Levulinic Acid Is a Key Strategic Chemical from Biomass †

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† Dedicated to the legendary Indian Chemist Professor C. N. R. Rao on his 88th birthday on 30 June 2022.

Abstract: Levulinic acid (LA) is one of the top twelve chemicals listed by the US Department of Energy that can be derived from biomass. It serves as a building block and platform chemical for producing a variety of chemicals, fuels and materials which are currently produced in fossil based refineries. LA is a key strategic chemical, as fuel grade chemicals and plastic substitutes can be produced by its catalytic conversion. LA derivatisation to various product streams, such as alkyl levulinates via esterification, γ-valerolactone via hydrogenation and N-substituted pyrrolidones via reductive amination and many other transformations of commercial utility are possible owing to the two oxygen functionalities, namely, carbonyl and carboxyl groups, present within the same substrate. Various biomass feedstock, such as agricultural wastes, marine macroalgae, and fresh water microalgae were successfully converted to LA in high yields. Finding a substitute to mineral acid catalysts for the conversion of biomass to LA is a challenge. The use of an ultrasound technique facilitated the production of promising nano-solid acid catalysts including Ga salt of molybophosphoric acid and Ga deposited mordenite zeolite, with optimum amounts of Lewis and Bronsted acidities needed for the conversion of glucose to LA in high yields, being 56 and 59.9 wt.% respectively. Microwave irradiation technology was successfully utilized for the accelerated production of LA (53 wt.%) from glucose in a short duration of 6 min, making use of the unique synergistic catalytic activity of $ZnBr_2$ and HCl.

Keywords: levulinic acid; biomass; solid acid catalysts; biochemicals; biofuels; biomaterials; heteropoly acids; zeolites; microwave irradiation; ultrasound

1. Introduction

Biomass is a renewable energy resource which is underutilized. Biofuels such as biodiesel and bioethanol, biochemicals such as glucose and levulinic acid (LA), and biomaterials such as biodegradable polymers can be produced from biomass [1]. On average, 32.8 papers/month were published on the subject with keywords, namely, LA and biomass, from the period 1 January 2022 to 30 June 2022, based on the Web of Science database [2–62]. Indeed, proliferation in this field of research is professed due to the strategic significance of LA. The unique feature of LA is that the molecule has two oxygen-containing functional groups, namely, carbonyl and carboxyl, which could be converted easily, making the derivatization of LA prolific. The intention of the authors in compiling this review is not to summarize the history of LA from biomass. On the contrary, the objective is to provide a possible solution to the war-torn and resource-depleted world.

The majority of the content of this review is devoted to the results from Professor Gedenkan's laboratory [63–71]. In addition, for want of time, only the major developments during the period from 1 January 2022 to 30 June 2022 are outlined [2–62].

2. Possible Biomass Feedstock for Levulinic Acid (LA) Production

Literally all lignocellulosic biomass (terrestrial), as well as unconventional glucosic feedstock such as marine and fresh water algae, and bacterial sources like cyanobacteria can be used for LA production. The diverse agricultural wastes (lignocellulosic biomass), namely, cotton, sugar cane bagasse, *Cicer arietinum*, rice straw, corn stover, sweet sorghum bagasse and miscanthus, that form a potential source of LA are shown in Figure 1.
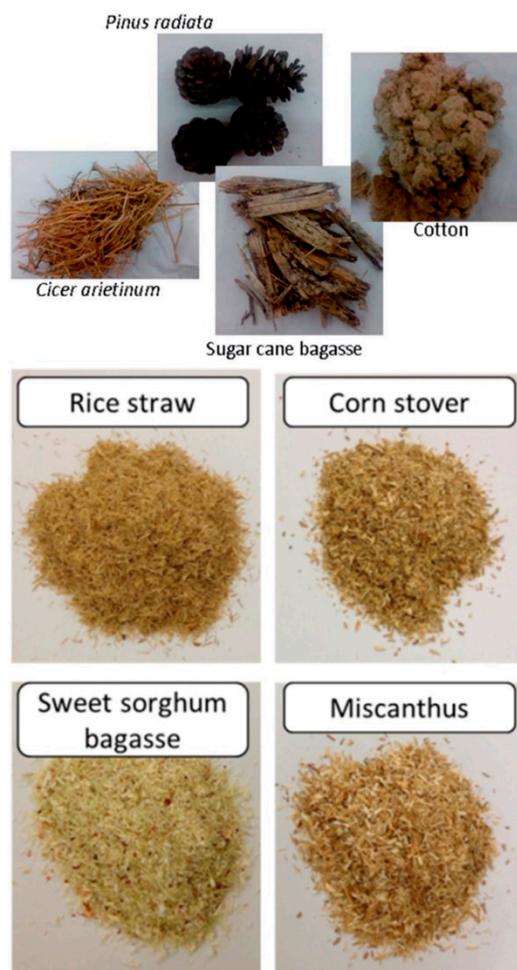
Figure 1. Diversity in cellulosic feedstock for levulinic acid production. Adapted with permission from ref. [63,70].

Fructose or fructose-containing feedstock, such as sugar cane juice, is an ideal feedstock [5,11,14,66] for LA production. This is because of the mechanistic steps involved in the direct conversion of cellulosic biomass to LA. The mechanistic steps involved in the conversion of cellulose to LA comprise the initial step of hydrolysis of cellulose to glucose catalysed by an acid; the glucose then isomerizes to fructose. By consecutive dehydration and rehydration steps, fructose is converted to hydroxy methyl furfural and LA, respectively. Each mole of fructose yields a mole of LA and formic acid, as shown in Figure 2. The difficult stages in the direct conversion of biomass to LA, namely hydrolysis of cellulose and isomerization of glucose, could be avoided if fructose/fructose-containing carbohydrates were used by industry as feedstock instead of cellulosic biomass, until the technology for the direct conversion of lignocellulosic biomass to LA is mature. This would hasten the appearance of LA based products in the market at the service of mankind, alleviating the problems of energy and environmental crises.
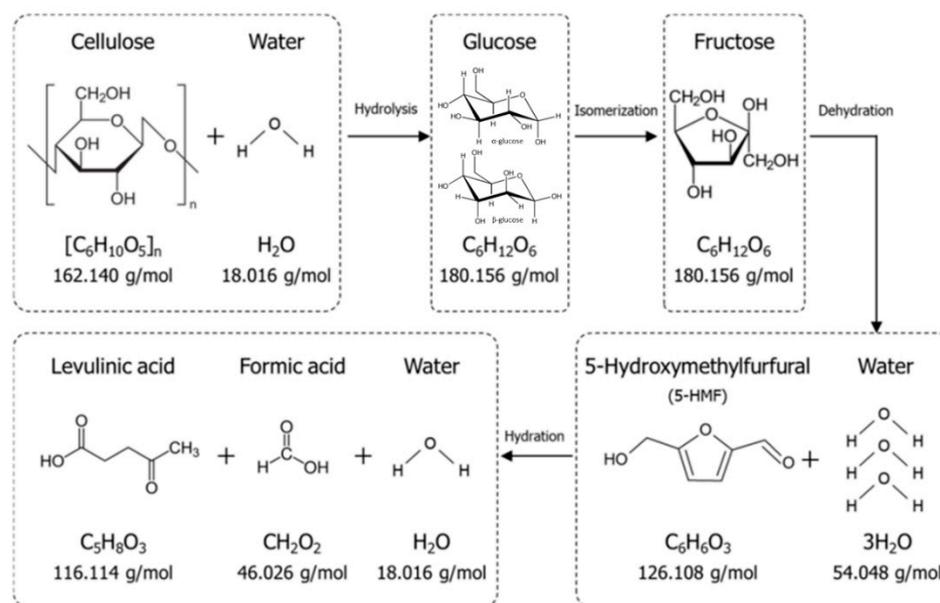
Figure 2. Consecutive reactions in the conversion of lignocellulosic biomass to levulinic acid. Adapted with permission from MDPI [63].

This is analogous to the use of sugar cane as a feedstock for the production of bioethanol in Brazil and the US, that has seen the light of the market as a gasoline substitute/additive. Until the technology for the direct conversion of cellulosic feedstock to fuels (bioethanol) and chemicals (LA) is ripe, facile carbohydrates (monomeric/dimeric) should be used as feedstock to meet the growing demand for fuel, as can be seen from the fuel and economic crises in Sri Lanka. A LA yield of 100 mol% and a conversion of 100% of fructose is achieved at 120 °C in 30 h using a commercial perfluorosulfonic acid resin in a pellet form as the catalyst (Aquivion®P98 PFSA) [5]. Such catalytic strategies need to be scaled up for the industrial production of LA. The diversification of LA to fuels, chemicals and materials requires a huge supply of this strategic chemical. The diversity in biomass (terrestrial, fresh water and marine) feedstock, and various catalysts innovatively used for the production of LA are shown in Table 1.

The use of an unconventional reaction medium such as γ-valerolactone (GVL), as a solvent, reduced the activation energy of the process of conversion of biomass to LA. The reaction kinetics of glucose conversion to LA was accelerated by the use of GVL as a solvent instead of water. The adsorption of glucose on the surface of the solid acid catalyst (CH_3-SBA-15-SO_3H) was enhanced. Moreover, the rate determining step, namely, direct dehydration of glucose to 5-HMF was accelerated in the GVL medium as the intermittent step of isomerization of glucose to fructose was completely eliminated in this medium. The activation energy for the conversion of glucose to LA was reported to be 62.66 kJ/mol. The yield of LA was enhanced by five times when the reaction was carried out in GVL medium instead of water, with the reaction conditions being a temperature of 160 °C for 120 min [10]. Another new avenue in this field of research is the use of environmentally friendly organic solvents, namely, deep eutectic solvents (DESs), for the pretreatment of lignocellulosic biomass to reduce the recalcitrance of the biomass and to improve the accessibility of the reaction site by the acidic catalyst. The reaction site in question is the β-1,4 glycosidic bond, as shown in Figure 3.

Table 1. Diverse biomass feedstock and catalysts used for levulinic acid (LA) production.

Feedstock for LA Production	Catalyst	Yield of LA	Reference
Fructose	Aquivion®P98 PFSA, a commercial perfluorosulfonic acid resin in a pellet form	100 mol% at 120 °C for 30 h;	[5]
Glucose	$LaMnO_3$	69.5 mol%;	[6]
Glucose	MOF (UIO-66-NH-R-SO_3H)	71.6 mol% at 170 °C;	[7]
Corn cob	Mo doped carbon microspheres; presence of Lewis acid sites, namely, Mo_2C and Mo^{6+} promoted the isomerization of glucose to fructose	33.02 (% of theoretical maximum) yield of LA at 195 °C in 90 min;	[8]
Glucose	Para-toluene sulfonic acid (PTSA) functionalized activated carbon with $CaCl_2$	61 mol% at 175 °C in 120 min with MIBK-H_2O solvent system;	[9]
Fructose	ZrO_2-SiO_2-SnO_2 Solid super acid catalyst with $H_0 = -14.52$	80 mol% at 180 °C in 3.5 h;	[14]
Laminaria digitata (wild brown seaweed)	4 wt.% H_2SO_4	12.5 wt.% at 200 °C in 30 min;	[15]
Spirulina platensis residue	1 M H_2SO_4	16.36 wt.% at 180 °C for 30 min;	[16]
Glucose	Cr-MCM-22	60 wt.% at 200 °C in 1 h;	[17]
Glucose and cellulose	Cu HZSM-5-HMS (hexagonal mesoporous silica) hybrid catalyst	45 and 30 mol% from glucose and cellulose, respectively. Ideal conditions for glucose conversion are: 200 °C; 10 bar N_2; 5 h; Ideal conditions for cellulose conversion are: 230 °C; 5 h;	[18]
Newspaper wastes with crystalline cellulose	0.5 M H_2SO_4	23–27 wt.% obtained from sanitary papers, tracing/parchment papers and paper food box; 180 °C; 5 min, 1:1 GVL/H_2O solvent;	[19]
Rice straw	1.5 wt.% HCl	52 mol% obtained from rice straw pretreated with choline chloride—oxalic acid deep eutectic solvent; Pretreatment: 100 °C for 2 h; Acid hydrolysis: 120 °C for 2 h;	[20]
Rice straw	Polyehtyleneimine functionalized acidic ionic liquid (PolyE-IL) with HSO_4^- counter cation	65.5 (% of theoretical maximum) from pretreated rice straw; Hydrolysis conditions: 210 °C for 120 min;	[21]
Safflower stalk with 45.2 wt.% cellulose content	0.3 M PTSA	30 (% of theoretical maximum) at 200 °C for 120 min;	[22]
Cellulosic residue from corn stover	Phosphoric acid activated lignin based activated carbon	67.9 mol% at 190 °C in 150 min in MIBK/H_2O-NaCl medium;	[23]
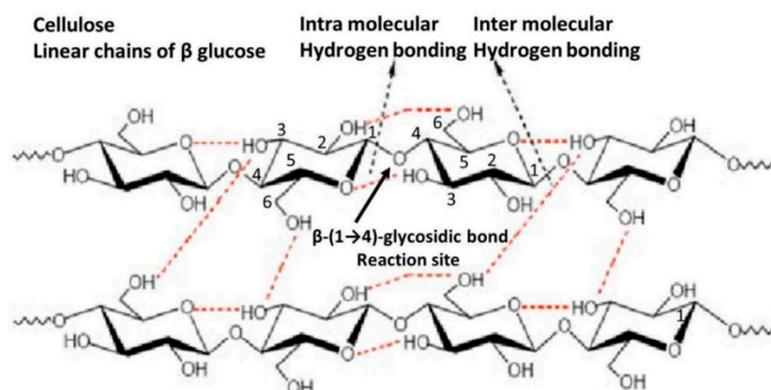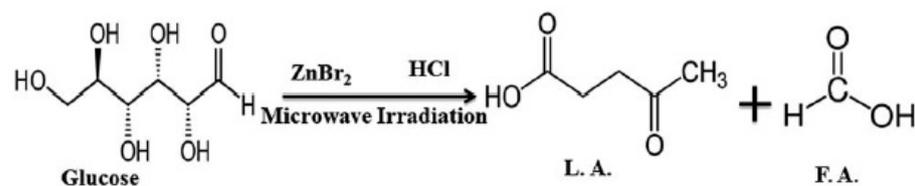
Figure 3. The reaction site β-1,4 glycosidic bond in cellulosic biomass surrounded by extensive hydrogen bonding network. Adapted with permission from Peertechz [71].

The use of DESs for pretreating the biomass improves the accessibility of the catalytic acid site (H^+) to the reaction site in the substrate by a two-fold action, namely, by dissolving the hemicellulose component as well as by weakening the inter and intramolecular hydrogen bonding that hinders the accessibility to the reaction site. Typical examples of such DESs include choline chloride-acetic acid, choline chloride-succinic acid, choline chloride-oxalic acid, choline chloride-malonic acid, and choline chloride-lactic acid [20,23]. Innovation in catalyst design includes heteroatom doping or heteroatom functionalization in activated carbon materials, making them environmentally benign catalysts for biomass conversion. Strategies for sulphur functionalization of biomass (*Ipomoea carnea*) derived activated carbon material using elemental sulphur/hydrazine solution under modest reaction conditions (400 °C) resulted in the sulphur loading of 0.34 wt.%, and the resulting material was used as an adsorbent for Hg for environmental applications [72]. Sulfonate/sulphate functionalized carbon nitride (g-C_3N_4) with a sulphur content of 9.2% catalysed the conversion of glucose to LA with a yield of 48 mol% and a selectivity of 57 mol% [12].

3. Possible Catalysts for Accelerated Levulinic Acid (LA) Production from Biomass

In addition to the catalysts summarized in Table 1, innovation is achieved in the design of heteropoly acid based solid acid catalysts with optimal amounts of Lewis and Bronsted acidity, a combination that is vital for the conversion of biomass to LA. Gedanken's group made a significant contribution to the use of microwave technology and the design of solid acid catalysts for the accelerated production of LA from biomass [63–71]. A total of 53 wt.% LA yield was obtained from glucose by the synergistic catalytic activity of HCl and $ZnBr_2$ under microwave irradiation for 6 min. The improved catalytic activity was attributed to the in situ generation of HBr (Scheme 1).

Scheme 1. Synergistic catalytic activity of HCl and $ZnBr_2$ under microwave irradiation leading to in situ generation of HBr for accelerated production of levulinic acid [67].

Pretreatment with a simulated green liquor (Na_2CO_3-Na_2S, 20 wt.% total titratable alkali, TTA, and 40 wt.% sulfidity) at 200 °C for 15 min was an effective strategy to delignify (64.8–91.2 wt.%) various herbaceous biomasses, namely, rice straw (RS), corn stover (CS), sweet sorghum bagasse (SSB), and Miscanthus (MS). As a consequence, the cellulose content of the delignified biomasses increased from 33.0–44.3 to 61.1–68.4 wt.% depending

on the source of the biomass. However, under similar conditions of biomass conversion to LA, namely, 1 M HCl, 150 °C, 5 h, 20 g/L solid loading, the yield of LA from the original untreated and delignified biomasses was 60.2–78.5 and 50.4–56.0 wt.% (% of the theoretical maximum). The variation of the yield of LA as a function of reaction time in the untreated and pretreated biomass is shown in Figure 4. The concentration of LA in the products from the pretreated biomass increased by a factor of 1.5.
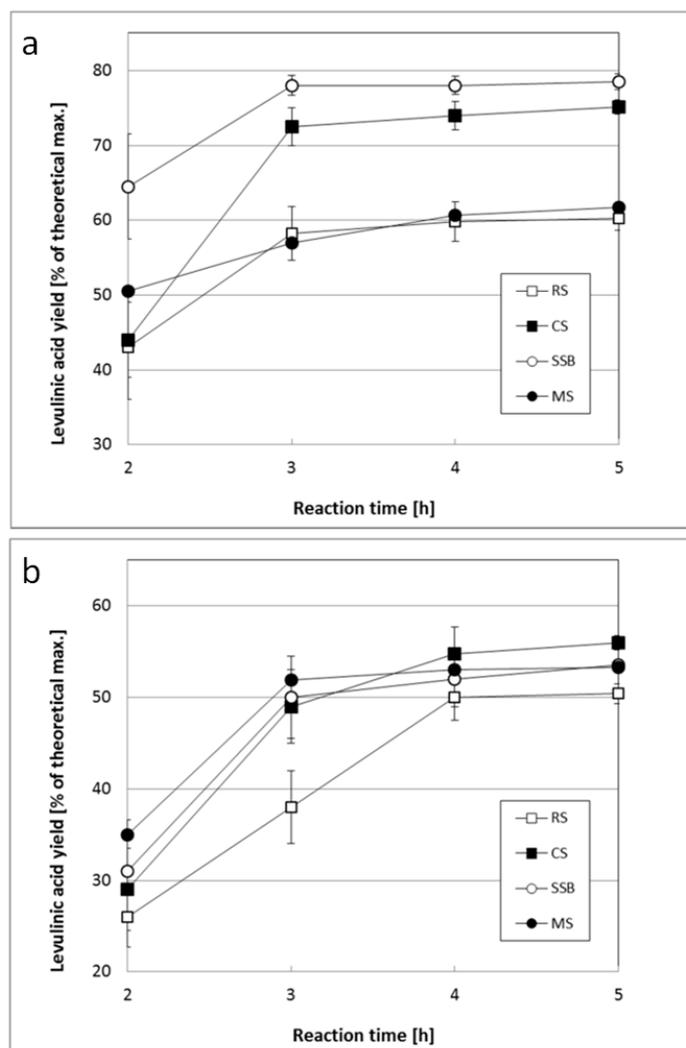
Figure 4. Variation of the yield of LA as a function of reaction time from (**a**) untreated and (**b**) green liquor pretreated biomass (rice straw, RS; corn stover (CS); sweet sorghum bagasse (SSB) and miscanthus (MS) [Reaction conditions: 1 M HCl, 150 °C, 50 g/L solid loading; biomass particle size > 2000 μm]. Adapted with permission from MDPI [63].

The lower yield of LA in RS and MS compared to either CS or SSB could be partially attributed to the higher lignin contents of 17.1 and 19.6 wt.% respectively. As expected, the biomass with the lowest lignin content (~13.3%) showed the highest LA yield (78.5 wt.%). However, the relationship between the lignin content of the biomass and the yield of LA is unclear and indirect as other factors, such as the relative binding strength of lignin to cellulose as well as the location of the lignin in the biomass and the ash content of the biomass also play a role in the conversion of biomass to LA. This is because the yield of LA from corn stover (75.1 wt.%) is higher than that of RS (60 wt.%), even though the lignin contents of both are ~17 wt.%. The distinguishing feature between CS and RS is their ash content, which is 1.5 and 8.2 wt.%, respectively. The higher ash content of the RS could have retarded the activity of the catalyst (HCl) leading to a lower yield of LA [63].

Among the various agricultural wastes, namely, *Cicer arietinum* (CA), cotton, *Pinus radiata* (PR) and sugar cane bagasse (SCB), cotton showed the best performance with the highest yield of LA (44.0 wt.%) under modest hydrothermal reaction conditions (423 K, 1 M HCl, 2 h) (Figure 5). This could be attributed to cotton containing the highest cellulose content (>99 wt.% from Milouban cotton linters pulp, MCP Ltd., Israel). Biomass with a high cellulose content is an ideal feedstock for obtaining high yields of LA [70].
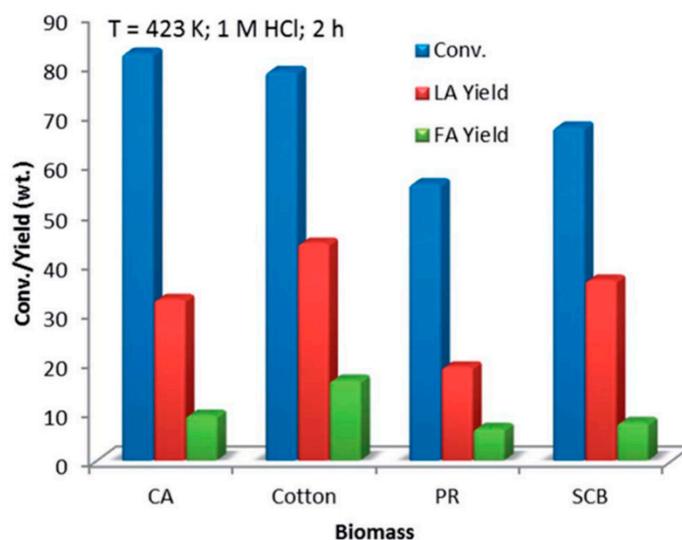
Figure 5. Hydrothermal conversion of agricultural wastes, namely, *Cicer arietinum* (CA), cotton, *Pinus radiata* cones (PR) and sugar cane bagasse, to levulinic acid. Adapted with permission from RSC [70].

Heteropoly acids are ideal solid Bronsted super acids with a potential to catalyse vital reactions, such as alkylation, esterification, hydration, dehydration, polymerization and many others that are involved in the conversion of biomass to biochemicals and biofuels [64,65,68,69,73–77]. Supporting heteropoly acids on activated carbon materials is an innovative strategy to exploit their unique selectivity for catalytic reactions involved in biomass conversion [68,69]. Silicotungstic acid supported on activated carbon showed high activity and selectivity (94 wt.% glucose) for the conversion of starch to glucose, a precursor to LA. The catalyst, prepared by wet impregnation, could be used for five reaction runs without appreciable loss of activity (Figure 6). By suitably tuning the reaction conditions, the catalyst, 20 wt.% $H_4SiW_{12}O_{40}$/activated carbon, could be exploited for high yield and selective production of LA from biomass, and efforts in this direction are awaited [68].
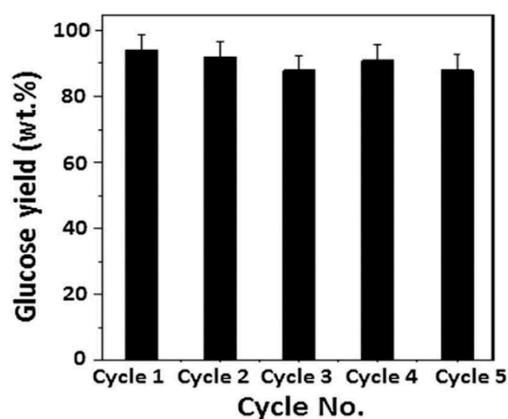
Figure 6. Reusability of the solid acid catalyst, 20 wt.% $H_4SiW_{12}O_{40}$ nH_2O/activated carbon for the conversion of starch to glucose (reaction conditions: starch, 0.5 g; catalyst, 0.5 g; H_2O, 20 mL; 423 K; 4 h). Adapted with permission from Elsevier [68].

To obtain optimal amounts of Lewis and Bronsted acid sites, efforts were devoted for preparing Ga salt of molybodphosphoric acid (GaHPMo) [64] and Ga deposited on mordenite zeolite (Ga@mordenite) [65] using an ultrasound irradiation technique. SEM images of GaHPMo with elemental mapping and the EDS plot are shown in Figure 7. Likewise, the TEM images of Ga@mordenite with elemental mapping and the EDS plot are shown in Figure 8. Uniform distribution of the constituent elements throughout the surface of the catalyst are shown in the images showing elemental mapping (Figures 7 and 8). High yields of LA, 56 and 59.9 wt.% respectively, were obtained from glucose using GaHPMo and Ga@mordenite catalysts [64,65].
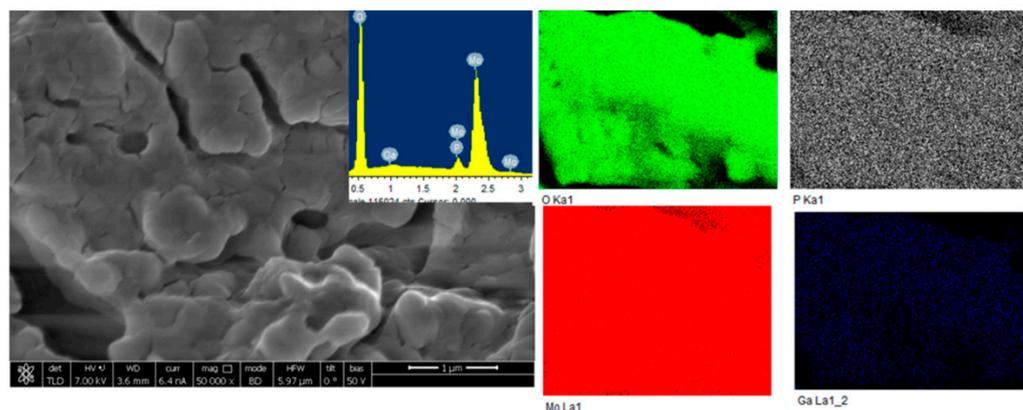
Figure 7. SEM image of Ga salt of molybdophosphoric acid (GaHPMo) with the EDS plot and elemental mapping. Adapted with permission from ACS [64].
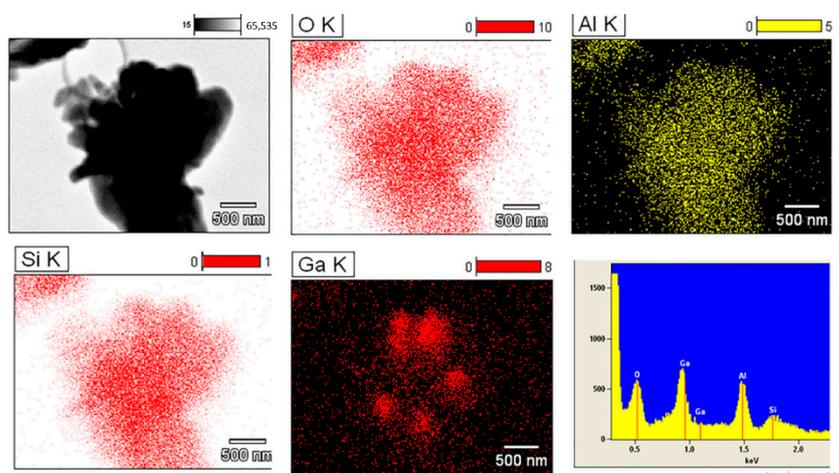
Figure 8. TEM image of Ga deposited on mordenite zeolite (Ga@mordenite) with elemental mapping (O, Al, Si, Ga) and EDS plot. Adapted with permission from Wiley-VCH [65].

Thus, heteropoly acids supported on activated carbon as well as Ga modified heteropoly acids and Ga modified zeolites are promising solid acid catalysts for LA production from glucose.

4. Possible Biochemicals from Levulinic Acid

4.1. Alkyl Levulinates from Levulinic Acid

Alkyl levulinates are potential fuel blends and additives [25,26,28,32,33,35,36,45,49]. Upgrading LA to levulinates via esterification using a variety of catalysts, namely, zeolites, mesoporous silica, carbon materials, metal organic frame works (MOFs), ion exchange resins and enzymes has received considerable attention globally, owing to their potential as fuel-blending chemicals used in biofuel production. Use of such blending agents reduce the emission of polluting gases and thereby global warming. Use of alkyl levulinates as

additives improve the physical, chemical and combustion properties of fuels. Moreover, the performance of the engine is also enhanced. Catalytic strategies for the production of alkyl levulinates, either linear (with varying chain length) or branched, are being developed. Alkyl levulinates are excellent additives to gasoline and diesel, resulting in an improvement in engine performance and a reduction in the emission of polluting gases. In addition to being used as fuel additives, alkyl levulinates find application in pharmaceutical, polymer, agriculture, cosmetic, resin and coating and solvent industries [2]. Currently, ~90% of industrial research and development is devoted to heterogeneous catalysis owing to the advantages of solid acid catalysts, such as zeolites, mesoporous silica, carbon materials, polyoxometalates, metal organic frame works, ion-exchange resins and biocatalysts. Tuning the porosity and acidity of zeolites has been an active area of research. Constraints with conventional mesoporous silica, namely, high reaction temperatures, reaction times and consumption of alcohol are being solved using hybrid mesoporous inorganic-organic silica as catalysts. As a result, improvements in green chemistry metrics, namely, E-factor, atom economy, recyclability and product yield were achieved. Though carbon materials are active and promising catalysts for the esterification of LA, the high cost of production and harsh production conditions (high temperature and the use of corrosive acids and alkalies) impose restrictions on large scale production. Moreover, strong affinity between the sulfonic acid functional groups on the carbon surface and the substrate, namely LA, causes problems of reduced activity and recyclability. Efforts in the direction of functionalization of carbon materials with solid acids, namely, zeolites or hetropoly acids, are being made to surmount these problems [64,65,68,69,71]. Moreover, efforts are dedicated to produce carbon materials from wasteland weeds (such as *Calotropis gigantea* and *Ipomoea carnea*) and agricultural wastes (such as *Borassus flabellifera* and *Limonia acidesima*) using environmentally friendly activating agents, such as alkali salts of organic acids (for example, sodium oxalate) under mild production conditions so as to reduce the cost of production and make the process more environmentally friendly [72]. Typical wasteland weeds and agricultural wastes exploited for the production of high surface area microporous activated carbon materials are shown in Figure 9 [72,78,79].

Figure 9. Wasteland weeds, (**a**) *Calotropis gigantea*, (**b**) *Ipomoea carnea*; and agricultural wastes, (**c**) spikes of *Borassus flabellifera* and (**d**) shells from *Limonea acidissima* used for the production of microporous high surface area activated carbon materials [72].

Recent developments in the esterification reaction of LA to alkyl levulinates are highlighted in Table 2.

Table 2. Biochemicals from levulinic acid (LA).

Biochemical from LA	Catalyst	Product Yield	Reference
GVL	Hf-FDCA (catalyst prepared from the hybrid of a metal precursor and 2,5 furan dicarboxylic acid	88% yield of GVL at 180 °C in 24 h;	[24]
Hexyl levulinate	Sulfated silica prepared by the sulfonation of amorphous bamboo leaf ash	95.2% conversion of LA at 90 °C in 7 min with 98.0% selectivity to hexyl levulinate; catalyst reused six times;	[25]
GVL	2 wt.% Pt on ZrO_2	97% GVL yield; formic acid used as hydrogen source; T = 140 °C; t = 180 min; triethyl amine used to facilitate formic acid decomposition; catalyst reused for four consecutive cycles;	[27]
Methyl levulinate	MOF containing Zr metal cluster with amino terephthalic acid (UiO-66-NH_2) ligand	85.89% yield of methyl levulinate in an autoclave in 1 h; T = 130 °C; P = 30 bar N_2 pressure; k = 3.57×10^{-3} min^{-1}; activation energy = 48.99 kJ/mol;	[28]
Chiral GVL	Nickel phosphine complex; Ni(OTf)$_2$; (S, S) Ph-BPE/(R, R) Ph-BPE; TFE; 50 °C; 12 h; in a gram scale preparation	78.6% yield of (R)-GVL with 96% ee; 79.05% yield of (S)-GVL with 96% ee;	[29]
GVL	Ru nanoparticles anchored on hierarchical porous N-doped carbon nanospheres (3 wt.% Ru/HPNC)	GVL yield > 99% at 100 °C in 2 h under solvent-free conditions; 2.5 MPa H_2; catalyst reused for six reaction cycles;	[30]
n-butyl levulinate (BL)	LiCl·$3H_2O$ + $AlCl_3$ (molten salt hydrates) with microwave irradiation	95.5% yield of n-butyl levulinate; T = 100 °C; t = 2.5 h; activation energy of n-butyl levulinate formation with LiCl $3H_2O$ and LiCl. $3H_2O$ + $AlCl_3$ were 70.9 kJ/mol and 31.8 kJ/mol respectively;	[35]
GVL	Zr-Al beta	85.5% yield of GVL; isopropyl alcohol used as hydrogen donor;	[36]
(R)-4-amino pentanoic acid	Glutamate dehydrogenase coupled with formate dehydrogenase	97% conversion of LA with a (R)-4-amino pentanoic acid stereoselectivity of >99% in 11 h;	[37]
GVL	Ru/PEG (ruthenium nanoparticles stabilized by water soluble polymer PED)	82 mol% conversion of LA with 99.2 mol% selectivity for GVL; T = 140 °C; t = 15 min;	[38]
GVL	Zr@PS-FA (successful coordination observed in the catalyst between Zr^{4+} and OH and COOH groups of the partially hydrolysed *Pinnistum sinese* in formic acid)	95.6 mol% yield of GVL; T = 180 °C; t = 1.5 h; TOF = 9.76 h^{-1}	[39]
2-methyl tetrahydrofuran	Ni-Cu-OMA (ordered mesoporous alumina)	73.0% selectivity towards 2-MTHF; two steps are involved in the production of 2-MTHF; Step 1: 190 °C; 30 bar H_2; 4 h Step 2: 230 °C; 50 bar H_2; 12 h	[41]
GVL	Ru@GOF (Ru nanoparticles confined in the gallery space of graphene oxide frameworks pillared with organic linkers)	93 mol% yield of GVL; T = 90 °C; t = 8 h; TOF = 7240 h^{-1}; catalyst reusable for at least five reaction runs	[42]

Table 2. *Cont.*

Biochemical from LA	Catalyst	Product Yield	Reference
GVL	5% Ru/Sn-SBA-15	LV conversion—99%; GVL selectivity—98%; T = 250 °C; t = 3 h; H_2 flow = 25 mL/min;	[43]
GVL	10 wt.% Re supported on activated carbon	LA conversion—100% GVL selectivity—99% T = 120 °C; t = 4 h;	[44]
Ethyl levulinate	$H_3PMo_{12}O_{40}$/Activated carbon	Ethyl levulinate yield = 80%; T = 80 °C; t = 15 h;	[45]

4.2. Hydrogenation of LA to γ-Valerolactone

　　Apart from the esterification of LA to levulinates, hydrogenation of LA is a promising route for the production of the biochemical and biofuel precursor γ-valerolactone, using either H_2 or formic acid or alcohols as the hydrogen source, and this has been extensively studied [27,29,30,36–44,46,50]. Promising catalysts developed for the conversion of LA to γ-valerolactone are summarized in Table 2.

4.3. Reductive Amination of LA to N-Substituted Pyrrolidones and N-Substituted Pyrrolidinones

　　Production of biobased nitrogenous chemicals is of vital significance to food security and for the pharmaceutical industry. Studies on the conversion of LA to N-containing organic compounds, especially N-substituted pyrrolidones [31,34] and N-substituted pyrrolidinones [47] are highlighted in Table 3.

Table 3. Production of biobased nitrogenous chemicals.

Nitrogenous Chemical	Catalyst	Product Yield	Reference
N-substituted pyrrolidones	No catalyst; HBpin used as reducing agent	28–94% yield of N-substituted pyrrolidones;	[31]
5-methyl-2-pyrrolidone	20 molar percent of Zr in the Co, Zr bimetallic carbon-nitrogen doped catalyst (Co-Zr@chitosan-20)	92.5% yield of 5-methyl-2-pyrrolidone; ammonia as N source; T = 130 °C; P = 30 bar H_2; 24 h;	[34]
N-butyl-5-methyl-2-pyrrolidinone	Cu_{10}/AlB_3O	*N*-butyl-5-methyl-2-pyrrolidinone yield = 94%; LA conversion = 99%; stable catalytic performance for 200 h; T = 200 °C; LHSV = 0.3 h^{-1}; 1,4-dioxane solvent; LA:n-butyl amine mole ratio = 1:1; H_2 pressure, 3 MPa;	[47]

5. Possible Biofuels from Levulinic Acid (LA)

　　Hydrocarbons such as ethylene and propylene can be produced from LA via bio 1-butene through a series of reactions, namely, hydrolysis, hydrogenation, decarboxylation, metathesis and cracking [51]. Ethylene and propylene are produced from sugar cane bagasse by the hydrolysis of the cellulose component to glucose, followed by the isomerization of glucose to fructose and subsequent dehydration of the fructose to 5-HMF, followed by the dehydration of 5-HMF to LA. The LA thus generated is hydrogenated to GVL. GVL is decarboxylated to 1-butene using an SiO_2/Al_2O_3 catalyst at a WHSV of 0.18 h^{-1} at 375 °C and 36 bar N_2. Bio 1-butene thus obtained is converted (81.5%) to propylene (selectivity: 42.02 wt.%) and ethylene (selectivity: 19.36 wt.%) at 500 °C and 1 bar and at a WHSV of 6 h^{-1}. 2-MTHF is another promising biofuel derived from LA. MTHF is a more promising biofuel and gasoline additive than bioethanol owing to its lower miscibility with

water, high heating value, energy density, and higher stability, despite its lower octane number (87 vs. 108.6) [53]. Hydrodeoxygenation of LA over a bimetallic Ni_5Co_{25}/γ-Al_2O_3 catalyst gave high activity with 73.4% yield of 2-MTHF at 240 °C. Commercial production of 2-MTHF is based on corn cob derived furfural. Recently, advances have been made for the production of 2-MTHF from a cellulose base biochemical such as LA. The existence of metal as well as metal oxide species in the $NiCo/\gamma$-Al_2O_3 bimetallic system is necessary for the conversion of LA to 2-MTHF as the metal sites activate the H_2, promoting the hydrogenation, while the metal oxides provide the necessary acid sites for the dehydration reaction. 2-proponal was found to be a promising reaction medium for the dehydration of 1,4-pentandiol to 2-MTHF [53]. Dimers (C_{10}) of LA, namely, tetrahydro-2-methyl-5, γ-dioxo-2-furanpentanoic acid (TMDFA), 3-(2-methyl-5-oxotetrahydrofuran-2-yl)-4-oxopentanoic acid (MOTOA) and 3-acetyl-2-methyl tetra hydro-5-oxo-2-furan propanoic acid (AMTOFA) are potential biojet fuel (C_8-C_{16}) precursors from the dimerization of LA using an H-Beta 19 catalyst at 148 °C for 24 h with a LA conversion of 79 mol% and a selectivity towards LA dimers of >98 mol% [53]. Valeric acid is a strategic platform chemical derived from the hydrogenation of LA that yields a new class of biofuels called valeric biofuels [61].

6. Possible Biomaterials from Levulinic Acid (LA)

Polyhydroxy-alkanoates (HPAs) are a viable alternative to non-biodegradable plastics derived from fossil resources [62]. Chiral GVL derived from the asymmetric hydrogenation of LA leads to the production of diverse natural products [29].

7. Conclusions

The use of microwave technology for the conversion of biomass to biochemicals, biofuels and biomaterials offers a solution to the resource depleted world. The use of concentrated solar energy combined with activated carbon supported heteropoly acids hold a promise for the energy efficient and selective conversion of biomass to levulinic acid (LA). The use of simulated green liquor pretreatment effectively delignified the herbaceous biomasses used in this study. However, it is not only the amount of lignin but also the relative location of the lignin and the strength of the bonding between the lignin, cellulose and ash content in the biomass that are crucial for obtaining high yields of LA from biomass. Biomass with a high cellulose content (>99%), such as cotton, is an ideal feedstock for LA production. Until the technology for the direct conversion of lignocellulosic biomass to LA using solid acid catalysts is mature, fructose could be used as the starting material and Ga@mordenite could be used as the solid acid catalyst for the large-scale production of LA. Though significant progress has been made in the diversification of LA to biofuels and biochemicals, progress is awaited in the production of plastic substitutes, natural products and chiral nitrogenous biomaterials from LA.

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