ability to catalyze the isomerization of glucose to fructose, and the latter consequent dehydration.

Although high yields might be achieved, homogeneous acid catalysts present major processing drawbacks (*e.g.* equipment corrosion, inefficient separability and reusability, polluting waste) as well as alcohol dehydration to its diether. A preferential focus was shifted toward heterogeneous catalytic systems.

2.2. Heterogeneously catalyzed MeL production

For instance, methyl levulinate yields of 88% were obtained over a methylated polymer–supported triazene (Me-PST) [36], while >95% methyl levulinate yields were achieved in mesoporous structures. In particular, Melero et al. [38] reported a 95% yield of the levulinate ester in methanol at 117 °C over SBA−15−(CH$_2$)$_3$−SO$_3$H, which decreased to only 93% after four consecutive runs. This was attributed to an enhanced mass diffusion of levulinic acid and relative ester in the mesopores. Similar trends were also observed in the use of solid heteropolyacids (HPA). HPA possess higher intrinsic acidity comparable to H_2SO_4 but these catalytic systems often display limited surface area and often high solubility in water and/or polar solvents, which leads to leaching of the active phase. The use of a porous catalyst support is often employed in order to avoid these problems. Yields of 73 to 99% of methyl levulinate were reported for levulinic acid conversion for $H_4SiW_{12}O_{40}$ incorporated on mesoporous SiO_2 [39] and $H_3PW_{12}O_{40}$−ZrO_2 with benzene moieties [40]. The remarkable activity of these catalysts is given by (i) the presence of hydrophobic moieties facilitating faster formation of methyl levulinate thanks to their capacities of facilitating levulinic acid adsorption over H_2O, and (ii) the larger pore structure, rather than acid sites density, type, and activity, factors that in nonporous catalysts (*e.g.* sulfonated oxides) are key for the observed activity [41].
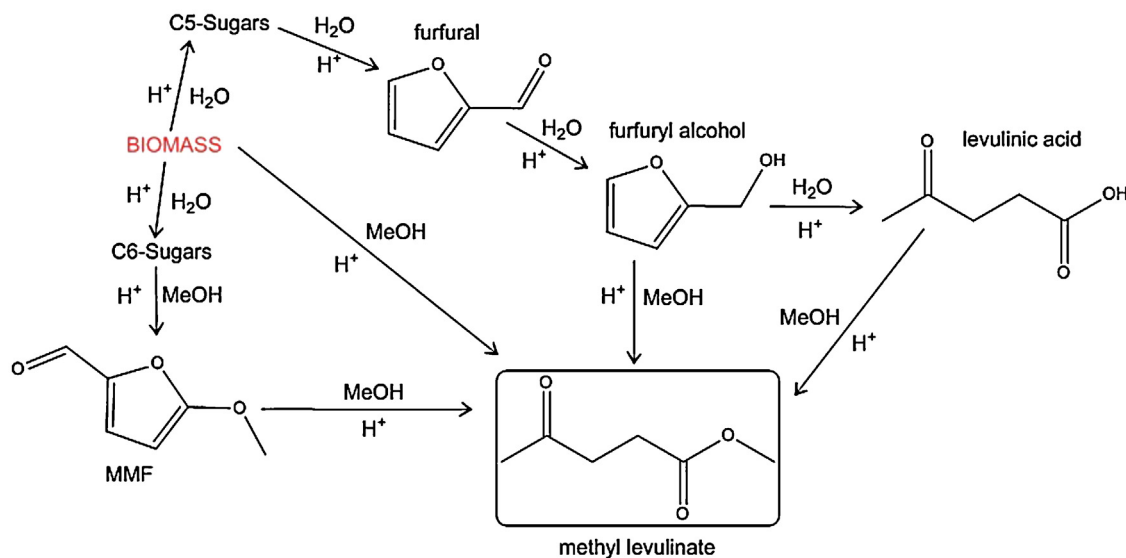
Scheme 1. Different pathways in the formation of methyl levulinate.

Tominaga et al. [42] employed Lewis acid In(OTf)$_3$ in combination with Brønsted *p*-toluene sulfonic acid (PTSA) and obtained 70% methyl levulinate at 180 °C with an optimum Lewis/Brønsted acid ratio of 0.2. Substitution of PTSA with 2-naphtalenesulfonic acid improved alkyl levulinate yields to 75%, suggesting that sulfonic acids are highly active in the hydrolysis of cellulose to sugars, while metal triflates catalyze methyl levulinate formation. An optimum acidity (Brönsted + Lewis) was required for these types of reactions. In fact, methyl levulinate yields dropped in pure Brønsted (20%), or pure Lewis (52%) acid catalyzed reactions.

Shape selectivity and tunable acidity are well known characteristics of zeolites. Their use as catalysts was investigated in the formation of methyl levulinate from glucose. Conventional zeolites such as H-Beta, H-mordenite, or H-ZMS-5 resulted in lower methyl levulinate yields than those typically reported for their homogeneous counterparts [32]. Only H-USY reported by Saravanamurugan and Riisager [43] yielded 49% methyl levulinate. Acid site densities of 300 μmol g^{-1} and optimum strong/weak acid ratio of 0.8 (0.3–1.1 range) were best suited for quantitative conversions of glucose into MeL. The same group also reported MeL yields of 13, 51, and 53% from cellulose, maltose, and cellobiose, respectively. Peng et al. [22] obtained yields of 10, 33, 43, and 59 mol% of MeL from cellulose, glucose, sucrose, and fructose, respectively, in near-critical methanol using sulfated TiO$_2$ as catalyst, with much reduced yields observed for the use of ZSM-5 (25 and 36), NaY, H-mordenite, sulfated ZrO$_2$, and pristine TiO$_2$ as catalysts. Zeolites performed comparatively worse than sulfated titania (which exhibited mainly strong acid sites) despite their larger amounts of acid sites, stressing the importance of strict catalyst tuning. In addition, 5-methoxymethylfurfural (MMF) and methyl glucosides were found as by products under the investigated reaction conditions.

Recently, zirconia–zeolite hybrid ZrY6(0.5) was found to be remarkably active in the conversion of a variety of substrates, yielding to 68% methyl levulinate from glucose, 70% from mannose, 73% from galactose, 78% from sucrose, 46% from cellobiose, and 53 and 27% from starch and cellulose, respectively[44]. In particular, the acid–base bifunctionality of the catalyst was effective in glucose isomerization and consequent dehydration. Njagi et al. [45] further investigated mesoporous sulfated TiO$_2$-based catalysts, comparing pristine TiO$_2$ and co-precipitated sulfated TiO$_2$–ZrO$_2$ (TZ) (Zr content = 10–50%). Sulfated metal oxides with the highest percentage of Zr exhibited the highest catalytic activity in the production of methyl levulinate in methanol at 200 °C after 1 h. Significant yields

of methyl levulinate were obtained from fructose (71%), sucrose (54%) and glucose (23%). Sulfated TZ50 presented large mesopores that favored internal diffusion. However, the type of acid site types and strength were not reported in this work, perhaps of strong nature due to the claimed low catalyst stability (and the need of thermal treatment for reactivation) probably due to insoluble humins adsorbed on the catalyst surface originated on the strong Brönsted acid sites of the sulfated catalyst. On the other hand, sulfonated carbons derived from biochar have been proven effective in the conversion of polysaccharides, yielding 30% methyl levulinate [46].

In order to provide environment-friendly and cheap heterogeneous alternatives to those reported, Xu et al. [47] tested inexpensive montmorillonite (MMT) in the conversion of carbohydrates at 200 °C. The highest yield was obtained with 20-SO$_4^{2-}$/MMT, *i.e.* 65% methyl levulinate from fructose, while glucose and cellulose conversion yielded 65 and 24%, respectively. A substantial drop in catalytic activity could be observed upon catalyst recycling, with deactivation correlated to humin deposition on catalytic surface. However, calcination treatments were ineffective in recovering any catalytic activity, possibly due to sulfur loss, which, at industrial level, would increase production costs of waste disposal.

Hu et al. [24] investigated the conversion of levoglucosan in methanol rich medium in order to hinder humins formation, obtaining >90% MeL yield, with a *ca.* 95% selectivity (while levulinic acid selectivity is attested at *ca.* 25%). The same group also proposed a reaction mechanism from levoglucosan which undergoes methanolysis to a glucose acetal (methyl α-D-glucopyranoside, MGP) at low temperatures (<130 °C), followed by the formation of intermediate 2-(dimethoxymethyl)-5-(methoxymethyl)furan (5-MMF, acetal and ether of HMF) at higher temperatures (150–170 °C), eventually decomposing into methyl formate and levulinate.

A more recent mechanistic study [48] confirmed the reaction pathway proposed by Hu et al. (*vide supra*) and stressed the influence of Lewis and Brønsted acid sites. In fact, Brønsted acids were further reported to favor methyl glucoside conversion into 5-MMF, while Lewis acids promote the formation of C—C cleavage products (*e.g.* 1,1,2-trimethoxymethane) and prevent further conversion of 5-MMF to MeL [48]. However, Lewis acids promoted cellulose alcoholysis to methyl glucoside, consequently improving overall MeL yields. In conclusion, improved yields of methyl levulinate could

be achieved utilizing solid acid catalysts featuring (i) fine-tuned Lewis/Brønsted acid sites ratios, (ii) medium strength acid sites, and (iii) regular pore size distribution to avoid diffusional issues.

Promising yields to alkyl levulinates (52%) could be obtained from furfuryl alcohol conversion in methanol under acidic conditions [49]. Similarly to levulinic acid conversion into its esters, furfuryl alcohol conversion to alkyl levulinates also showed a strong dependence on the accessibility of the reactant to the acid sites rather than acid site strength itself. In fact, acid sites density and strength only play a minor role in the conversion to alkyl esters as compared to substrate internal diffusion limitations, although suitable acid sites must exist.

Yields close to 90% were recently obtained by preparing Nb_2O_5 hybrid bifunctional catalysts containing $H_3PW_{12}O_4$-type HPA, with phenyl-bridged organosilica moieties [50]. These hybrid catalysts combined hydrophobic moieties and strong Brønsted with moderate Lewis acidities that favored the reaction. Interestingly, the highly ordered structures used in this study showed systematically higher activities with respect to their disordered counterparts.

Hengne et al. [51] also reported the use of functionalized ionic liquids in the alcoholysis of furfuryl alcohol to γ-valerolactone and alkyl levulinates. In particular, 95% selectivity to methyl levulinate with 99% conversion of furfuryl alcohol was given using ionic liquid [BMIM-SH][HSO$_4$]. Combination of the latter with 5% Ru/C catalyzed ring cyclization of the alkyl levulinate led to the formation of γ-valerolactone. Although attractive, this strategy is highly cost ineffective because of the expensive technology currently needed for ionic liquids mass production. Table 2 summarizes a comprehensive overview of results in MeL production reported in this review from different heterogeneous catalysts.

3. Furfural

Different from 5-hydroxymethylfurfural (HMF) [52], another member of the furan family (furfural) was identified as one of the top 10 biomass-derived chemicals by the US Department of Energy [8]. First discovered in 1821 by Döbereiner [53], furfural has taken hold of the scientific community as a potential chemical platform, thanks to its high versatility. In fact, furfural (and its derivatives) are highly versatile molecules, finding numerous applications including their use as selective solvent for extractions of conjugated molecules, non-toxic fungicides and nematicides, food and drinks flavor enhancers and as building blocks for transportation fuels, gasoline additives, resins, biopolymers, pharmaceuticals, and similar [54,55].

Furfural has been synthesized both in stand-alone processes from C5-rich carbohydrates (i.e. xylose, arabinose content in hemi-cellulose [54]) and as a co-product of a variety of biomass valorization processes including the *Biofine* process for levulinic acid production (*vide supra*) as well as HMF production via the dehydration of lignocellulosic biomass[56,57]. Current industrial production of furfural involves mineral acid-catalyzed processing of xylose-rich lignocellulosic residues (e.g. bagasse, corn cobs, oat hulls, almond husks) in aqueous media under high steam stripping conditions for product recovery [58,59]. Though this particular process utilizes a *green* resource, it has significant drawbacks due to equipment corrosion, high amounts of acidic and toxic waste, energy intensiveness, homogeneous catalyst loss, and, last but not least, an elevated number of possible of inevitable side reactions (e.g. degradation, condensation) that generate low value byproducts and limit furfural yields to *ca.* 50% [60] (theoretical yield of 73 wt% from pentose, 64 wt% from pentosan [61]).

In order to improve operation conditions, a better understanding of the reaction mechanism is required. The mechanism of this dehydration step has not yet been fully elucidated. Owing to different reaction pathways proposed, it is still a nowadays matter of debate. Neutral media conversions present low furfural production rates which find a slight increase at the occurrence of autocatalysis by means of the biomass degradation product acetic acid [62], therefore indicating a positive effect of the presence of Brønsted-type acids.

3.1. Homogeneously catalyzed production of furfural

Danon et al. [59] extensively addressed mechanistic and kinetics aspects of homogeneous acid catalysis dehydration. Different mechanisms have been proposed for xylose conversion in aqueous acidic media, comprising of open ring enolization or β-elimination, and cyclic intermediates pathways. In acidic medium such as sulfuric or hydrochloric acid (up to 2.5 wt% [63]), pentosans hydrolysis comparably proceeds at a faster rate to that of the dehydration of the C5-carbohydrates into furfural, therefore making the latter the rate determining process and the focus of mechanistic insights [64]. By analyzing isotope-labeled experimental evidence and activation energies, a comprehensive reaction mechanism that involves only acyclic intermediates was proposed, excluding the closed-ring mechanism proposed by Antal et al. [65], due to a particularly low activation energy for the O-5 protonation and subsequent ring opening of the cyclic intermediate 2,5-anhydroxylose.

In particular, it is suggested that xylose undergoes (i) aldose-ketose isomerization *via* 1,2-hydride shift to xylulose that eventually leads to furfural *via* the 1,2-enediol or side-reactions and humins, predominant at pH < 1 with higher conversion rates, (ii) enolization to 1,2-enediol followed by two consecutive dehydration reactions to furfural *via* the 2,3-(α,β)-unsaturated aldehyde, catalyzed by halides anions and favored at pH *ca.* 3, (iii) β-elimination that follows the pattern *via* 2,3-(α,β)-unsaturated aldehyde (*vide supra*), and (iv) equilibrium with D-xylopyranose that leads to unspecified side products, as shown in Scheme 2. The proposed reaction pathway validated the open ring mechanisms suggested by Ahmad [66] and Feather [67] by combining them both.

Further experimental evidence is required in elucidating this complex mechanism. Nonetheless, it can be drawn out that the key steps that require catalysis in order to derive higher furfural yields are isomerization/enolization and dehydration reactions which are catalyzed under basic and acid media, respectively.

Current industrial production of furfural still relies on homogeneous acid catalysts. The first furfural production was reported by *Quaker Oats*, based on oat hulls conversion in the presence of sulfuric acid at 153 °C for 5 h. Heating of the process was achieved by continuous steam injection, which also stripped furfural from the reaction environment, with yields of *ca.* 50% [64]. The biggest furfural exporter of modern times (accounting for 70% of furfural production), China, has based their own process on the 1921 *Quaker Oats*, employing sulfuric acid (3–4 wt%) and steam stripping in the conversion of corncobs, with a similar furfural yield of the former process. The moderate yields of furfural are mainly due to the formation of solid humins (*vide infra*), deriving from the occurrence of undesired polymerization reactions. As mentioned above, furfural is produced as co-chemical in the levulinic acid *Biofine* process. A furfural yield of 70% can be achieved from cellobiose at a 20 min residence time, operating at 210–220 °C with 3% of sulfuric acid under 25 bar pressure of steam [68].

Alternatively, recent scientific progress provided significant advances in furfural production. Several mineral acids were also investigated in the production of furfural from a variety of biomass sources. Rice husks have proven to be ineffective in the production of furfural (9% yield [69]), while olive stones conversion yielded 65% furfural at 230 °C with sulfuric acid [63]. A screening of various mineral acids (*i.e.* HCl, H_2SO_4, HNO_3, and H_3PO_4) along with organic Trifluoroacetic acid (TFA) catalysts in the production of furfural

Table 2
Summary of literature reported MeL yields from various substrates using heterogeneous catalysts.

Catalyst	Substrate	T (°C)	t (min)	Yield (%)	Ref.
Me-PST	Levulinic acid	25	120	88	[37]
SBA-15-(CH$_2$)$_3$-SO$_3$H	Levulinic acid	117	120	95	[36]
H$_4$SiW$_{12}$O$_{40}$–SiO$_2$	Levulinic acid	65	360	73	[38]
H$_3$PW$_{12}$O$_{40}$/ZrO$_2$–Si(Ph)Si	Levulinic acid	65	180	99	[40]
H-USY	Glucose	160	1800	49	[43]
H-USY	Cellulose	160	1800	13	[43]
H-USY	Maltose	160	1800	51	[43]
H-USY	Cellobiose	160	1800	53	[43]
SO$^{2-}_4$/TiO$_2$	Cellulose	200	120	10	[22]
SO$^{2-}_4$/TiO$_2$	Glucose	200	120	33	[22]
SO$^{2-}_4$/TiO$_2$	Sucrose	200	120	43	[22]
SO$^{2-}_4$/TiO$_2$	Fructose	200	120	59	[22]
ZrY6 (0.5)	Glucose	180	3	68	[44]
ZrY6 (0.5)	Mannose	180	3	70	[44]
ZrY6 (0.5)	Galactose	180	3	73	[44]
ZrY6 (0.5)	Sucrose	180	3	78	[44]
ZrY6 (0.5)	Cellobiose	180	3	46	[44]
ZrY6 (0.5)	Starch	180	3	53	[44]
ZrY6 (0.5)	Cellulose	180	3	27	[44]
TZ50	Fructose	200	60	71	[45]
TZ50	Sucrose	200	60	54	[45]
TZ50	Glucose	200	60	23	[45]
Sulfonated biochar	Cellulose	200	75	30	[46]
PW$_{12}$/Nb$_2$O$_5$-Si(Ph)Si	Levulinic acid	65	180	90	[50]
[BMIM-SH][H$_2$SO$_4$]	Furfuryl alcohol	130	120	94	[51]
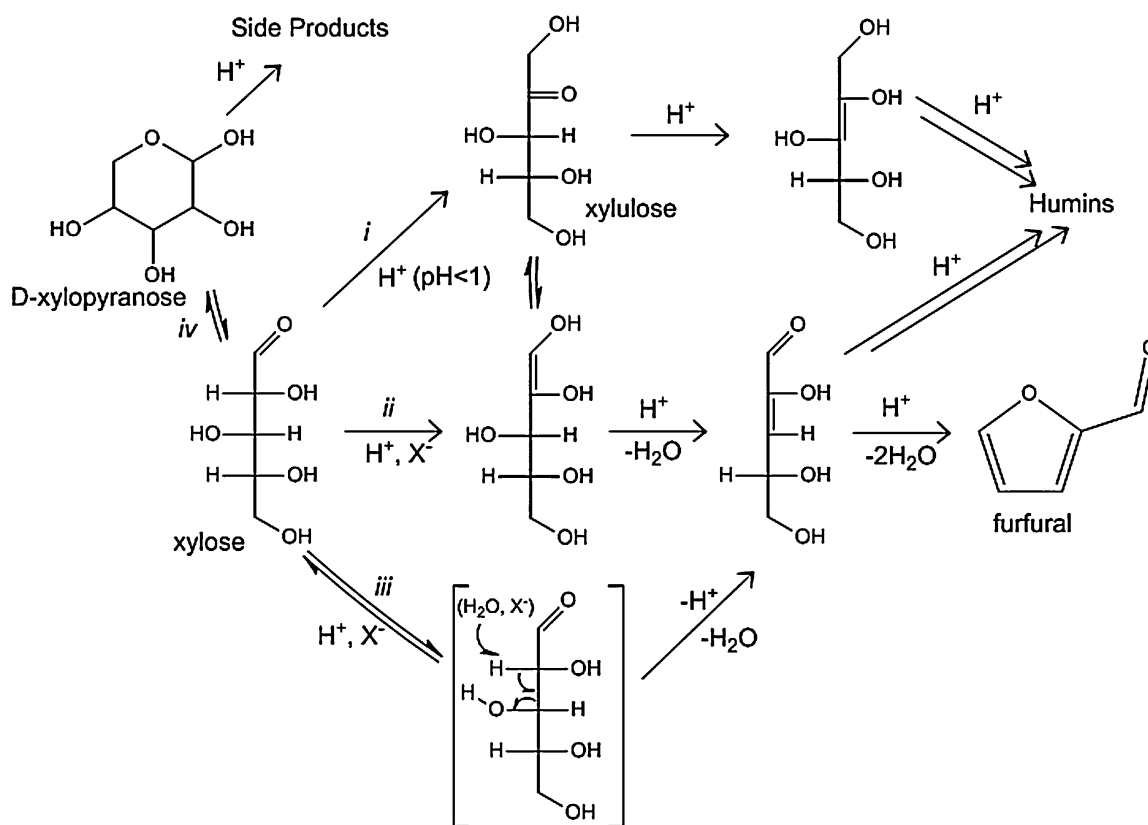
Scheme 2. Furfural formation mechanism proposed by Danon et al. adapted from Ref. [59].

from loblolly pine was conducted by Marzialetti et al. [70], finding reasonable furfural yields (and HMF and hexoses as by-products) at 200 °C for the TFA and sulfuric acid systems (57 and 34%, respectively). Barbosa et al. [71] also screened mineral acids HCl, H$_2$SO$_4$, and H$_3$PO$_4$ in the homogeneous liquid phase dehydration different biomasses, and found the best activity was given by chloridric acid, which yielded 30, 26, and 14% furfural from corn stalk, sugar-cane bagasse, and eucalyptus wood, respectively. Phosphoric acid was found to be fairly active in the conversion of sorghum straw with furfural yield of 38% [72], while maleic acid yielded 55% furfural from switchgrass liquor [73]. Heteropolyacids were also employed in the dehydration of xylose. For instance, Dias et al. [74] reported furfural yields of 58–67% at 140 °C employing H$_3$PW$_{12}$O$_{40}$ (PW), and H$_4$SiW$_{12}$O$_{40}$ (SiW) after 4 h, while H$_3$PMo$_{12}$O$_{40}$ showed

Table 3
Overall view of homogeneous catalysts employed in furfural production.

Catalyst	Substrate	T (°C)	t (min)	Yield (%)	Ref.
H_2SO_4	Oat hulls	153	300	50	[63]
H_2SO_4	Cellobiose	210	20	70	[68]
H_2SO_4	Rice husks	230	288	9	[69]
H_2SO_4	Olive stone	230	2.5	65	[63]
H_2SO_4	Loblolly pine	200	60	34	[69]
TFA	Loblolly pine	200	60	57	[69]
HCl	Eucalyptus wood	170	180	14	[71]
HCl	Sugarcane bagasse	170	180	26	[71]
HCl	Corn stalk	170	180	30	[71]
H_3PO_4	Sorghum straw	134	300	38	[72]
Maleic acid	Switchgrass liquor	200	15	55	[73]
$H_3PW_{12}O_{40}$	Xylose	140	240	67	[74]
$H_4SiW_{12}O_{40}$	Xylose	140	240	58	[74]
HCl + NaCl	Xylose	200	3.3	81	[75]

the lowest activity. A combination of acid–base catalysts has also been employed, reaching 76% furfural yield as reported by Choudhary et al. [75]. Addition of halide salts to mineral catalysts has also proved the increase of furfural production. In particular, Marcotullio et al. screened NaCl, KCl, KBr, $CaCl_2$, and $FeCl_3$, finding sodium chloride as the most effective [76]. In fact, halide salts not only possess the ability of salting-out furfural in biphasic systems [77,78], therefore reducing overall residence time and possible side-reactions, but also enhance furfural selectivities to up to 90% at 200 °C as seen by Marcotullio et al. [76] in the co-presence of HCl, and NaCl. Higher selectivity is reported to be given by an acceleration in the 1,2-enediol formation by the weak base behavior of chlorine ions. Although the use of mineral acid catalysts simplifies operations, and fairly high yields of furfural can be obtained, these homogeneous acid systems present numerous drawbacks including corrosion, acidic waste disposal, and catalyst loss. Therefore, solid acid catalysis might seem a *greener* choice in the production of furfural. An overview of the homogeneous catalysts reported in this review is presented in Table 3.

3.2. Heterogeneously catalyzed production of furfural

As for heterogeneous catalysis is concerned, a distinctive reaction pathway has yet to be described as just few mechanistic investigations are being advanced in this matter. In the presence of Brønsted-acid catalysts, a cyclo-dehydration mechanism is most likely to occur where a pseudo-cycle undergoes ring-opening and subsequent ring closing to furfural, described by Zeitsch [64]. In particular, xylose undergoes as a sequence of two proton-catalyzed 1,2-eliminations that open the pentose ring, followed by a 1,4-elimination that closes the ring yielding furfural. Instead, in the case of Brønsted acids combined with Lewis acid sites (either in homogeneous or heterogeneous phase), all experimental evidence suggest that the synergistic effect of the two types of acids promote xylose isomerization to xylulose, and overall increasing furfural yields by accelerating overall xylose conversion rate. For instance, Choudhary et al. [75] reported a 10% increase of furfural yields in water, and a 47% increase in a water/toluene medium (toluene acts as furfural-extracting solvent) when a Lewis acid (*i.e.* $CrCl_3$) is added to a homogeneous Brønsted acid (*i.e.* HCl), suggesting a mechanism *via* isomerization to xylulose (and the other isomer, lyxose) only in the presence of a Lewis acid catalyst but without proposing a full reaction mechanism.

Recently, Shirotori et al. [79] studied the xylose conversion in the presence of Brønsted acid Amberlyst-15 and acid–base catalyst Cr/hydrotalcites. The research group proposed a reaction mechanism based on ring opening and Lobry de Bruyn-Alberda van Ekenstein transformations (aldose-ketose). The suggested mechanism does not exclude a catalytic activity of dispersed Cr_2O_3

particles in the direct hydride shift for xylose–xylulose isomerization, however, a much lower furfural yield of solely Cr_2O_3 (4%) compared to solely HT Brønsted base catalyst (19%) suggest that the latter is indeed the main active site. With this in mind, a first xylopyranose-Cr_2O_3 coordination initiates the reaction by increasing the positive charge on the C1 oxygen atom and favors HT-catalyzed deprotonation to open-chain xylose. Subsequently, another deprotonation occurs at the C2H of xylose by means of HT, generating an 1,2-enediol which complexes with the Cr-Lewis acid that undergoes proton shift from C2 to C1, generating xylulose. Ultimately, it is reported that xylulose will be dehydrated to furfural thanks to the catalytic activity of Brønsted acid Amberlyst-15. However, these mechanisms do not take into consideration the numerous side reactions that limit furfural yields including polymerization or degradation reactions that lead to humins (*vide infra*) and decomposition products (e.g. formic acid, lactic acid, pyruvaldehyde [65]), respectively.

In conclusion, a defined scheme of this complex mechanism has yet to be elucidated, but a co-existence of Lewis and Brønsted acids may remarkably improve furfural yields.

The tunable acidities, excellent thermal and chemical stability and pore selectivity properties of zeolites make them attractive catalysts in xylose dehydration to furfural. Moreau et al. [80] first reported the use of microporous zeolites in the selective preparation of furfural, studying H-Y Faujasite (Si/Al = 10 and 15), H-Mordenite (Si/Al = 11 and 12) in water/toluene and water/methylisobutylketone (1:3 by volume) in the conversion of xylose at 170 °C for 30 min. Furfural selectivity of 96% was achieved with H-Mordenite (Si/Al = 11) in water/toluene medium (96% after 30 min of reaction), while in water/methyl isobutyl ketone furfural selectivity for H-Mordenite (Si/Al = 12) was 51%. The highest xylose conversion was observed for the catalyst with the lowest Si/Al (HY Faujasite, Si/Al = 10), due to the accessibility of xylose into the 3D structure of HY–Faujasite and pores of *ca.* 13 Å. However, large pore volumes also favor further rearrangements of furfural into degradation and/or polymerization compounds. Along these lines, Bruce et al. [81] investigated small pore zeolite catalysts (both synthesized and commercial) in the conversion of xylose in a γ-valerolactone/water system. Lessard et al. [82] tested higher temperatures (260 °C) for xylose conversion over a variety of zeolites, finding that phosphoric acid treatment on mordenite 13 catalysts could increased furfural yields to 98 mol% with almost quantitative xylose conversion (99%). O'Neill et al. [83] obtained 46% furfural yield at 200 °C over protonic H-ZSM-5 (pore size of 1.2 nm) in water environment. Different zeolites were investigated by Kim et al. [84] in different reaction media (*i.e.* H_2O, H_2O/toluene, and DMSO), reporting lower conversion and furfural yields in water medium, and a general decrease of catalytic activity in furfural production with increasing SiO_2/Al_2O_3 ratios, which is closely correlated to acid sites accessibility.

This indicates that furfural yields critically depend on residence time in water media (therefore, validating biphasic systems), and on reagent/product diffusion limitations in porous systems. As an attempt to avoid this phenomenon, Lima et al. [85] attempted to achieve single crystalline sheets of layered aluminosilicates precursors through swelling and ultrasonication. The delaminated zeolites showed a remarkable increase in surface area and a slight decrease of the Si/Al ratio, and yield to 47% furfural at 170 °C in a water/toluene solution. The same research group, in a later paper[86], reported 58% furfural selectivity of the medium-large pore size silicoaluminophosphates (SAPOs 5, 11, 40) with the highest Brønsted acid content and surface area. SAPOS are known to possess less but stronger acid-sites, thanks to the phosphorous substitution with Si. Overall, studies employing SAPO-5, -11, -40, and -44 reported furfural yields of 40–65% in biphasic systems [86,87]. Similarly, Valente et al. [85,87] prepared delaminated zeolites by

swelling and ultrasonication from ferrierite, Nu-6(2), and MCM-22 (ITQ-2). Higher surface area and porosity of the delaminated compounds lead to higher furfural yields by favoring internal diffusion.

Mesoporous acid catalysts, such as SBA-15 and MCM-41 have been receiving increasing attention in biomass conversion. Xylose conversion to furfural was achieved with a 68% yield by Shi et al. [89] over SBA-15-SO$_3$H in water/toluene environment. MCM-41 showed low thermal stability of the acid sites and furfural yields lower than 40% in DMSO or water/butanol (48% in water/butanol with the addition of NaCl [90]), while modified MCM-41-SO$_3$H showed increased activities in water/methyl isobutyl ketone and water/toluene, with furfural yields of 51% and 76%, respectively [90,91]. For these catalytic systems, the higher activity was due to the nature of the MCM acid sites, and not its porous structure. In fact, as mentioned before, Lewis acid sites favor the isomerization of xylose to xylulose that possess overall faster reaction kinetics to furfural rather than the direct xylose-furfural pathways catalyzed by Brønsted acid sites. Increasing acid strength may increase reaction rates, but also further catalyze polymerization side-reactions [61,75,86,92]. An optimum Lewis/Brønsted acid sites ratio has been reported between 30 and 80% [93]. Among other mesoporous acid catalysts investigated, high furfural yields of 82–86% were obtained with propylsulfonic-SBA [94] and arenesulfonic-SBA [95], respectively, thanks to their optimum BET surface area and pore size. Yields of 78% were reported for flurosulfonic modified MgF$_2$ catalysts (71 wt% HF) in water/toluene at 160 °C [95], and Nb$_2$O$_5$/Cabosil in water at 175 °C [96], with good Lewis/Brønsted acid sites ratio. Strong acid PTSA-POM catalyst also resulted into high furfural yields (ca. 80%) at 170 °C for 10 min in GVL/water [97]. Furfural yields reported in literature from xylose conversion are summarized in Table 4.

Heterogeneous conversion of whole biomass has been also attempted (Table 5). One-pot hydrolysis/dehydration of raw biomass (softwood hemicelluloses) to furfural has been carried out by Dhepe et al. [98] using HUSY, H-Beta, and H-mordenite, however only ca. 12% of furfural was recovered. Corn cob conversion with mixed metal oxide ZrO$_2$–TiO$_2$ at 300 °C yielded only 10% furfural [99]. A higher furfural yield of ca. 56% was instead achieved for bagasse conversion with HUSY in water/p-xylene at 140 °C after 300 min [98,100].

Even though furfural traditionally is derived from C5-carbohydrates, recently its production from hexoses has also been attempted using microporous ion exchanged H-Beta zeolites [101] (Table 5). A synergistic effect of textural properties (i.e. pore size comparable to furfural, and shorter pore pathways), Lewis/Brønsted acid sites ratio (ca. 1.3, with the presence of mainly weak acid sites and small amounts of medium-strength) made Sn-Beta the most active catalyst, reaching 95% glucose conversion, ca. 68% furfural yield with a ca. 72% selectivity in 25 min at 170 °C.

Comprehensively, a strict correlation of optimum surface areas, pore size, and acid type and strength exists in the xylose/biomass conversion in furfural. Limitations of this particular heterogeneous process are given by internal diffusion limitations, and optimized Lewis/Brønsted acid sites ratio. Comparable pore size to xylose and furfural molecular sizes (6.8 and 5.7 Å, respectively) must be obtained, with ease accessibility given by a larger surface area; moreover, the right acid content and strength must be achieved, limited by the presence of too strong acid sites that catalyze secondary reactions [93].

In conclusion, environment-friendly heterogeneous catalysts are attractive possible alternatives to current homogeneous mineral acid catalysts employed in the industrial production of furfural.

Peleteiro et al. [58] wrote a recent review on the application of ionic liquids in furfural production. For sake of completeness, a very general overview is given herein. Their high boiling point, optimum dissolving capacity [103], chemical and thermal stability, recy-

clability, and non-toxic nature (except for chloride-based) make ionic liquids an attractive green alternative to conventional solvents, however, their industrial application is still limited by their cost, and separability. Nonetheless, remarkable high yields were obtained in the dehydration of a variety of biomasses into furfural. The most notable examples will be given as follows. High activities were obtained when [BMIM]Cl (1-butyl-3-methylimidazolium chloride) was employed as solvent over a variety of substrates (lyxose, ribose, arabinose, xylose, pine wood), combined with a wide range of catalysts (Amberlyst-15, H$_3$PW$_{12}$O$_{40}$, PEG-OSO$_3$H, CrCl$_3$, AlCl$_3$) [101–106]. Remarkable yields of ca. 94% from xylan were reported when [BMIM]Cl was combined to H$_3$PW$_{12}$O$_{40}$ [103] at 160 °C for 10 min. [BMIM]Cl and CrCl$_3$ yielded ca. 31% furfural from pine wood [105]. Overall, moderate-high furfural yields were reported for all systems (48–84% from xylose, 75% from lyxose, 90% from ribose, 72% from arabinose).

The possible release of halogens in the environment or consequences of its thermal decomposition, be it very slow, lead to the prevailing of scale-up studies for non-halide ionic liquids. [BMIM]HSO$_4$ (1-butyl-3-methyl-imidazolium hydrogen sulphate) has yielded also to promising results when employed as both co-solvent and acid catalyst. For instance, Lima et al. [107] utilized [EMIM]HSO$_4$ (1-ethyl-3-methylimidazolium hydrogen sulphate) combined with toluene, obtaining 84% furfural from xylose. Peleteiro et al. [108] reported yields of up to 82% when [BMIM]HSO$_4$ was in the presence of dioxane, and of up to 80% with MIBK, in xylose dehydration at 140 °C. Attempts on whole biomass conversion were also attempted, yielding to 33% furfural from Miscanthus giganteus at 120 °C for 22 h [109], and yields of 36% were reported from wheat straw dehydration, with up to 3% co-yield of HMF [110]. Ionic liquids, in conclusion, seem to have optimum employability for future furfural productions. However, the scarce technology knowledge of industrial production and unknown consequences of long-term use of ionic liquids, alongside their elevated cost and yet inefficient recovery and recycling, set some major drawbacks in the use of these systems. A number of furfural yields in ionic liquid systems are reported in Table 6 [54].

In general, furfural industrial production is feasible when yields exceed 50 wt%, but many technological aspects can still be improved.

4. Humins

The limited yields of the products mentioned before (i.e. methyl levulinate, and furfural), alongside other products of dehydration reactions of biomass-derived carbohydrates (e.g. HMF, levulinic acid), are due to the formation of waste by-products. Among the latter, the most undesired by-products are given by the formation of so-called humins. These dark, tarry to solid, insoluble polymeric structures are favored by the aqueous acidic media of most ligno-cellulosic biomass homogeneous transformations, although most likely also present also when heterogeneous catalytic treatments are carried out in both water and/or organic solvents (Scheme 3).

For instance, 37–39% yields of humins were reported in the mineral acid dehydration of aldose [111], while yields of even 50 wt% of humin by-products can derive from HMF production [112], and the typical furfural yields do not exceed 55% because of this side-reactions [113]. Although not yet unequivocally determined, the humin structure is known to depend on reaction time, temperature, and feedstock structure and its concentration [114–116]. Several kinetic studies on humin formation were performed. Values of 85–130 kJ mol^{-1} were reported for the activation energy for humin formation from HMF [52,117,118]; lower activation energies were found for the humins formed from furfural in the presence of either xylose or glucose, compared to furfural alone [119–121].

Table 4
Overall view of heterogeneous catalysts employed in furfural production from xylose.

Catalyst	Substrate	Solvent	T (°C)	t (min)	Yield (%)	Ref.
H-Mordenite	Xylose	Water/toluene	170	50	33	[78]
H-Mordenite	Xylose	Water/methylisobutylketone	170	50	20	[78]
HY-Faujasite	Xylose	Water/toluene	170	50	42	[78]
HY-Faujasite	Xylose	Water/methylisobutylketone	170	50	30	[78]
ZSM-5	Xylose	Water/γ-valerolactone	190	15	70	[81]
Amberlyst-70	Xylose	Water/γ-valerolactone	190	15	67	[81]
SAPO-34C	Xylose	Water/γ-valerolactone	190	360	40	[81]
SAPO-56	Xylose	Water/γ-valerolactone	190	360	38	[81]
SAPO-34	Xylose	Water/γ-valerolactone	190	360	31	[81]
H-Mordenite	Xylose	Water/toluene	260	3	98	[82]
H-ZSM-5	Xylose	Water	200	30	46	[84]
H-ZSM-5	Xylose	Water/toluene	140	240	42	[84]
Del-Nu-6	Xylose	Water/toluene	170	240	47	[85]
SAPO-11	Xylose	Water/toluene	180	240	51	[86]
H-MCM-22	Xylose	Water/toluene	170	960	70	[88]
ITQ-2	Xylose	Water/toluene	170	960	66	[88]
SBA-15-SO$_3$H	Xylose	Water/toluene	160	240	68	[89]
MCM-41 + NaCl	Xylose	Water/1-butanol	170	120	48	[90]
MCM-41-SO$_3$H	Xylose	DMSO	140	1440	75	[91]
Propylsulfonic-SBA	Xylose	Water/toluene	160	1200	82	[94]
Arenesulfonic-SBA	Xylose	Water/toluene	160	1200	86	[95]
Fluorosulfonic MgF$_2$	Xylose	Water/toluene	160	1200	78	[96]
Nb$_2$O$_5$/Cabosil	Xylose	Water (N$_2$ stripping)	175	180	78	[97]
PTSA-POM	Xylose	Water/γ-valerolactone	170	10	80	[98]

Table 5
Overall view of heterogeneous catalysts employed in furfural production from substrates different from xylose.

Catalyst	Substrate	Solvent	T (°C)	t (min)	Yield (%)	Ref.
Amberlyst-70	Switchgrass	Water/γ-valerolactone	190	30	60	[81]
SAPO-34C	Switchgrass	Water/γ-valerolactone	190	1440	30	[81]
SAPO-56	Switchgrass	Water/γ-valerolactone	190	1440	29	[81]
HUSY	Softwood hemicelluloces	Water	170	180	12	[99]
ZrO$_2$-TiO$_2$	Corncob	Water	300	5	10	[100]
HUSY	Bagasse	Water/p-xylene	140	300	56	[99,101]
Sn-Beta	Glucose	γ-valerolactone	170	25	68	[102]

Table 6
Overall view of furfural production employing ionic liquids.

| Catalyst	Substrate	Solvent	T (°C)	t (min)	Yield (%)	Ref.
H$_3$PW$_{12}$O$_{40}$	Xylan	[BMIM]Cl	160	10	94	[105]
CrCl$_3$	Pine wood	[BMIM]Cl	(400 W)	3	34	[107]
[EMIM]HSO$_4$	Xylose	[EMIM]HSO$_4$/toluene	100	360	84	[109]
[BMIM]HSO$_4$	Xylose	[BMIM]HSO$_4$/dioxane	140	360	82	[110]
[BMIM]HSO$_4$	Xylose	[BMIM]HSO$_4$/MIBK	140	360	80	[110]
[C4C1im][HSO$_4$]$_{80\%}$ and [C4C1im][MeSO$_4$]$_{80\%}$	*Miscanthus giganteus*	–	120	1320	33	[111]
[BMIM]HSO$_4$	Wheat straw	–	160	157	36	[112]

The kinetic study of glucose conversion to levulinic acid conducted by Girisuta et al. [122] reported higher activation energy for the formation of humins (165 kJ mol^{-1}) than all of the other activation energies of glucose conversion. However, both Weingarten et al. [121], and Eifert and Liauw [123] obtained lower activation energies for humin formation compared to xylose dehydration to furfural, making humins thermodynamically favored. Moreover, Eifert and Liauw observed a linear correlation between the reaction rate of humin formation and temperature. Even nowadays, structural characterization is the main research focus, and still object of debate. One of the first studies on humin structure is given by F. A. H. Rice [111] in 1958, who performed IR analysis on homogeneously dehydrated aldoses, reporting the presence of hydroxyl, carbonyl and, possibly, carbon-carbon double bonds, as well as, highly similar spectra of the soluble and unsoluble humin fractions.

Sumerskii et al. [113] studied the multistep humin formation in acidic medium from monosaccharides. It was noted that the investigated pentose (*i.e.* arabinose) yielded more humins than the hexoses counterparts. This finding was suggested to be caused by

the high reactivity of furfural, readily formed from pentose sugars, to undergo further condensation reactions to humin, while lower thermal stability would cause HMF to decompose in two stable acids (levulinic and formic acid). ^{13}C NMR analysis showed 35.1% of relative amount of carbons as carbon and hydrogen substituted C atoms in furan compounds; and 27.3% as oxygen-substituted C atoms in furans. Among the rest, in low percentages (2–4%) each, carboxyl and esters, methoxy, -CH$_2$O- fragments, and acetal carbon atoms were found. The same group, proposes also two reaction pathways for humin formation in pentoses and hexoses. For xylose dehydration, furfural polycondensate to humins *via* electrophilic substitution, forming C—C bonds between furan rings. As hexoses concern, humin formation from HMF proceeds *via* aromatic electrophilic substitution, leading to ether or acetal bonds between rings.

Recently, pyrolytic humins were found to possess mainly carbonyl functional groups [124]. Horvat [125] first proposed the formation of highly reactive 2,5-dioxo-6-hydroxyhexanal (DHH), crucial molecule regarding humin formation, although DHH has
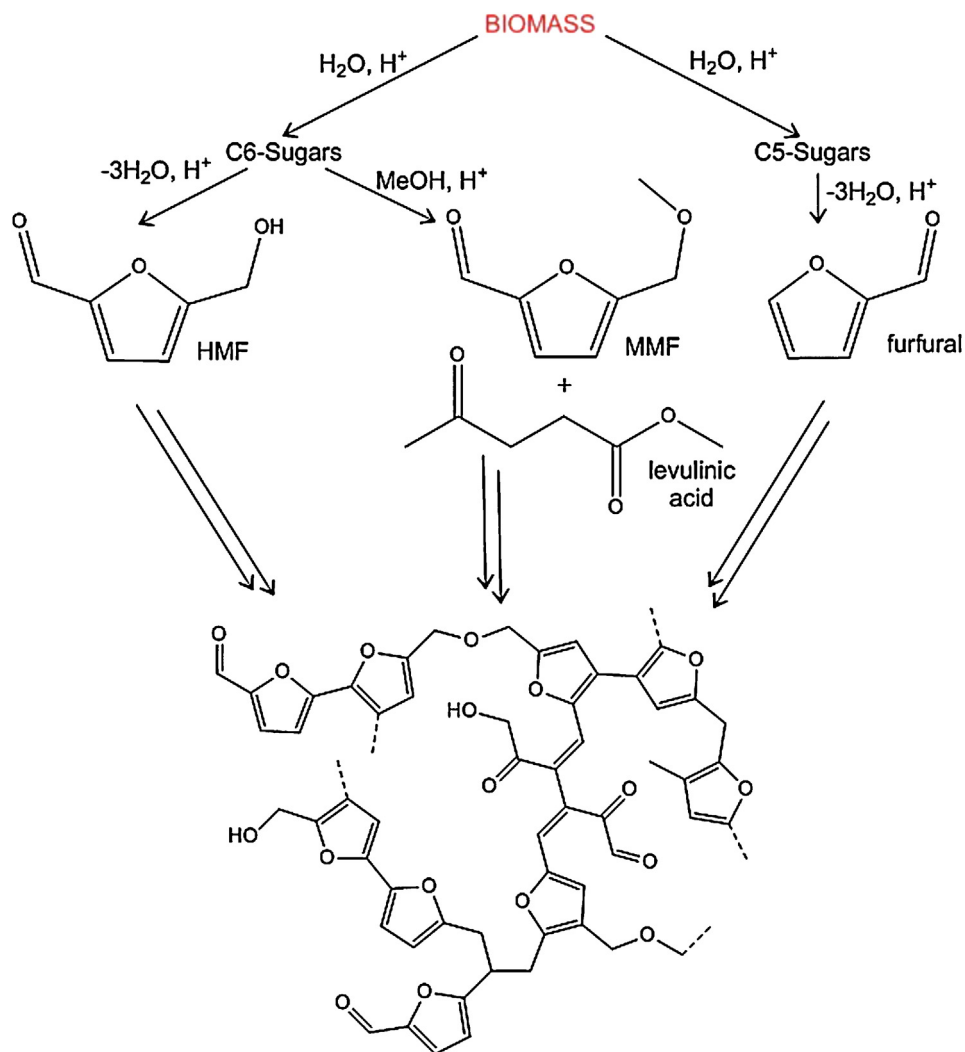
Scheme 3. Pathways formation of humin by-products.
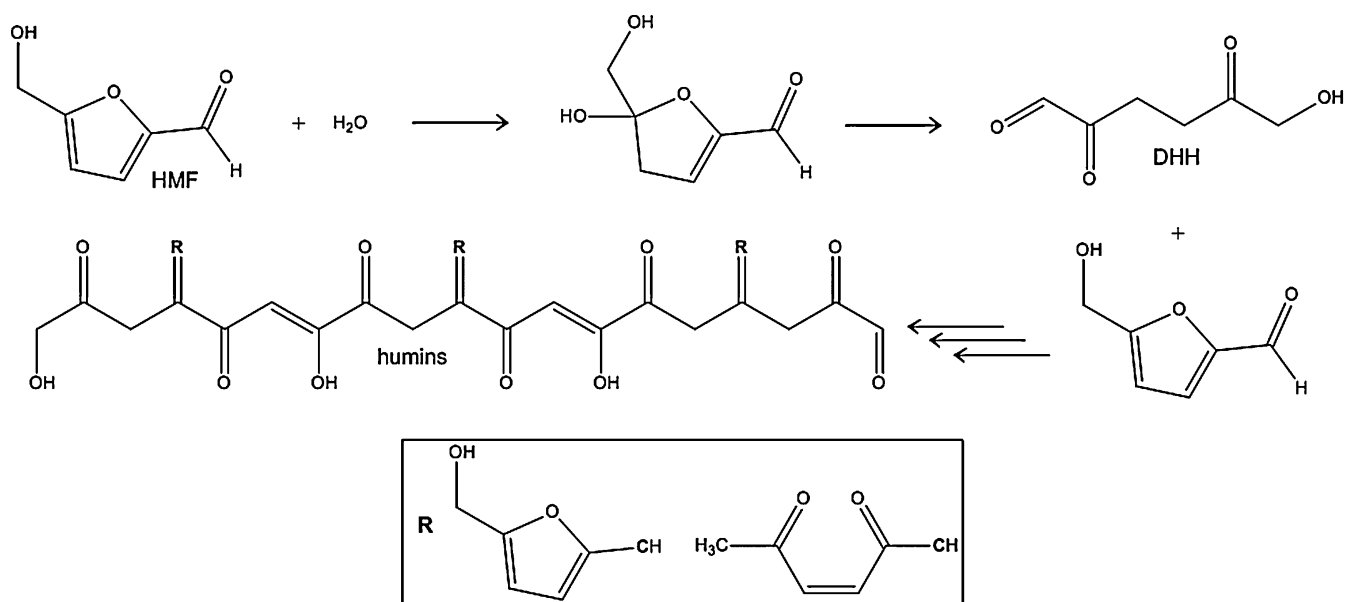
Scheme 4. Humins formation mechanism as proposed by Lund et al., adapted from Ref. [126].

Table 7
Humins transformations reported in literature.

Process	Catalyst	Conversion (%)	T (°C)	t (min)	Yield (%)	Ref.
Gasification	Na_2CO_3	100	750	30	81 (H_2) or 75 (syngas)	[114]
Fast pyrolysis	–	–	500	12 s	30 (volatile)	[143]
Hydrotreatment	Ru/C	69	400	360	65 (phenolics)	[144]
Hydrotreatment	Ru/Al_2O_3	59	400	360	70 (phenolics)	[144]

yet to be identified spectroscopically. This hypothesis was further accredited by Lund et al. [118,126] in the humin formation from HMF. IR spectra showed the presence of an extensive conjugated network, and furan rings with aldehyde or ketone functional groups were supposed. The proposed mechanism involves DHH as key intermediate, formed by 2,3-addition of water to HMF. In particular, the highly reactive intermediate undergoes aldol condensations with the carbonyl group of HMF, yielding to humins (Scheme 4). However, the mechanism has not yet been unequivocally established.

Self-condensation of HMF or furfural has been postulated [127]; however, this possibility has been discarded by others [128]. Molecules such as HMF and furfural cannot undergo condensation reactions due to the absence of an α H-atom, pushing forward the theory that humins are formed *via* cross-polymerization reactions between HMF and either sugars or reactive HMF-derivatives [52]. Dee et al. [129] reported up to 30% humin yield in the hydrolysis of cellulose to glucose in ionic liquids and sulfuric acid. The research group observed an increase of humin yields with increasing HMF concentration, confirming the important role this molecule plays in humins formation. It was postulated that humins are formed *via* polymerization reactions of HMF with glucose, initiated by protonation of HMF aldehyde group followed by condensation with a sugar molecule. Similar findings were reported by Herzfeld et al. [130], who suggested that furan units act to cross-link sugar molecules. Akien et al. [131] investigated the dehydration of fructose to HMF with *in situ* NMR and ^{13}C labeling studies, intermediates that are believed to polymerize to humins. In particular, it was proposed that the furanose-type intermediate lead to HMF while pyranose forms lead to humins.

The formation and morphology of humins as a function of feedstock and operating conditions was recently studied [116]. It was found that humin formation is strongly influenced by reaction temperatures and acid concentrations but little effect was given to sugar concentrations. A dependence on the feedstock type was nonetheless observed, with higher humin formation from fructose due to the fast formation of HMF. Condensation reactions were attributed to nucleophilic attacks resulting in linkages at the α position of HMF, or substitution at the β position.

Combination of elemental analysis, IR, ^{13}C ssNMR, and pyrolysis–GC–MS, lead to speculate a furanic structure formed *via* dehydration, with alcohol, acid, ketone and aldehyde groups. It was also noted that xylose-derived humins presented a more conjugated structure due to the reactivity of the free 5-position of furfural, as it is well-known in the formation of resins [132]. 1D and 2D ssNMR were performed by the same research group on ^{13}C-labeled humins, in a later publication [133]. This study revealed that in the acidic dehydration of glucose, the major linkages in humins include $C_\alpha-C_{aliphatic}$ and $C_\alpha-C_\alpha$ bonds, while C_β linkages were minor. Moreover, reactive solubilization *via* alkaline treatment on the humins formed a more aromatic structure, at the expense of the furan rings.

Tsilomelekis et al. [117] validates the proposed nucleophilic attack of a HMF carbonyl group to the α or β position of the furanic ring, and ATR-FTIR indicated that humin formation involves a multitude of parallel reactions to the aldol condensation. Recent work by Wang et al. [134] reported FTIR and ^{13}C NMR analysis on glucose- and xylose-derived humins, finding *ca.* 50% of carbon in furanic rings, and an abundance of oxygenated functional group. Xylose-derived humins, however, contained higher aliphatic content. Analysis of the volatiles from the pyrolysis of the two different humins showed similar compositions, with furans and phenols as the main products. Aromatic products and carbonization were favored by the high pyrolysis temperatures.

In conclusion, humin formation mechanism is largely unknown, alongside the various feedstocks intermediates. Nonetheless, some attempts in upgrading this humin waste have been attempted. Traditionally, the minimization of humic substances is usually preferred [135,136]. For example, less humins were observed with toluene extraction in the ethanolysis of carbohydrates [135], and addition of co-solvents such as GVL and methyl-THF [137,138]. However, different approaches have been taken into consideration for upgrading this unavoidable waste. Steam reforming of humins was reported by Hoang et al. [112] at 750 °C over a variety of alkali- and alkaline-earth based catalysts, Na_2CO_3 was found to be the most effective giving a complete conversion of humins with a 75% selectivity to syngas (81% H_2 yield). Byun et al. [139] proposed the integration of a heat exchanger that utilizes lignin and humins as combustible in the production of butene oligomers from cellulose. Humins have also been integrated in polyfurfuryl alcohol (PFA) polymeric structure, creating a new composite with lower brittleness than the pure PFA sample [140]. These various material applications might seem direct and simple for the undesired substances. Humins offer the potential also to liberate highly added-value chemicals. Rasrendra et al. [141] reported, in fact, that liquefaction of humins by fast pyrolysis yielded low molecular furanics such as furfural and 2,5-dimethylfuran, which show a potential of obtaining important platform chemicals from the humic waste. Wang et al. [142] reported the hydrocracking and hydrodeoxygenation of low molecular weight humins, with a mixture of formic acid and isopropanol over ruthenium-based catalysts at 400–500 °C. The main products obtained were naphthalenes, alkylphenolics, and cyclicoalkanes. Other products included alkanes, aromatics, and polyaromatic hydrocarbons. Remarkable humin conversions of 69% were obtained on Ru/C with formic acid, while Ru/Al_2O_3 gave only 59% humin conversion. These results pointed out the potential of humins as new feedstocks rather than traditional waste (Table 7).

5. Conclusions and future prospects

This manuscript was aimed to provide a general overview on the various possibilities to valorize three key biomass-derived side products from hemicellulosic fraction processing. MeL, as well as in general levulinate esters, have *per-se* remarkable properties with potential applications in the fragrances and flavoring industries and additional possibilities to be converted into a number of useful derivatives (e.g. gamma-valerolactone) and can be simply produced from a number of biomass feedstocks under both homogeneous and heterogeneous catalysis. Interestingly, fine-tuning Lewis/Brønsted acid sites ratios, the presence of medium strength acid sites and a regular pore size distribution to avoid diffusional

issues in MeL production (only for solid acid catalysts) seem to be critical to develop in order to maximize MeL yields for its subsequent conversion to valuable chemicals and fuels.

Furfural is one of the most promising furanic compounds that can be obtained from C5 sugars via dehydration. Furfural production can be industrially feasible when yields exceed 50 wt% for which both homogeneous and heterogeneous systems have been reported starting from a number of biomass-derived feedstocks (also different from xylose). The key in maximizing furfural yields from C5 sugars lies in the design of catalytic systems featuring optimum acidities (strength *vs* type of acid sites), surface areas, pore sizes, etc. to minimize humins and side products formation – generally produced under mineral acid catalyzed dehydration or in the presence of too strong acid sites – in the dehydration step.

Last, but not least, humins as generated intractable furanic polymers originate from dehydration reactions of biomass-derived carbohydrates which have a remarkable potential for their conversion into valuable chemicals and fuel precursors (e.g. furanics and aromatics) as well as materials. Their unknown and poorly characterized structures to date make such catalytic processing a significant challenge which however can provide alternative research avenues to companies currently producing humins as waste product from sugar-related chemistries.

The selected examples illustrate the potential in the production of biomass-derived side products in view of their potential valorization to chemicals, materials and fuels, with substrates including humins that will play a major role in future biorefineries to provide additional revenues to companies working on sugars processing.

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