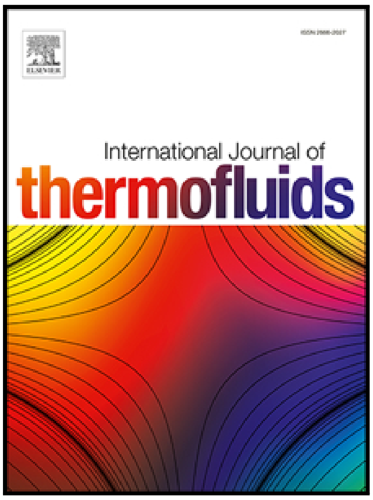

Lignocellulosic biomass conversion to levulinic acid via acid catalysis: current methods, opportunities and challenges for self-sustaining biorefineries.

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Highlights

- Cheaper levulinic acid from lignocelluloses requires full by-products valorisation.
- Nature of solid by-products depend on feedstock composition and catalytic variables.
- Heterogeneous/homogeneous catalyst synergies are positively correlated.
- Solid residues from acid hydrolysis of lignocellulose are the largest by-product.
- Hydrochar use as promoter of anaerobic digestion is a novel valorisation route.

Lignocellulosic biomass conversion to levulinic acid via acid catalysis: current methods, opportunities and challenges for self-sustaining biorefineries.

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Abstract

In recent years, integrated biorefineries have received growing interest as to maximise the extractable value from biomass in the form of green platform chemicals in order to support the establishment of a low carbon economy. Research and development in this area has focused on the conversion of lignocellulosic biomass, regarded as second-generation feedstocks, into a multitude of biochemicals from numerous different plant-based feedstocks with a wide range of catalytic systems, particularly the production of levulinic acid. This work critically reviews the most significant and pertinent literature of the methods and challenges of second-generation feedstock for levulinic acid production, identifying heterogeneous/homogeneous catalyst synergies can improve yields between 28-58% depending on mineral catalyst promoter used. In addition, areas of particular focus of this review regards solid residues potential applications in a circular biorefinery context, revealing the novel role of hydrochar as booster additive in anaerobic digestion, which results in increased methane yields and, potentially, better soil amending digestate. The review also highlights the gaps in knowledge and synthesise new concepts to bridge these gaps in research, most pertinently applied to the solid residue formation and properties, with key links between multiple fields defined for the first time.

Keywords: Levulinic Acid; Value Added Chemicals; Lignocellulosic feedstock; Biorefinery; Catalysis; Solid residues.

Abbreviations: anaerobic digestion (AD); 2,5-dioxo-6-hydroxyhexanal (DHH); gamma-valerolactone (GVL); hydrothermal carbonisation (HTC); Higher Heating Values (HHV); 5-hydroxymethylfurfural (5-HMF); Klason-lignin (KL); microvawe (MW); plug-flow reactors (PFR).

1. Introduction

The global transition towards a low-carbon economy has driven a in growing interest in low-carbon green chemicals [1]. Lignocellulosic biomass can be converted into a range of both bulk and fine chemicals, carbon emissions partially negated by the use of carbon-neutral biomass feedstocks [2]. Due to the complexity of biomass composition focus has been on the development of platform chemicals, such as levulinic acid and furfural, that can be utilised in the production of fuels, herbicides and solvents among other high value applications, as shown in Figure 1 [3]. For example, hydrogenation of levulinic acid to valeric acid (pentatonic acid) and subsequent esterification to valerate esters will yield petrol and diesel-grade compounds [4], as shown in Figure 2. Levulinic acid can also be oxidised to succinic acid [5], which is a complementary C4 platform chemical [6]. It can be hydrogenated to gamma-valerolactone (GVL), a useful solvent and polymer precursor [7], or undergo amination to form the herbicide amino-levulinic acid, among other applications. Similarly furfural, commonly produced during levulinic acid synthesis has shown a diverse range of applications including polymers, resins fuels and solvents [8–10]. The development of these applications of levulinic acid as part of a green chemical sector requires the efficient low-cost production of the platform chemical itself. Levulinic acid production from lignocellulose is therefore imperative.

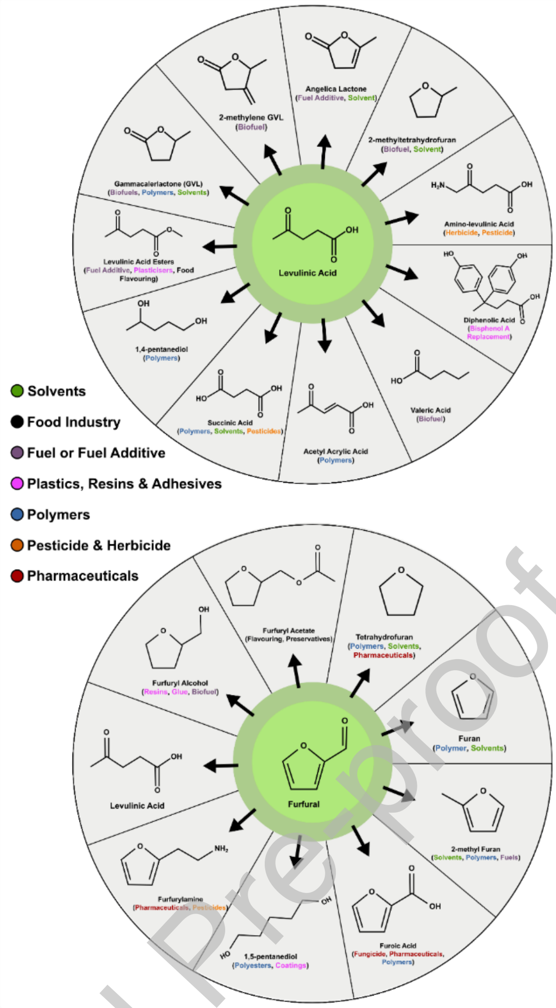

Figure 1: Levulinic acid as a platform chemical for multiple applications

Levulinic acid can be synthesised directly from the lignocellulosic materials, in conjunction with furfural and formic acid, with minimal biomass pre-treatment using “one-pot” or sequential acid catalysis [11–14]. Acid-catalysed hydrolysis employs relatively mild temperatures (120-250 ^{o}C) to selectively hydrolyse β-1-4-glycosidic bonds in cellulose, while simultaneously catalysing the dehydration and conversion of the resulting monomeric sugars to high value chemicals [15]. The combination of low temperature and catalysts reduces the quantity of side products reducing the difficulty of separation and producing higher value platform chemicals. The application of acid catalysts can selectively transform two of the largest lignocellulosic fractions, cellulose and hemicellulose, directly towards multiple platform chemicals offering a greatly simplified process with comparable methods. This can be further improved using heterogenous acid catalysts that very much reduce catalyst separation costs compared with homogenous ones such as HCl and H_2SO_4 [16]. Solid acid catalysts include metal oxides, modified metals, zeolites, acidic polymers, and metal oxide frameworks [17–19]. Despite solid acid catalysts achieving comparable yields for the conversion of sugars to levulinic to mineral acids, difficulties have been found with cellulose and biomass, due to reduced solid-solid interactions and catalyst deactivation [20]. As such, mineral acid catalysis is among the most developed lignocellulose conversion methods with several pilot and demonstration plants in Italy, Minnesota (USA) and the Netherlands, for the production of platform chemicals including furfural, 5-hydroxymethylfurfural (5-HMF) and levulinic acid [21].

The further development of commercial levulinic acid using acid catalysts has proven more troublesome in recent years, despite the ever-growing attention it has received. Several studies have modelled various levulinic acid production processes from lignocellulose, which highlighted several issues limiting full commercialisation [22–24]. Most notably, the low weight yields of levulinic acid (10-25 wt.%) require either higher selling prices or the complete valorisation of the biomass by-products [25]. For example, typical acid hydrolysis processes can yield 5-10 wt.% of both furfural and formic acid from biomass, requiring furfural valorised for the production of solvents, polymers and fuel additives [26,27] [28–31], while formic acid is extensively used as a commodity chemical in multiple industries with multiple applications. Valorisation of by-products is thus seen as essential for lowering the cost of levulinic acid production, with significant attention placed on the two aforementioned by-products. Large quantities of quantities of currently low-value aqueous and solid waste products are produced as both degradation products and unreactive lignocellulose fractions [32]. Amongst these, the solid residue is the largest fraction accounting for 30-60 wt.% of the starting biomass and is most-frequently utilised for energy recovery as a post-reaction solid fuel [33]. This represents a key element to be valorised appropriately (higher value) for modern, self-sustaining biorefineries. The process operating conditions have a significant effect on the formation of solid by-products, most notably humins from the dehydration of sugars through aldol condensation [34,35]. The formation mechanism of humin by-products via aldol-condensation of 5-HMF has been elucidated in great detail by literature and it can include lignin and protein fractions [33,36–39]. The valorisation of humin-rich solid residue has proven a difficult challenge for biorefinery design [25]. In fact, high value applications have included utilisation as a building material, pyrolysis feedstock and anaerobic digestion supplement [40–44]. As such, the minimisation of solid residue and other by-product yields is commercially advantageous via process optimisation, advanced separation, and novel catalysis solvents [45–48]. However, the by-product yields have been found to depend on the nature of the biomass feedstock utilised for acid hydrolysis as well as the different operating conditions [49]. The effects of biomass composition thus not only affect the by-product (in yield and type), but also the levulinic acid yield. There are no extensive reviews investigating this link in great details. Accordingly, this study focused on the conversion of lignocellulosic biomass towards levulinic acid with specific consideration on the effects of all biomass fractions on the overall process including by-product yields.

2. Lignocellulosic Biomass Composition

The abundant availability of lignocellulosic biomass across major global regions, manifests in a diverse scalable multi-source supply of up to 1.3 billion tons annually [50]. Lignocellulosic biomass by definition includes all feedstocks containing cellulose, hemicellulose and lignin as their primary components with, forestry residues, paper residues, agricultural by-products and dedicated energy crops [51].The variety in lignocellulosic biomass manifests itself in varying biomass composition in both regards to the largest constituents, namely structural polysaccharides, as shown in Table 1. The exact composition and local availability of each lignocellulosic feedstocks will vary significantly, however, the commonality of primary constituents, facilitates the transfer of processing methods from one feedstock to another [52–54]. Therefore, the heterogeneous nature of lignocelluloses necessitates an investigation of all constituent fractions to understand the overall conversion process, the interaction between breakdown products and their impact on final levulinic acid yield.

Table 1 Examples of varying composition of the main structural components in lignocelluloses

Lignocellulosic Biomass	Cellulose / wt.%	Hemicellulose / wt.%	Total Lignin / wt.%	Reference
Rapeseed	30.5	18.7	15.1	[55]
Corn Stalk	39.0	42.0	7.3	[56]
Wheat Straw	38.2	30.0	15.7	[57]
Rice Straw	40.4	18.1	26.0	[58]
Miscanthus x Giganteus	38.3	24.7	18.0	[20]
Poplar Wood	48.9	21.7	23.3	[59]

2.1 Cellulose

The largest single constituent of lignocellulosic biomass is cellulose, accounting for up to 50% of the dry weight and it is considered the primary target of lignocellulosic conversion to platform chemicals or biofuels. Cellulose is composed of 15-20 nm wide microfibrils that contain β-1-4-glycosidic bonds linked glucose units that form the plant cell wall [60]. The arrangement of the cellulose microfibrils provides structural strength to the cell wall and plant, by utilising a rigid crystalline structure that causes significant intramolecular hydrogen bonding networks [61]. The crystalline structure is recalcitrant and insoluble under normal conditions, however the linking glycosidic bonds are susceptible to acidic and enzymatic hydrolysis, as well as ionic liquids. Transitionary zones of less organised cellulose chains (identified as amorphous cellulose), exist between crystalline cellulose microfibrils, as shown in Figure 2. Where the accessibility of cellulose and thus the β-1-4-glycosidic bonds have been shown to be directly proportional to the amorphous cellulose content [62]. Previous studies have shown that accurate conversion of cellulose requires the modelling of both amorphous and crystalline cellulose degradation. The crystalline – amorphous variation is often overlooked in cellulose valorisation and has been proposed as a source of lower than expected product yields.

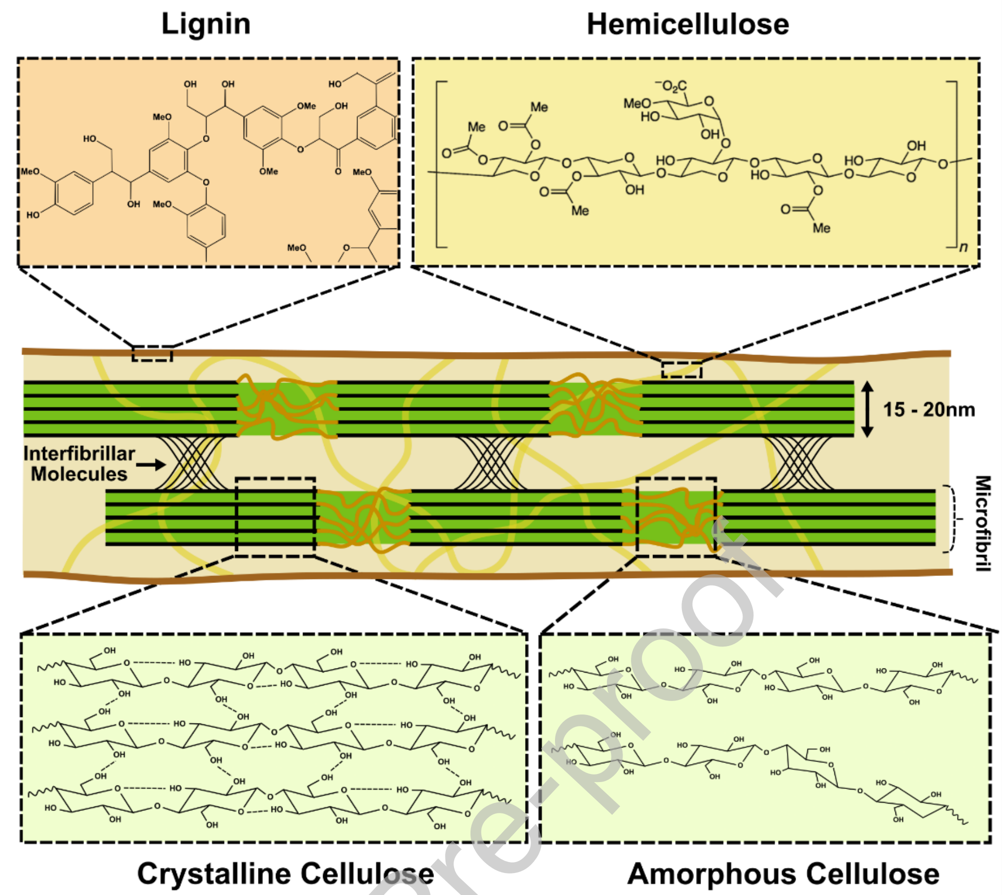

Figure 2: Difference between crystalline and amorphous cellulose

Particle size reduction pretreatment of lignocellulose has shown that dry ball-milling reduce cellulose crystallinity, which results in an increased rate of cellulose hydrolysis to glucose [63]. More recently, wet ball milling has been found to have reduced effects on crystallinity, due to recrystallization of cellulose during drying [64]. Wet milling has a well-known energy advantage over dry-milling processes that would make it a preferred and much more cost-effective initial pre-treatment method [65].

2.2 Hemicellulose

Hemicellulose is the next largest component of lignocelluloses, characterised by an amorphous structure, as it is composed primarily of xylose, but also includes a variety of other sugars including galactose, glucose, mannose and arabinose, as well as acetic acid [66]. Its primary function in the cell wall is to bind cellulose to lignin and it is inherently amorphous with very few protecting groups to the linking glycosidic bonds. Hemicellulose plant content and sugar composition differ significantly between species, with switch grass showcasing values of nearly 30% compared with woods, which frequently contain less than 10% [67]. The primary constituent (xylose) is a five carbon (C5) sugar; hence, it differs from glucose (C6 sugar), and these undergo different reaction pathways during hydrolysis. Currently, the largest application of xylose is for the production of the platform chemical furfural. Xylose can be separated from lignocellulosic biomass via sequential hydrolysis or steam explosion [68]. Despite that, due to the relatively small abundance compared with cellulose, its valorisation is not prioritised in current biorefineries.

2.3 Lignin

Finally, lignin is a three-dimensional polymer of phenylpropanoid units [53]. Its biological purpose is to provide stiffness and strength to the plant material, and is primarily composed of a non-repeating structure, primarily derived from p-coumaryl, coniferyl, and sinapyl alcohols [69]. Lignin is most commonly classified in two types by literature as Klason lignin (also known as acid insoluble lignin) and acid soluble lignin. Lignin can be liberated into is aromatic monomers using oxidative processes (including white fungi, alkaline, oxidation, fast pyrolysis and hydrogenolysis) [70–72]. These aromatic compounds are currently of great commercial interest for use in production of vanillin, biofuels and styrenes [73], but for the most part lignin is refractory to degradation under non-oxidative conditions [74,75]. Several other methods have been developed to increase lignin accessibility, including catalytic, ionic liquids and enzymatic processes [76–78]. During non-oxidative conditions [79], such as acid hydrolysis, the hydrothermal conditions can induce aromatisation and dehydration of lignin [80]. This is further discussed in Section 6.2.

Acid soluble lignin is composed of short-chained hydrophilic phenolic compounds [81,82] and its content in lignocelluloses varies between 3-10% of plant dry matter. Acid soluble lignin has been observed to react with various sugar compounds under hydrothermal and acidic conditions to produce pseudo-lignin [83,84]. Pseudo-lignin is an aromatic material, which contributes to Klason lignin content but is not derived thereof. The individual reactions of acid soluble lignin under various operating conditions are not well understood, though they can be broadly described as condensation reactions forming insoluble materials akin to Klason lignin.

2.4 Minor constituents

Alongside these three constituents, there are a range of other simple sugars, proteins, pectin and oils as well a multitude of trace chemicals that make up to 20% of biomass. The quantity and composition of extractives from lignocelluloses varies significantly between feedstocks and processing conditions [85]. These other components can either be inert and/or reactive under different operating conditions. The removal of extractive aromatic compounds such as tannins has received significant attention using solvents such as water, ethanol and deep euletic solvents, as well as via dilute acid or alkaline hydrolysis [86]. However, selective extraction processes have demonstrated low selectivity with high sugar losses [87,88]. Other extractives such as proteins are mostly insoluble though have demonstrated flocculation properties [89] , while uronic acid composed pectins are effectively insoluble under non-alkaline conditions [90]. Determining the relative reactivity of the extractive fraction is possible through experimental methods only; which is one of the reasons why a multitude of feedstocks must be trialled.

3. Polysaccharide fractionation pre-treatments

Given the complexity and insolubility of the polysaccharide matrix, it is beneficial to degrade the long-chained polymers into individual monomers before further valorisation. This includes the hydrolysis of cellulose and hemicellulose to primarily glucose and xylose respectively, in addition to feedstock-dependent trace quantities of mannose, galactose, arabinose and rhamnose sugars [70]. The polysaccharide hydrolysis can be achieved through several processing conditions most importantly, but not limited to, hydrothermal hydrolysis, acid hydrolysis, solvatic processes (such as organosolv, deep euletic solvents, and ionic liquids) and microwave assisted heating systems [91–95].

Under hydrothermal conditions the hydrolysis of polysaccharides towards simple sugars can be achieved using processing methods such hot water extraction and steam explosion [96–98] . The advantages of hydrothermal processes are the reduction in the catalyst consumption and cost, with no requirements to remove corrosive acids. However, specific hydrothermal hydrolysis processes such as steam explosion and sub-critical water extraction have been found to not fully hydrolyse sugar-based polymers, though they do not produce significant by-products from hydrothermal decomposition such as levoglucosan, furfural and glycolaldehyde [99]. Another disadvantage is that hydrothermal hydrolysis produces significant quantities of oligosaccharides that have lower conversion yields to that of monomeric sugars, further reducing levulinic acid yields [102,103]. Acid catalysed hydrolysis can selectively hydrolyse β-1-4-glycosidic bonds between repeating sugars at moderate temperatures (120-250 °C) with mineral and organic acids such as hydrochloric, sulphuric, formic and oxalic acid [69]. In the last 20 years, the acid hydrolysis of large variety of materials including crystalline cellulose, bagasse, wood, energy crops, grasses and agricultural wastes, has been extensively investigated for the production of monomeric sugars [67,104–106]. Alternative non-aqueous solvents with ionic properties such as ionic liquids and deep euletic solvents can hydrolyse by disrupting the polysaccharide structures [115]. Ionic liquids have been described as “designer solvents” that can be further tailored for specific applications including the catalysis of sugars to levulinic acid [118]. However, ionic liquids are currently expensive for commercial uses and can easily precipitate with ash impurities in lignocellulosic feedstocks [119,120]. Recent works have sought to reduce ionic liquid costs by utilising inorganic anions combined with organic cations [115], though work is ongoing. In recent years the use of microwave heating has been actively investigated as an alternative to conventional thermal conduction/convection heating for biomass processing. Despite the benefits of microwave heating, its wide scale commercial adoption has been limited. Previously, its use has been constrained by high electricity costs, high capital costs and low scalability [136]. More recent developments however have sought to reduce these costs by adopting modular microwave approaches that increase scalability and reduce capital costs via process intensification. While the price of electricity will remain comparatively higher than fossil fuel derived low pressure steam, the development of low-carbon electricity grids can potentially significantly reduce the carbon impact of process heating [137]. The electrification of industrial processes is considered a key challenge in meeting carbon reduction emissions and the use of microwave heating would help meet these goals [138].

4. Acid catalysis of sugars

4.1 Homogeneous catalysis

The acid catalysed conversion of sugars can be combined with the polysaccharide hydrolysis, resulting a “one-pot” process for the direct production of biochemicals from lignocellulosic biomass. Using Brønsted and Lewis acid properties, cellulose can be hydrolysed to glucose, as previously discussed, before transformation into levulinic acid, following the paths shown in Figure 3 [34]. Lewis acids can readily isomerise glucose to fructose, in which the pyranose structure is converted to furanose fructose, which is known to be more unstable [96]. Fructose can then undergo the Bronsted acid catalysed triple dehydration to form the intermediate, and highly reactive, 5-HMF [97]. The subsequent double rehydration of 5-HMF produces a stoichiometric equal mixture of levulinic and formic acid. Formic acid is a versatile biochemical that can be utilised in a multitude of processes in a biorefinery context [31]. [98]

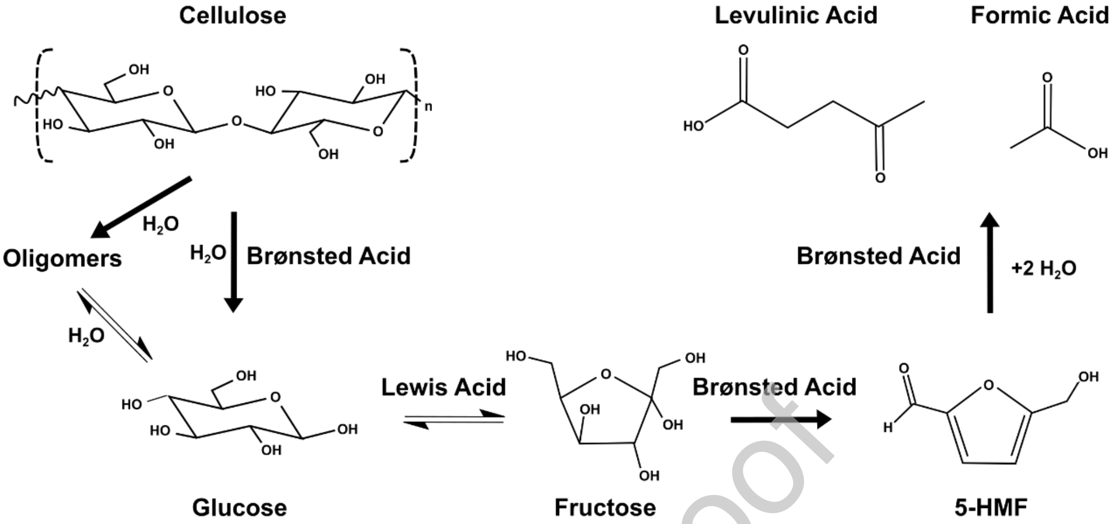

Figure 3: Production of levulinic acid from cellulose with intermediate glucose, fructose and 5-HMF

Homogenous catalysts such as mineral acids, metal salts and organic acids have been used for the conversion of sugars, cellulose and real lignocellulosic biomass, as shown in Table 2. Levulinic yields have varied from 30 to 80%, from a variety of feedstocks and reaction conditions. In 2006, Girisuta *et al.* [99] utilised H_2SO_4 (0.05-1.0 M) to achieve levulinic acid yields exceeding 80% using glucose as a feedstock at 140 °C. The accompanying kinetic model identified that the lower operating temperatures (towards 140 °C) improved the selectivity of glucose towards levulinic acid over side reactions. While higher operating temperatures around 200 °C is required for selective cellulose hydrolysis. The difference in optimum operating temperature between cellulose hydrolysis and levulinic acid synthesis can complicate optimisation of lignocellulose conversion. This limitation is not an issue for the conversion of simple sugars such as glucose and fructose, leading to yields of over 70% with catalyst HCl, H_2SO_4 and $AlCl_3$. Several studies report that fructose is nearly 100 times more reactive than glucose [100,101] and that metal ions, such as Al^{3+}, Sn^{2+} and Cr^{3+}, can greatly improve the isomerisation of the glucose to fructose [102]. However, levulinic acid yields from sugars are limited by the formation of by-products, which reduce molar yields to below 80%.

Table 2: Summary of levulinic acid yields from a range of feedstocks with homogenous catalysts

Catalyst	Substrate	Substrate Loading (w/w%)	Temperature (°C)	Reaction time (Hours)	Other	Yield (mol. %)	Reference
2M H_2SO_4	Fructose	5	170	8		69	[103]
30 w/w% NaCl	Fructose	10	110	24		75	[104]
0.1 M HCl	Glucose	10	160	4		51	[105]
0.5 M H_2SO_4	Glucose	0.18	140	8		80	[99]
$SnCl_4$	Glucose	1.90	190	1.5		45	[106]
0.01M $AlCl_3$	Glucose	2	180	2		71	[107]
1M H_2SO_4	Cellulose	1.70	150	-		76	[34]
0.75M HCl	Cellulose	2	155	1.6	GVL*/H_2O Solvent	71	[108]
1.37 M HCl	Cellulose	1	200	0.05	MW	43	[11]
0.01M $AlCl_3$	Cellulose	2	180	2		24	[107]
0.02M $CrCl_3$	Cellulose	5	200	3		67	[107]
[HO$_3$S-(CH2)3-py]Cl-FeCl$_3$	Cellulose	1.67	180	10		49	[17]
0.1M H_2SO_4	Euctalyptus	5	190	1		29	[109]
2.5M H_2SO_4	Kernel grain sorghum	10	200	40 mins	MW	33	[110]
1 M H_2SO_4	Corn-cob	10	180	0.5		75	[111]
5% w/w H_2SO_4	Poplar Wood	10	190	50 mins		54	[112]
37 w/w% HCl	Poplar Wood	7.2	200	1	MW	71	[113]
2 M HCl	Corn Starch	1	165	0.25		55	[114]
0.37 M HCl	Bamboo	10	160	3	MW	48	[115]
0.6M HCl	Pre- treated Cow-Dung	3.3	180	2.5		81	[116]
[C$_3$SO$_3$Hmim]Cl$_2$	Rice straw	-	180	1.5		21	[117]

[BMIMSO$_3$H] HSO$_4$	Corn Stover	-	95	1		70	[118]
2M Maleic acid + Al$_2$(SO$_4$)$_3$	Mandarin Peel	4.3	180	0.63		86	[119]

*GVL = gamma-valerolactone

Using microcrystalline cellulose, it is possible to achieve levulinic acid yields exceeding 60 % with HCl, H_2SO_4 and $CrCl_3$ as shown in Table 2. Mineral acids are of greatest interest for this application, due to their availability, low-cost and high yields however, their corrosive properties have been reported to damage vessels and pipeline systems [24]. Transition metal chlorides also received attention in this area, due to the low concentrations required (<0.1 M) to achieve high yields compared with HCl (0.1-1.0 M) and H_2SO_4 (0.5-2M) [107]. It has been hypothesised that the chloride counter ion has an additional positive effect of stabilising intermediate products [120]. More recently, neutral NaCl salts have been reported to achieve yields over 75% from fructose under relatively mild conditions (<150 °C) [104], however chloride ions under neutral conditions have not been reported to fully depolymerise cellulose or isomerise glucose to fructose.

Due to the complexity of lignocellulosic biomass, its composition must be screened to estimate the interference of other compounds on catalysis. This is most evident with metal salt catalysts such as $AlCl_3$, which tend to precipitate with counter ions found in real lignocellulosic biomass [121], despite achieving similar yields to that with pure cellulose. Ion precipitation is a considerable expense for ionic liquids conversion of real biomass, due to the low catalyst recyclability, especially with toxic transition metal elements [122]. The salt precipitation issue is less significant with mineral acids, primarily HCl and H_2SO_4, due to the wide solubility of their respective salts under aqueous conditions. Antonetti *et al.* [113] achieved levulinic acid yields exceeding 70% with a range of feedstocks including poplar wood, wastepaper and olive tree prunings at 200 °C for 1 hour with microwave heating, with similar yields being achieved with bamboo, cow dung and rice straw by other authors [115,116,123]. Despite the high yields consistently achieved with hydrochloric acid, the high corrosivity of the catalyst requires advanced alloy materials, greatly adding to initial capital costs [124]. Sulphuric acid has therefore been used as the compromise catalyst in several pilot plants in Caserta (Italy) and Minnesota (USA) [21], despite the possible $CaSO_4$ fouling issues with certain feedstocks such as wastepaper and tobacco waste [113,125]. Sulphuric acid has achieved yields of 50-70% with poplar wood, bagasse and food wastes [15,126,127]. The Biofine process reported sulphuric acid recyclability of over 98% with minimal fouling on a large scale [24] which has also been demonstrated on a lab scale [98,103].

The kinetic model of the cascade catalytic process shown in Figure 3, including by-products, has been investigated in great depth from both cellulose [34,128] and real lignocellulosic biomass [35,129,130]. Using the reaction kinetics continuous plug-flow reactors (PFR) have been designed for the large-scale production of levulinic acid and also implemented in pilot plants [21,105]. One of the advantages of PFR reactors is the minimisation of by-product yields, when using the Biofine process, to ~50 wt.% of the feedstock. Dussan *et al.*[131] proposed two PFRs in series, operating at 185 °C and 180 °C respectively, to achieve overall 72% levulinic acid yield from *Miscanthus x Giganteus*, with 27 % furfural yields in under 20 minutes. The modelling of the reaction kinetics with multiple feedstocks have found similar reaction rates for the conversion of glucose towards levulinic aid across multiple studies, while the differences in cellulose structure result in widely differing the kinetic data for polysaccharide hydrolysis. The variance in cellulose structure and crystallinity has been attributed as the cause of such difference along with the presence of inert fractions such as lignin and pectin [132]. Nevertheless, this results in each feedstock needing an individual and custom evaluation for this application.

4.2 Heterogeneous Catalysts and recyclability

Heterogenous catalysts compared with mineral acids have several advantages including reduced corrosive wear, improved separation, reduced environmental concerns and lower energy consumption [133]. In recent years, a large variety of solid acid catalysts has been investigated for the catalysis of sugars, cellulose and real biomass, as shown in Table 3. Such catalysts include insoluble metal oxides, zeolites, acidic ion-exchange resins and functionalised hydrochars. The use of solid catalysts significantly decreases the catalyst separation costs compared with homogenous catalysts, with minimal corrosion concerns [134]. Another key advantage of solid acid catalysts is their high temperature stability as well as the tunability of their surface acidity to improve catalyst selectivity by reducing by-product formation [135]. As an example, the carbonaceous solid acid catalysts obtained from lignin [150] is an interesting route to catalyse the conversion of cellulose into high-added value chemical, mostly because it can be obtained from natural and cheap raw materials, such as sugarcane straw [151]. It is also beneficial to use a solid catalyst instead of a liquid catalyst because the former is easier to isolate from the reaction mixture and has potential to be reprocessed [152]. These properties make heterogeneous catalysts suitable for large scale commercial application in this field, including levulinic acid production.

Table 3: Summary of levulinic acid yields from a range of feedstocks with heterogenous catalysts

Catalyst	Catalyst to Biomass ratio (w/w%)	Substrate	Substrate Loading (w/w%)	Temperature / (°C)	Reaction time (hours)	Other	Yield (mol. %)	Reference
Amberlyst 15	2.2	Glucose	10	140	8		59	[136]
ZSM-5	0.75	Glucose	4	180	3		53.2	[137]
Graphene-SO_3H	0.025	Glucose	15	200	2		78	[138]
Amberlyst 15	2.2	Glucose	10	140	8		26.7	[136]
Amberlite IR-105	0.7	Sucrose	10	130	0.05		19	[139]
Zirconium Phosphate	1	Cellulose	4	220	2		18	[140]
Amberlyst -70	3	Cellulose	2	160	16		23	[141]
C-SO_3H-Fe_3O_4	1.6	Cellulose	12	190	3.5	MW Magnetic	25.3	[142]
Sulfated TiO_2	1	Cellulose	2.5	240	0.25		32	[143]
Zirconium	1	Cellulose	2	180	3			[144]
Al-$NbOPO_4$	0.8	Cellulose	5	180	24		53	[145]
PTA doped carbon foam	5	Cellulose	1	180	4		89.4	[146]
Amberlyst 36	1	Paper Towels	5	150	0.33	MW	30	[147]
$CrCl_3$/HY	12	Kenaf	1	145	2.5			[148]
Amberlyst 36	20	Sugar Beet Molasses	0.1	140	180		78	[149]
SCSTc-x	3.6	Sugarcane	1	140	6		38.55	[150]
Cr-A15 (4 wt%, 6 wt%, and 8 wt%)	0.5	glucose, sucrose, MG,	1	200	2		1.2, 17.3, 4.6, 11.2,	[151]

	cellobiose, fructose, 5-HMF, and cellulose		10.6, 11.3, 5.8

4.2.1 Acidic ion-exchange catalysts

The first solid acid catalyst for levulinic acid production utilised acidic ion-exchange resin, Amberlite IR-105, to achieve yields of 19 wt.% (28 mol. %) from sucrose at 130 °C in 5-6 minutes under reduced pressures [139]. The use of this solid acid catalyst was able to significantly drop the reaction temperature and time compared with mineral acids. Acidic ion-exchange catalysts are made from functionalised polymers, most commonly sulfonated polystyrene, that can be produced at large scale with highly tuneable surface, porosity and ion exchange capacity. The sulphonic acid group (-SO_3H) is a strong acid that has similar acidic properties to sulphuric acid, without the associated corrosion issues. More recent works with Amberlyst has achieved levulinic acid yields of the 57% with fructose, 27% with glucose and 30% with wastepaper sludge [136,140,147]. The limiting factor with ionic polymers is the low isomerisation of glucose to fructose which can be mitigated by active basic catalytic sites [153] or the addition synergistic catalysts with soluble Lewis acids [104]. More recent works have utilised carbon foams to support acid exchange functional groups with over 80% yields over 5 recycles from cellulose [146].

4.2.2 Metal oxide catalysts

The cationic metal centres of metal oxides act as Lewis acids that can isomerise glucose to fructose, with high selectivity at low temperatures of <100 °C [134]. Zirconium dioxide has been reported to produce a molar levulinic acid yield of 32% at 180 °C for 3 hours from cellulose [144]. However, the direct conversion of cellulose to levulinic acid with a single metal oxide has mostly proven difficult, due to imbalances in the acid functional sites. This is due to the high catalytic activity of many metals, which can catalyse the formation of formic, acetic acid lactic acid from sugars [154], along with the further conversion of levulinic acid into higher value products such γ-valerlactone [155]. Ding *et al.* [145] suggested that the optimum Brønsted/Lewis acid ratio for the conversion of cellulose to levulinic acid is 1.2:1. Hybrid metal catalysts can easily be tailored to optimise acids sites with catalysts such as Al-Zr, zirconium phosphate and Ru/C for the conversion of sugars [140,145,156]. Nonetheless, it should be noted the use of metal catalysts has been limited for the production of levulinic acid for many reasons, but primarily for the strong adsorption of LA and degradation products onto the catalysts surface area, which can decrease levulinic acid yields over multiple cycles[160].

Surface modification can be utilised to tune acidic properties of metal oxides to improve levulinic acid yields such as sulphation or metal doping. Sulphated titanium dioxide and zirconia catalysts achieved levulinic acid yields of 32% and 59% respectively from cellulose [143,158]. Kobayshi *et al.* [159] developed a recyclable heterogeneous catalyst from the sulphated carbon chars resulting from the production of glucose from eucalyptus. Heterogeneous catalysts surface modification by sulphation has been found to increase the number of overall acid sites as well as allow the tunable modification of the Brønsted/Lewis acid site ratio [160]. The sulphation of zirconia increased the catalysts selectivity for levulinic acid from cellulose from 32% to 53% and showed remarkable stability over 5 recycles with lignocellulose [144]. However, with lignocellulosic biomass, humin deposition can deactivate surface modified sites which can be partially negated by the incorporation of organic hydrogels onto the surface structure[161] .

4.2.3 Zeolite catalysts

Zeolite catalysts such as ZSM-5, X/Y, β, and A are aluminosilicate minerals that exhibit a wide variety of tuneable catalytic crystal structure [162] [163]. As early as 1987, Jow *et al.* [164] used LZY zeolite to convert fructose to levulinic acid at 140 °C for 15 hours with a 43.2% yield, with the high selectivity attributed to molecular sieving ability, in addition to Lewis acid sites. Also, H-USY zeolite (Si:Al of 30) has shown remarkable selectivity (>90%) for the isomerisation of glucose to fructose at temperatures as low as 120 °C [165]. Ya'aini *et al.*[166] found that $CrCl_3$/HY catalyst can reach levulinic acid yields of 55.2 and 53.2% from cellulose and kenaf respectively, at 145 °C for 2.5 hours. In this case, the high yields were attributed to pore structure trapping intermediate 5-HMF [148]. The reduced steric freedom reduces the humin formation from the aldol-condensation 5-HMF reducing by-product yields. In addition, the catalytic activity of zeolites for the conversion of sugars and cellulose has shown remarkable stability of up to 5 recyles [165,167,168]. However, the recyclability of zeolites for the conversion real lignocellulosic biomass has proven more challenging, with yields decreasing by up to 60% over 3 recycles [169]. Low recyclability was attributed to several phenomena, including coking [170] and acid site leaching [171]. The coking phenomena also include the catalytic formation of insoluble humins via dehydration of intermediate compounds and also lignocellulosic extractives blocking the catalyst the surface area. Specifically the beneficial steric hinderance of furanic compounds can catalyse the decomposition of aromatic compounds inside the porous structures causing micro-channel blockages. Bianasari *et al.* utilised delignified rice husks to reduce coking with Mn_3O_4/ZSM-5 with H_2O_2 [172]while Magyarova *et al.* proposed the inclusion of metal cations into the zeolite structure to facilitate coke decomposition [173].

4.2.4 Metal-organic catalysts

Metal-organic catalysts utilise organic frameworks to support metal oxides or metal oxide nanoparticles have been investigated for an increased surface area and tuneable pore structure [174]. Metal-organic frameworks have primarily been investigated for the further conversion of levulinic acid via hydrogenation or ketalization[175,176]. Wang *et al.* achieved yields of nearly 32% levulinic acid using Ga2O3-UiO-66 with a high selectivity (68%) with regards to levulinic acid [17]. More recently, Lee *et al.* found that UiO-66-NH-R-SO_3H could produce levulinic acid from glucose with 71.6% yield at 170 °C [177]. The study by Lee found that the addition of alkyl spacers into the organic framework allowed tailoring of the spacing between Bronsted and Lewis acid site further improving levulinic acid yields. Metal organic frameworks offer many of the same advantages of ion-exchange catalysts, specifically the chemical inertness of the underlying structure, but with a far higher degree of functionalisation and optimisation options. Although the stability of such catalysts has not been demonstrated with biomass and have not been largely explored for cellulose conversion.

4.3 Synergistic Catalysis

Heterogeneous catalysts can be synergistically promoted by the addition of salts or acids in the aqueous phase, as shown in Table 4.

Table 4: Promotion of heterogeneous catalysts

Catalyst	Feedstock	Yield Without Promoter	Catalyst Promoter	Yield With Promoter	References
DOWEX DR-2030	Glucose	28% Levulinic acid	1:1 Salt:sugar	71% Levulinic Acid	[104]
Nanofin	Cellulose	14% Levulinic Acid	25 wt% NaCl	72% Levulinic Acid	[178]
Ru(1.8)/H–USY	Cellulose	1% Sorbitol	1 mM	29% Sorbitol	[179]
Sulfonated Carbon	Eucalyptus	31% Glucose	13 mM	78% Glucose	[159]

Previous studies have found that high concentrations of NaCl (20 wt.%) under hydrothermal conditions could partially depolymerise cellulose and, simultaneously, reduce the average molecular weight of cellulose by up to 50% without forming free sugars [177]. In this regard it was proposed that the Cl^- anion could disrupt the cellulose hydrogen bonding network. Other works have proposed that cellulose depolymerisation is enhanced in the order of CO_3^{2-}> F^- >> Cl^- > NO_3^- > SO_4^{2-} . Similarly, Pyo *et al.* [104] proposed Cl^- >CO_3^{2-} >SO_4^{2-} for the dehydration of the fructose to levulinic acid. The use of NaCl has been found to drastically increase the yields of levulinic acid with sulphated polymers however, it was shown to require high salt concentrations, exceeding 10 wt.%. Kobayshi *et al*. [159]was able to substitute concentred NaCl with dilute 13 mM HCl for the promotion of glucose formation from real biomass, which increased from 31% to 78%. While Geboers *et al*.[176] was instead able to improve sorbitol production via hydrogenation from cellulose by nearly 27-fold with only 1 mM HCl. Similar results were found with homogenous catalysts by Hu *et al.* where NaCl improved levulinic acid yields with benzenesulfonic acid from 45% to 60% from wheat straw [181]. These remarkable improvements with trace mineral acids can be used with a wide range of heterogeneous catalysts, by debottlenecking both the cellulose hydrolysis and 5-HMF hydration stages with Cl^- anions [103,106][200]

5. Post-reaction products and their applications

Catalytic reactions of lignocellulosic biomass yield a variety of liquid and solid by products, in conjunction to the target compound of levulinic acid. For practicality these products will be discussed separately in the following sub-sections based on their form (liquid or solid) and their chemical formula is shown in association with their main application in Figure 4.

5.1 Aqueous by-products

The production of levulinic acid from lignocellulosic biomass results in a range of aqueous and solid by-products [24,32]. Most notably, organic acids such as formic and acetic acid, acid soluble lignin and aliphatic hydrocarbons [182]. Aqueous by-products have been under reported despite the possibility for interactions that could reduce primary product yields. The most commonly reported by-product, acid-soluble lignin, has been reported by multiple authors to react with xylose under acidic conditions. Dussan *et al*. found that the formic acid by-product from levulinic acid synthesis could catalyse the reaction between lignin and xylose, reducing furfural yields by up to 24 %. The removal of acid soluble lignin is possible by dilute acid extraction which has also shown to improve cellulose hydrolysis [183].

Formic acid is a degradation product of multiple biomass products, including proteins, in addition to being formed in equimolar proportions to levulinic acid. The degradation of protein amino acids can result in the production of ammonia as well as multiple organic acids in trace quantities including, pyruvic, glutramic, and gylolic acid in addition to formic acid [184]. The presence of formic acid is often reported after acid hydrolysis, but rarely quantified. Formic acid has been found to be stable during the mineral acid hydrolysis [185,186] However, Świątek *et al.* [49] identified that formic acid degraded during the dilute hydrolysis with sugars, suggesting its consumption to be linked to the nature of the lignocellulose feedstock. In fact, formic acid reacts with acid soluble lignin and formylation of solid residues from acid hydrolysis could be possible [187,190]. Acetic acid is also naturally present in biomass in the form of acetylated hemicellulose. The acetate content of biomass varies up to 2 wt.% in certain woods, and is considered easily hydrolysable [189]. Several authors have shown that the acetic acid is independent of processing conditions and is not formed during the levulinic production, but it has been found to react with hydrochars, increasing the carbon content and Higher Heating Values (HHV) [190] This suggests that acetic acid becomes incorporated into the humin structures, though Wang *et al.* found acetic acid (~1 wt.%) had minimal effect on hydrochar surface properties [191]. The interactions between aqueous by-products and solid-by-products could have significant effects with solvent and catalysts recycling. Further investigation between trace aqueous products is required.

Levulinic acid recovery by solvent extraction or esterification, results in the separation of organic acids that must be further purified [192,193]. Previous studies have found that formic and acetic acid can be separated from levulinic acid during solvent recovery with levulinic acid as the bottom product [22]. Larger trace organic acids with similar boiling points to levulinic acid have not been investigated. Errico *et al.* modelled the extractive separation of levulinic acid, furfural and formic acid with furfural as the extractive solvent. The accumulation of acid soluble lignin and other organic by-products may thus accumulate in the extractive solvent necessitating further investigation. T

5.2 Solid By-Products

Solid by-products from acid hydrolysis of lignocellulose are the largest single by-product and can exceed the combined levulinic acid furfural weight yields [32]. The residual solid fraction complex, as the solid residue not only contains degradation products including humins, hydrochar and pseudo-lignin, but also unreacted biomass and unreacted lignocellulosic structures [41]. The relative ratio of these constituent fractions will vary as the reaction progresses, with unreacted cellulose constituting a decreasing fraction as the reaction progresses though is not completing eliminated. Therefore, the multiple constituent fractions can be defined from their source, as either an inert fraction present in the initial biomass or a process by-product.

The largest inert fraction of lignocellulose is Klason-lignin (KL) which can account for 10-30 wt.% of starting feedstock and has been found to be inert under sub 300 °C acidic reaction conditions [80]. Although Aftab et al. found that the acid removal of cellulose and acid-soluble lignin cause morphological changes to KL structure increasing the surface area and porous structure [194,195] . Klason-lignin properties are highly dependent on the reaction conditions due to its lipophilic properties that can result in the presence of long-chain hydrocarbons, alcohols, and ketones, sterols, stanols, and dioic acids. The aforementioned lipids are mostly inert under acidic conditions, have not been reported to react with KL matrix and are dispersed through the porous lignin structure that reduce wettability [196]. The wax and cutin derived structures can be mostly extracted using organic solvents such as ethanol, iso-propnal, acetic acid and hexane [197]. It has previously been reported that during compositional analysis the wax and cutin derived compounds are frequently erroneously reported as part of the KL fraction due to improper solvent extraction prior to analysis [198]. During levulinic acid production under aqueous conditions it assumed that the wax and cutin structures will be incorporated in the solid residue and would effectively be similar to KL.

The most frequently reported solid by-product during acid-catalysis are humins. Several humin formation mechanisms have been proposed by Lund and Patil [37], Huber *et al.* [105], Zandvoort *et al.*[39] and Heeres *et al.* [34] among others. These models have consistently proposed humin formation as an overall dehydration process via aldol condensation. Baugh *et al.* [199] found in 1985 that different C6 sugar isomers and processing conditions altered the elemental composition of humin formation (56-61 wt.% C). The variation of humin's elemental composition with reaction conditions was further investigated by the Heeres group (60-65 wt.% C) which suggested that the humins may be the result of multiple different reactions 165,166. However, Zandvoort *et al.* 157 demonstrated such differences in elemental composition can be explained as different degrees of dehydration of the overall structure. Sumerskii *et al.* [201] estimated the humin structural composition consisted of ~60 wt.% furan rings weight and ~20 wt.% linking aliphatic linkers. Furthermore, using C13 NMR, GC-MS and IR analysis, it was estimated that humins consisted of polymers chains varying in chain length with a similar composition of functional groups. IR spectra specifically suggested the presence of a significant number of oxygen functional groups, as well as furanic surface structures with acidic properties [33,38,202].

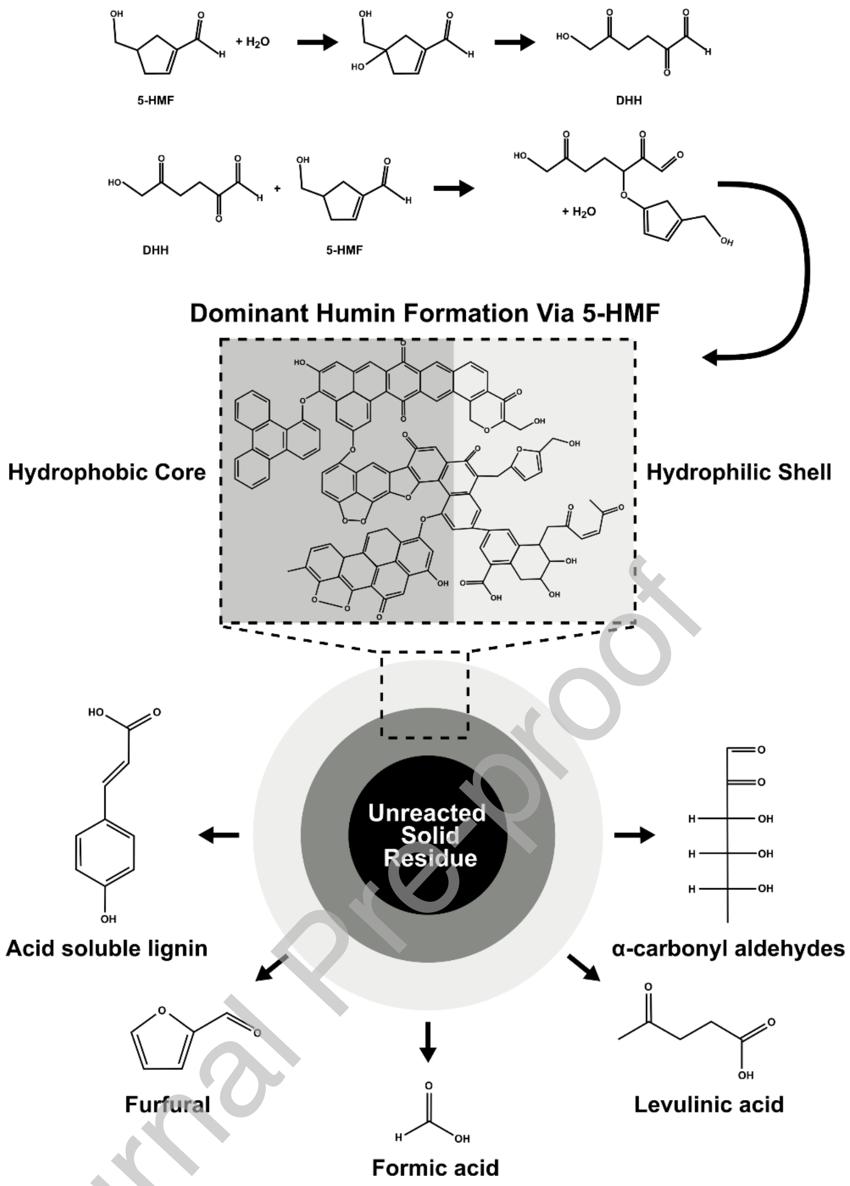

Figure 4: Composition structure of solid residue particle humin formation and minor compound incorporation

Patil and Lund [37] proposed a humin formation mechanism from 5-HMF explaining their findings on structural investigations, shown as the humin formation mechanisms in Figure 4. The proposed mechanism involved 2,5-dioxo-6-hydroxyhexanal (DHH) formed by rehydration of 5-HMF as an intermediate product for further polymerisation. Specifically, polymerisation between the carbonyl group of 5-HMF and DHH enolate group, with the subsequent product maintaining the enolate group for chain reaction aldol condensation. The solid residue from acid hydrolysis of sugars using ionic liquids, suggested that the primary humin formation rapidly occurred between soluble compounds, with slower solid-liquid and solid-solid interactions [203]. The particle size of the humins structures was found to increase with reaction time and could include levulinic acid fragments as part of the structure. Morphological SEM analysis suggested that the humins formed in the shape of spherical units [39,204]. Thus, the sugar-derived humins structures can be described as an oxygenated, time-dependant polymer with furanic cross-branching.

Multiple kinetic studies investigating the formation of levulinic acid have included the formation of humin by-products from both glucose and 5-HMF [15,34,128,131,202]. Humin formation has been considered an almost first-order reaction with regard to acid concentration [97] and Lund *et al.*[37] showed that levulinic acid selectivity could be increased over that of humins using high acid concentrations. In addition, both Girisuta and Dussan [34,131] estimated that the activation of energy for the formation of humins is much higher than all other activation energies during the acid catalysed dehydration, showing that lower reaction temperatures can limit humin formation. Resulting in lower humin yields with lower reaction temperatures, low residence times and high catalyst concentration.

Humic substances formed when using real lignocellulosic biomass is even more structurally complex, due to the incorporation of unconverted biomass fragments. Chars from the Biofine process showed (via TGA analysis) that the char included cellulose and hemicellulose, in addition to lignin [21]. Furthermore, C13 analysis indicates possible cross-linking between the humins and unreacted biomass fractions, as well as symmetric peak patterns that are indicative of fused polyaromatic rings. Similar results were found by Agarwal *et al.*[42]study, where the acid catalysed solid residue from pinewood, contained cross-linking cellulose and hemicellulose fragments. In contrast Runge and Zhang [112] reported "tar-like" substances on-top of unreacted lignocellulosic biomass during acid hydrolysis, which limited lignocellulose conversion. That study proposed that fast-forming furfural could undergo decomposition and polymerisation to form humin-like materials [206,207]. Zandvoort *et al.* [208] found that xylose derived humins were chemically and thermally more recalcitrant than glucose derived humins possibly due to their more conjugated structures. Further, C13 analysis indicated that levulinic acid, furfural and dihyroxyacetone was incorporated into the humin derived structures [209].

The presence of psuedo-lignin has been reported in addition to humins due to the condensation of acid-soluble lignin under acidic conditions. Acid soluble lignin has been reported to actively react with xylose under acidic conditions [81]. In support of this, Dussan *et al.* [84] found that soluble lignin could decrease furfural yields by up 24%, with the formation of an insoluble pseudo-lignin residue by-product. It was also proposed that acid-soluble lignin could react with itself to form pseudo-lignin in significant quantities under acidic conditions [210]. Another study by Aarum *et al.* [211] reports pseudo-lignin was incorporated into the humic structures on the particle surface and, as such, is difficult characterise pseud-lignin in detail. Nitrogen containing compounds were also found by Leng *et al.* [212]incorporated into the pseudo-lignin structures. The rate of the pseudo-lignin incorporation into humin structures is unknown to date and difficult to quantify, due to complexity of measuring acid soluble lignin.

5.3 Similarities Between Solid Residue and Hydrochar

The acid catalysis in aqueous conditions operates under similar reaction parameters to hydrothermal carbonisation (HTC) which are generally considered to be 180 – 250 °C at autogenous pressure [213]. HTC is primarily utilised as an energy densification process for wet lignocellulose for the production of bio-oil and hydrochar [214–217]. The hydrothermal carbonisation process has been proposed to include dehydration, decarboxylation, polysaccharide hydrolysis, retro-aldol cleavage and condensation as well as aromatisation [213]. However, at temperatures less than 250 °C, negligible direct aromatization of cellulose occurs, with the predominant hydrochar formation mechanisms being polysaccharide hydrolysis, followed by condensation of aqueous and furanic compounds [214]. Sevilla *et al.* [218] stated that low temperature hydrochars from sugars formed as carbon rich spheres, with an oxygen-rich outer shell and carbon-rich core. The aqueous compounds condense via aldol condensation on the surface structure, followed by subsequent aromatization. Shi *et al.*[215] suggested that humins are an intermediate product of hydrochar formation, in agreement with the 'shell and core' model, where aromatization of the furanic polymer network occurs via a combination of acetal-cyclisation, 1,2-hydride shift, intramolecular aldol condensation, and dehydration to form a polycyclic and phenolic rich polymer core.

The proposed aromatisation of furanic humin structures towards poly-aromatic during levulinic acid production with acids catalysis presents similarities with hydrochar formation mechanisms. Such similarities in formation mechanisms result in minimal differences between the two independently studied materials. However, the small differences in structures may affect the possible applications. In fact, hydrochars have been reported to have higher HHV than that of humins [36]. The more abundant polycyclic compounds found in hydrochars (primarily due to higher reaction temperature) have been reported to increase cation exchange capacity of the material, at the expense of increased microbial inhibition [219]. As the severity of the acid catalysis process increase, solid condensation increasingly dominate the residue's surface properties. Initially, humin formation enriches the surface area with oxygen-rich functional groups that increases the surface hydrophilicity. Higher reaction temperature however, will increase the rate of hydrochar formation, surface hydrophobicity and surface area. The carbon sphere condensation product also includes pseudo-lignin and nitrogen containing compounds, which are considered to exert minor effects on the solid residue surface area. These interacting condensation reactions will result in an overall dehydration process of the solid residue with significant surface and bulk property differences related to reaction conditions.

5.4 Solid By-product Applications

Several studies have looked at the application of humins and solid residues for the valorisation of waste products from levulinic acid production. Most commonly, the solid residue has been proposed as a solid combustion fuel, for the production of steam, to be utilised for the heating of the acid hydrolysis process as well as the separation of levulinic acid via distillation [106,200] . Techno-economic analysis results the aforementioned studies suggest that solid residue as fuel is sufficient to provide the heat required by the levulinic acid production process. However, due to its carbon content exceeding 60 wt.%, the solid residue combustion resembles that of coal with regards to CO_2 emissions [25]. This would significantly increase the carbon emissions associated to the manufacture of levulinic acid.

Sugar-derived humins were investigated by Rasrendra *et al.* [200] as a feedstock for pyrolysis. The primary reaction product was biochar (70-72 wt.%), with bio-oil and syngas yields of 8-10 wt.% and 17-22 wt.%, which was lower than that from lignin under similar conditions. Agarwal *et al.*[42] utilised catalytic pyrolysis to increase the bio-oil to 14 wt.% with ZSM-5. Using catalytic fluidised bed reactors, Sumbharaju *et al.* [220] managed to increase bio-oil yields to nearly 20 wt.% with the same catalyst. However, the low bio-oil yields are not sufficient to justify the high processing temperature of nearly 600 °C. Melligan *et al.* [41] as part of the Carbolea research group, was able to achieve bio-oil yields of 12-20 wt.% from the pyrolysis of solid residue from the acid *Miscanthus x Giganteus* without any catalyst. The higher bio-oil yield with real biomass may be attributable to the higher lignin content of solid residue although, biochar remained the primary pyrolysis product. These results indicate that significant further work is necessary for the successful valorisation of solid residues via pyrolysis.

Alternatively, novel applications of humins have gained increasing attention in recent years, which are related to their material properties. For example, humin-impregnated resins have been found as a promising substitute of plywood boards[40]. Humin-based solid foams exhibited remarkable insulation capacity with applications for the building sector [202] . Solid residue from bamboo hydrolysis can be activated with sulphuric acid to from a low-cost catalyst for further acid hydrolysis [159], while the residues from the acid hydrolysis of textile waste was found to be a promising electrode material [221]. Also, ionic liquid derived humins from sugars were shown to remove heavy metals from wastewater due to the high surface O/C ratio [203]. In which, the functionalised surface areas, exhibiting high cation exchange capacity, were able to selectively remove trace elements. Non-thermal applications of solid residue from acid catalysis would also facilitate the storage of carbon, acting as a form of carbon sequestration, thus reducing the CO_2 emissions of the resulting levulinic acid product.

Hydrochar applications are similar to those of humins, with a primary focus in this case, on use as a solid fuel however, in the literature they also found applications as an electrode material, soil amendment and heavy metal removers for soil remediation [217]. Among the novel and growing applications of hydrochar is its use as additive for the promotion of anaerobic digestion. Hydrochar has been found to increase methane yields during anaerobic digestion by improving buffering capacity, providing a source of trace metals, adsorbing inhibitors (such as ammonium and fatty acids) as well promoting microbial activity via direct interspecies electron transfer and acting as a microbial support material [260–264]. The energy consumption, and subsequent costs of carbonaceous material production, has been so far a limiting factor of their application for AD with lower cost analogous hyrochars sought [222,223]. The application of solid residue from the acid catalysis of *Miscanthus x Giganteus* for levulinic acid production were found to have up to +14% increase in methane yields from the anaerobic digestion of chicken manure [224]. This was further confirmed Madadi *et al.* that showed that levulinic acid could be produced alongside highly adsorbent solid residues with 85% energy recovery [225]. More recently Licursi *et al.* found that the adsorption properties of hydrochar from levulinic acid could be further upgraded by KOH activation [228].

It should be noted that there is remarkable similarity between the humins and the soil organic material humus, after which humins are named [208]. Soil humus is formed from the decay of animal and plant material with a complex aromatic structure, predominantly composed of furanic polymers with oxygen and nitrogen functionalities. Fulvic and humic acids found in soil have been found to have similar structures to catalytically derived humins, but also incorporate fatty acids, amino acids and lignin [227]. Soil humus is an essential fraction of healthy soil and has been proposed to improve soil fertility. Effective humus has additionally been proposed to provide a source of nutrients and organic matter for the soil microbiome, as well improving the bulk soil water retention [228]. The similarities between humins and soil humus indicate potential cross application of humin materials, more specifically as a form of carbon sequestration or microbial promotion.

6. Conclusions

Renewable low carbon levulinic acid, can be produced from a large variety of lignocellulosic biomass using a range of acid catalysts. Both homogeneous and heterogeneous catalysts can be employed (with varying degrees of success) for the conversion of lignocellulose towards levulinic acid and furfural in a one-pot process. However, for the full commercialisation of the levulinic acid biorefineries better consideration for the interactions between the individual biomass properties, catalysis and by-product valorisation must be conducted. Ideally, flagship demonstration of commercial biorefineries that exploit solid residues should be investigated from an economic feasibility perspective. The utilisation of novel heterogeneous catalysts and possible combination with aqueous modifiers such as salts or trace acid could potentially overcome the limitations of cellulose hydrolysis with solid catalysts. These novel catalytic platforms must be considered alongside by-products for specific biomass varieties. Complete valorisation of by-products has been shown to be necessary for commercial production of levulinic acid.

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CRediT

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship which are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

This manuscript has two corresponding authors as outlined in signature below. We understand that the Corresponding Author is the sole contact for the Editorial process (including Editorial Manager and direct communications with the office). He/she is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs. We confirm that we have provided a current, correct email address which is accessible by the Corresponding Author and which has been configured to accept email from s.tedesco1@salford.ac.uk

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CREDIT AUTHOR STATEMENT

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship which are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

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Additionally we wish to confirm the following CRediT roles for this research:

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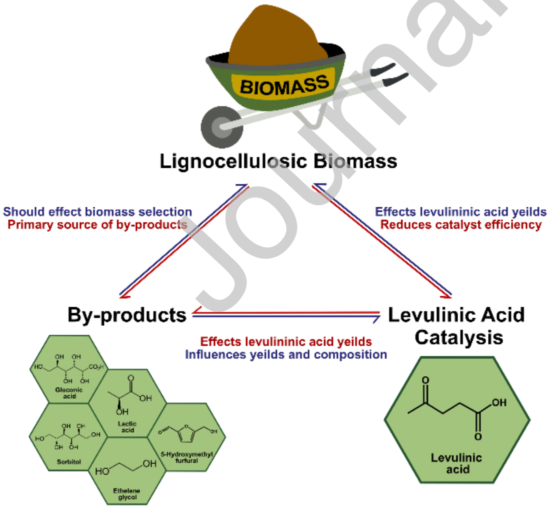
Graphical abstract



Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: