Production and catalytic transformation of levulinic acid: A platform for speciality chemicals and fuels

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ABSTRACT

Lignocellulosic biomass is a renewable and abundant source that can be used as a replacement for fossil resources in the sustainable production of speciality chemicals and transportation fuels. Over the last several decades, it has been demonstrated that one of the most effective methodology is to converse the high concentration of oxygen functionalized biomass monomers (e.g., cellulose, hemicelluloses) through de-functionalization into levulinic acid (LA) that has low oxygen content, followed by catalytic transformation of LA into fuels and valuable chemicals. This strategy currently seems to be the logical and promising alternative for sustainable development in the context of economic and environmental considerations. Besides, LA has been identified as one of the most promising platform chemicals for the sustainable production of fuels and commodity chemicals. This review is an up-to-date progress of literatures available on the subject of speciality chemicals and fuels derived from biomass through LA platform. The mechanism and current technologies for the production of LA are reviewed and compared. The potential theoretical calculation methods such as ab initio methods and density functional theories to predict the reaction pathway was also commented. The various transformation methods started from LA to speciality chemicals and fuels are critically reviewed. Among the various products, γ-valerolactone, 2-methyltetrahydrofuran and levuinate esters have been identified as promising fuels. The commercial diphenolic acid and delta-aminolevulinic acid have been widely utilized in many areas. The potential applications as well as fuel properties of these products are also discussed.

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1. Introduction

With the growth of emerging economies and increasing populations that is approximately quadrupled in the 20th century, the continued use of fossil fuels has resulted in a fast increase in global energy consumption with 16 fold [1,2]. The three most utilized fuels by industrial economies are oil, coal and natural gas [1–3], which accounted for ~87% of the global energy consumption in 2011 as shown in Fig. 1A. In the United States, fossil resources account for

Fig. 1. Global energy consumption in 2011 (A) and Primary energy consumption in the United States by source and sector in 2011 (all numbers in quadrillion BTU, (B), modified and redraw from [2]. *Note*: the waste (4.9%) is not accounted in (A).

~93% of the total energy consumption in the transportation sector as shown in Fig. 1B [1,2]. The global energy demand for liquid fuels was 85.7 million barrels/day in 2008 and it is estimated to be grown to ~97.6 million barrels/day by the year 2020 and ~105 million barrels/day by the year 2030 [2], while the existing energy resources of the crude oil can only support our society for another ~50 years at the current rate of consumption [3]. Besides, most speciality chemicals and fuels are directly or indirectly produced from the limited fossil resources [4–8]. To develop more sustainable routes for the production of fuels and commodity chemicals, our society has to explore and utilize alternatives such as renewable resources for this purpose. Additionally, the combustion of the primary energy sources (e.g., oil, natural gas and coal) has caused a significant increase in the concentration of carbon dioxide in the atmosphere [9–11], which has been widely considered as a greenhouse gas, trapping solar energy and changing global climate. To transform our society into a greener future, sustainable alternatives have been taken for environmental protection and rational utilization of renewable energy [9,12–16].

Biomass is the only abundant and concentrated source of nonfossil carbon that is available on Earth. The conversion of biomass to speciality chemicals and fuels has been the focus of industry and researchers within the past decade [9,17], because it not only aimed at the development of effective and environmentally benign technology, but also simultaneously solves the problem of agricultural and forestry waste use [18–23].

The DOE/NREL report, named "*Top Value Added Chemicals from Biomass*" [24] identified the twelve top chemical candidates for launching renewable chemical platforms that can be derived from biomass. Bozell et al. [25] presented an updated evaluation of potential target structures and extended the platform chemicals of biobased products from biorefinery carbohydrates. In most of the established chemical approaches being investigated, platform chemical levulinic acid (LA) [24,25], also named 4-oxopentanoic acid, was considered as one of the most promising platform chemicals from lignocellulosic biomass for fuels and chemicals (Figs. 2 and 3). It is also a speciality chemical that finds applications for several purposes, such as source of polymer resins, animal feed, food as well as components of flavoring and fragrance industry, textile dyes, additives, extenders for fuels, antimicrobial agents, herbicides and plasticizers [26,27].

LA can be obtained by the multiple steps in the hydrolysis of raw cellulose through dilute sulfuric acid treatment via
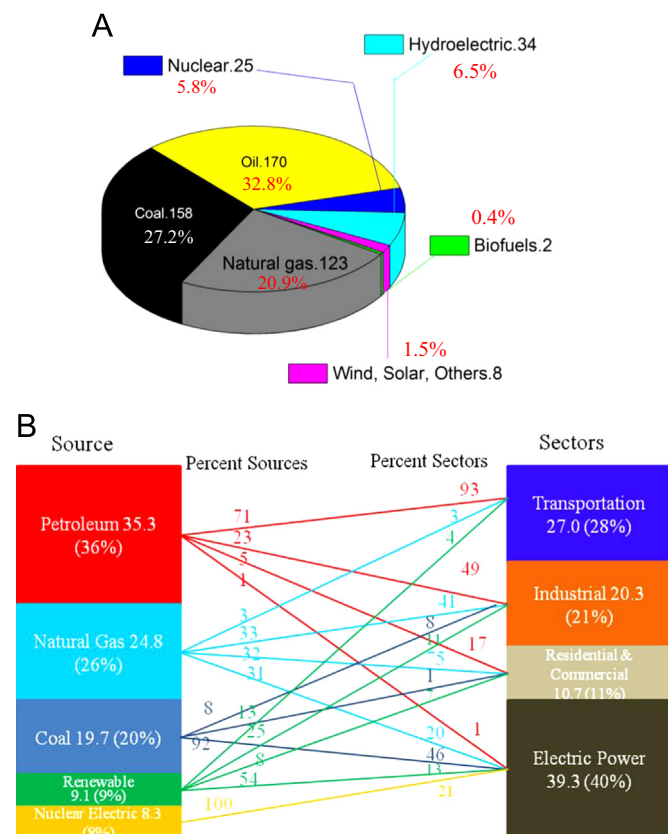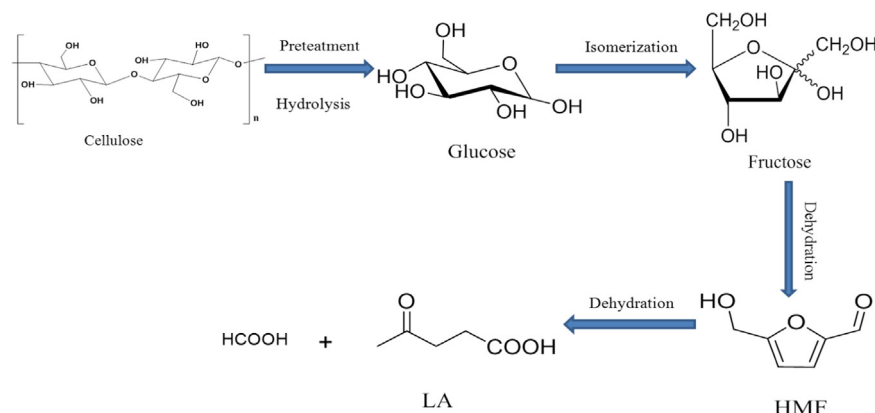

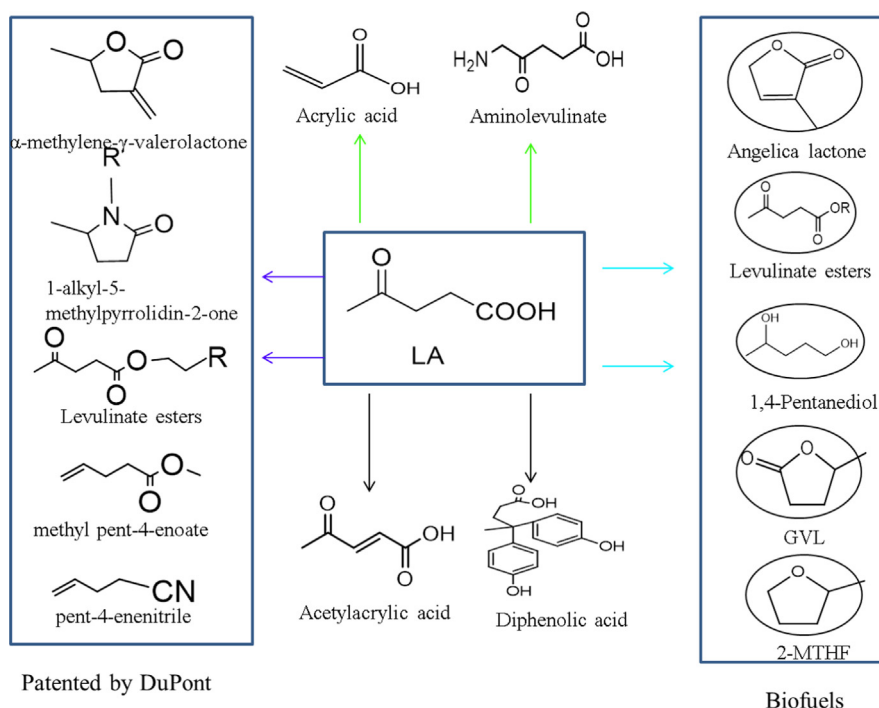**Fig. 2.** Production of LA from cellulosic biomass [8,18].

Fig. 3. Importantly value-added chemicals and biofuels from the conversion of LA [23,39].

Table 1
The main physical properties of LA.

Physical properties items	Values
Color	White
pKa	4.59
Melting point	37 °C
Boiling point	246 °C
Density	1.14
Solubility (water and polar organic solvents)	Soluble
Refractive index (20 °C)	1.447
Surface tension (25 °C)	39.7 dyn cm^{-1}
Heat of vaporisation (150 °C)	0.58 kJ mol^{-1}
Heat of fusion	79.8 kJ mol^{-1}

intermediate 5-droxymethylfurfurfural (HMF) as shown in Fig. 2 [27–29]. The raw cellulose often needs pretreatment and detoxification prior to the hydrolysis of cellulose [30,31]. Equimolar amount of formic acid is formed together with LA. LA is a water-soluble acid (pKa=4.59) with a high-boiling point (520 K), that crystallizes at room temperature (R.T.) (melting point 311 K). The main physical properties of LA are shown in Table 1 [8,9]. Being a bifunctional gamma-keto-carboxylic acid [30,31], LA has a rich chemistry as a platform and can be converted into a wide range of derivatives with numerous applications as polymer precursors, pharmaceutical intermediates and fuel additives as shown in Fig. 3.

Biofine process (Biofine Renewables LLC Company) utilizes dilute sulfuric acid (H$_2$SO$_4$) as a catalyst, but it differs from other dilute-acid lignocellulosic-fractionating technologies because the monomeric sugars are not the product [32,33]. The Biofine Process is a patented technology that has been demonstrated at pilot scale, producing LA, furfural, formic acid (HCOOH) and lignin char from lignocellulose by the hydrolysis in the presence of dilute sulfuric acid (H$_2$SO$_4$) [32–34]. The process involves a continuous two-stage reactor system operated at optimal conditions to produce LA with 70–80% theoretical yields, which corresponds to 50% mass yield on the basis of C6 sugars. Formic acid is a co-product accounting for

20% of the mass yield and the water-insoluble humins (side products) accounts for the rest of the product mass [35,36]. C5 sugars can also be used for the production of LA. This transformation is realized through the acid-catalyzed dehydration of xylose to produce furfural, followed by the metal-catalyzed hydrogenation of furfural to furfuryl alcohol, and completed by Brønsted acid-catalyzed hydrolysis of furfuryl alcohol to LA [34]. In these examples, the design of catalysts and selection of operating conditions are crucial to maintain high selectivity and the effectiveness of the catalytic process. These biomass-based processes are still early in their development, and as such, this represents a tremendous research opportunity for the development of effective catalytic materials with a variety of catalytic functions, including acid sites, basic sites, and metal hydrogenation sites, to accomplish the common goal of selectively removing oxygen functional groups. This review presented a detailed analysis of the conversion of the high concentration of oxygen functionalized biomass to LA that has low oxygen content, followed by catalytic transformation of LA into speciality chemicals and fuels. This review investigates potential methods, and current technologies to address these issues for the catalytic conversion of biomass to LA, then upgrading to speciality chemicals and fuels. The various production routes started from LA to speciality chemicals and fuels are critically commented and identified. Their potential utilizations and fuel properties will be also outlined.

2. Mechanism studies on the production of levulinic acid

A number of studies have been performed for the investigation of dehydration of carbohydrate into LA; however, only limited information of the pathway is available [37–40], thus making the nature of the dehydration very ambiguous. The available information briefly described the pathway that C$_6$-sugar was initially dehydrated to form the intermediate named HMF through loss of three molecular water, where the HMF was subsequently rehydrated to give the final product LA with formic acid in the presence of water [36,40]. Fig. 4 shows the proposed
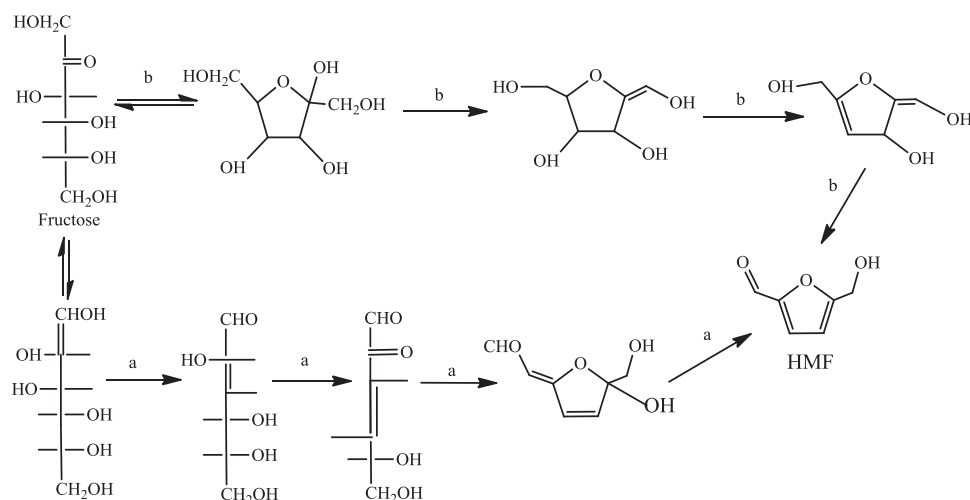
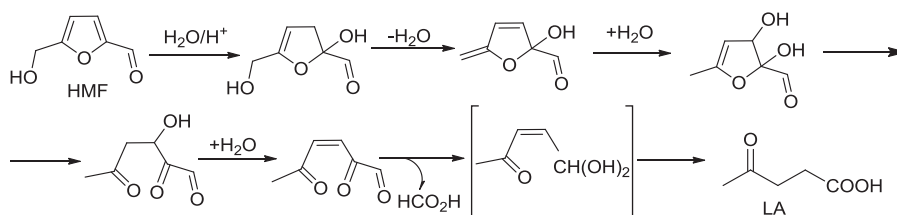**Fig. 4.** Possible dehydration mechanisms for formation of HMF (a) acyclic route; (b) cyclic route [40].

Fig. 5. Proposed mechanisms for the formation of LA from HMF [42].

Table 2
Production of LA from carbohydrates substrate[a].

No.	Substrate	Catalyst	Solvent	Time (h)	T (°C)	Y_{LA} (%)	Refs.
1	Glucose	HCl–$C_2H_4Cl_2$	–	3	80–100	79	[51]
2	Glucose	$FeCl_3$	H_2O	2	180	30	[56]
3	Glucose	$CrCl_3$	H_2O	2	180	60	[56]
4	Glucose	$CuCl_2$	H_2O	2	180	~23	[56]
5	Glucose	$AlCl_3$	H_2O	2	180	~71	[56]
6	Glucose	HCl/$ClCH_2CH_2$ Cl	$ClCH_2$–CH_2Cl	3	80–100	5–9	[57]
7	Glucose	HCl	H_2O	24	R.T.	15	[58]
8	Glucose	Amberlite IR-120	H_2O		124	5.8	[59]
9	Glucose	HCl	H_2O	0.25	160	41.4	[60]
10	Glucose	Clay	H_2O	24	150	12	[61]
11	Glucose	H_2SO_4	–	1	170–210	80.7	[62]
12	Glucose	HCl	–	1	220	57.7	[63]
13	Glucose	HCl	–	4	90	23	[64]
14	Glucose	H_2SO_4	–	12	98	38	[64]
15	Glucose	Al–Zr oxide	H_2O	2	180	6.1	[65]
16	Fructose	HCl	–	–	98	~75	[64]
17[a]	Fructose	Amberlite IR-120	H_2O	27	R.T.	23.5	[59]
18	Fructose	LZY	H_2O	15	140	43.2	[66]
19	Fructose	Lewatit SPC 108	H_2O+MIBK	0.5	80	79	[67]
20	Fructose	H_3PO_4	H_2O	~0.03	280	7	[68]
21	Fructose	$Cs_{2.5}H_{0.5}PWb$	H_2O+MIBK	1	115	12.6 ± 0.3	[69]

[a] R.T.: Room temperature.

mechanism for the conversion of C_6 sugars, such as glucose and/or fructose to HMF. A study by Antal et al. [40] suggested that HMF was formed from the dehydration of fructose in its furanose form and occurred through a series of cyclic furan intermediates (Fig. 4, b pathway). Moreau et al. [36,37] and Lamport et al. [41] have suggested that HMF was formed through an enediol pathway (Fig. 4, a pathway). The enediol was proposed as an intermediate in the isomerisation of glucose to fructose. The further conversion of HMF into LA was the result of water addition to the C_2–C_3 bond of the furan ring to give the final products LA and formic acid (see Fig. 5).

Assary et al. [39] have reported that the thermochemistry of the conversion of glucose to LA through fructofuranosyl intermediates was investigated using the high-accuracy Gaussian-n Methods. The method keywords G4 and G4MP2 perform high accuracy complex energy computations in Gaussian. They have calculated values of gas phase reaction enthalpies and indicated that the first two steps were highly endothermic involving water molecule elimination, while the other steps were exothermic, including the additional water elimination and rehydration to form LA. They calculated gas phase free energies and the results indicated that inclusion of entropic effects promoted the dehydration steps, although the

elimination of the first water was still endothermic. According to the calculated enthalpy and free energy values, it indicated that the first dehydration step in conversion of glucose to LA was likely a key step in controlling the overall progress of the reaction [42]. In combination with calculation and experimental results, the pathways through an enediol are more plausible.

The production of LA from biomass conveniently starts with acid hydrolysis. The raw material lignocellulosic biomass mainly composed of cellulose, hemicelluloses and lignin, where the first two can yield the desired hexoses, the key intermediates in the production of LA. Thereafter, sugars will be dehydrated under acidic environment and rearranged to HMF from hexoses and furfural from pentose. Consequently, HMF can be further rehydrated to LA. It should, however, be stated that the real yields of LA are typically lower than the theoretical yields due to occurrence of multiple side reactions and the harsh reaction conditions required for the hydrolysis of cellulose and hemicellulose.

Albeit a number of studies have performed and investigated the production of LA, how to disclose the actual mechanism is still a challenge. Many of the mechanism studies are still early in their development, and certainly require additional researches, especially for the In-situ studies (e.g., Nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR), and Isotope technologies) on elucidating reaction intermediate and kinetics.

3. Production of levulinic acid from biomass

As an alternative to fossil fuels, production of fuels from lignocellulosic biomass (e.g., cellulose, hemicelluloses) have been portrayed as a future leading supplier of energy sources that have the ability to increase the security of supply and reduce the vehicle emissions. Besides, this strategy offers the promise of numerous
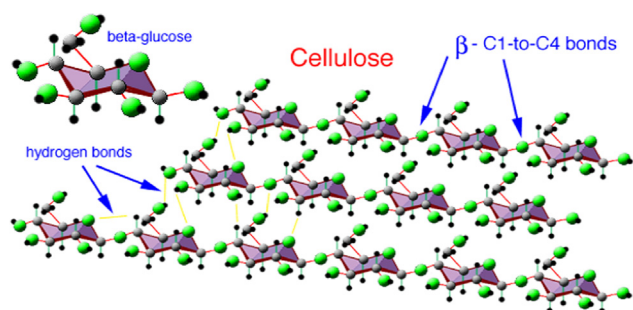

Fig. 6. Cellulose from intra-molecular condensation of β-glucose at the 1,4-position. Redraw from [17,19].

benefits related to energy security, economics, and the environment. As a platform intermediate LA, how to maximize the yield of LA is becoming crucial and emergent. The influences of various reaction parameters during the transformation of biomass to LA, including biomass type, reaction temperature, initial concentration of feedstock, liquid-to-solid ratio, agitation speed in the reactor, potential adjacent pretreatments of biomass as well as the influence of additives are commented in this section.

3.1. From sugars

The first study on the synthesis of LA from saccharose was reported in the 1840s by the Dutch professor Mulder [43], who prepared LA by heating sucrose with mineral acids (e.g., HCl, H_2SO_4) as catalyst at high temperature. LA is conventionally formed from the conversion of glucose, which is initially isomerised to fructose in the presence of alkaline catalyst. In the presence of acidic species, fructose is further dehydrated, producing a number of compounds such as HMF, LA, formic acid, and others (Figs. 4 and 5) [44–46]. During the acidic environment, HMF is prone to recombine with sugars or HMF itself via aldol-condensation, resulting in polymers with undefined structures and stoichiometry called humins [47,48]. To maximize the yield of LA, these side reactions must be hindered significantly. It is thus expected that by changing the solvent system as well as the amount and/or the nature of the employed catalyst using acid sites and basic sites, the reaction rates of different steps can be influenced to alter the distribution of products obtained [49,50].

Over the last several decades, a number of studies have employed the heterogeneous and homogeneous acidic catalysts. Due to the easy community between carbohydrate (e.g., fructose) and homogeneous catalyst (e.g., HCl), relatively high yield of LA was obtained. Typical works from literatures for the production of LA from carbohydrate as shown in Table 2. Mascal et al. [51] have reported the dehydration of glucose to LA with 79% yield under the conditions of HCl catalyst and dimethyl chloride solvent. The same catalytic system also works well for 5-(chloromethyl) furfural, where it was dehydrated into LA with 91% yield at 190 °C in water. Jin et al. [52] converted carbohydrate biomass to HMF and LA using mineral acid as catalysts. The highest yield of LA was 55%, which was obtained using HCl as catalyst at a pH of 1.5 and 5 min reaction time. Heterogeneous catalysis may provide an efficient methodology for the LA production, allowing for high reaction rates and high selectivity. Moreover, its easy recycle and environmental benign property appeared more attractive for the practical utilizations. For these reasons, the catalytic conversion of carbohydrate to LA over solid catalysts has received much attention over

Table 3
Production of LA from cellulose.

No.	Substrate	Catalyst	Solvent	T (°C)	t (h)	Y_{LA} (%)	Refs.
1	Cellulose	H_2SO_4	–	150	2	60	[74]
2	Cellulose	$CrCl_3$	H_2O	200	3	67	[56]
3	Cellulose	NafionSAC 13 or $FeCl_3$ /Silica	H_2O	130–190	12/24	0–5	[72]
4	Cellulose	HCl/$ClCH_2CH_2Cl$	$ClCH_2$–CH_2Cl	80–100	3	5–9	[75]
5	Cellulose	H_2SO_4	–	150	6	57	[75]
6	Cellulose	Sulfonated carbon	H_2O	190	24	~12	[76]
7	Cellulose	HCl containing NaCl and GVL (1:1)		155	1.5	72	[53]
8	Kernel grain sorghum	H_2SO_4	–	200	~0.67	32.6	[26]
9	Microcrystal-cellulose	HCl	–	220	1	35.4	[63]
10	α-cellulose	HCl	–	220	1	45.2	[63]
11	Cellulose	ZSM-5	GVL and water	–	16	35	[78]
12	Cellulose	Mordenite+Amberlyst 70	GVL and water	–	16	35	[78]
13	Cellulose	Nb_2O_5+Amberlyst 70	GVL and water	–	16	25	[78]
14	Cellulose	Amberlyst 70	GVL and water	–	16	69	[78]
15	Cellulose	CP-SO_3H-1.69	GVL and water	170	10	65.5	[72]

Table 4
A summary of other biomass feedstocks for production of LA from literatures.

No.	Substrate	Catalyst	Solvent	T (°C)	t (h)	Y_{LA} (%)	Refs.
1	Starch	HCl	–	220	1	53.7	66
2	Corn stover	HCl/ClCH$_2$CH$_2$Cl	ClCH$_2$–CH$_2$Cl	80–100	3	5–9	57
3	Water hyacinth	H$_2$SO$_4$	H$_2$O	175	0.5	53	78
4	Rice straw	S$_2$O$_8^{2-}$/ZrO$_2$–SiO$_2$–Sm$_2$O$_3$	H$_2$O	150	0.25	6.6	79
5	Rice straw	S$_2$O$_8^{2-}$/ZrO$_2$–SiO$_2$–Sm$_2$O$_3$	H$_2$O	180	0.25	8.2	79
6	Rice straw	S$_2$O$_8^{2-}$/ZrO$_2$–SiO$_2$–Sm$_2$O$_3$	H$_2$O	200	~0.17	70	79
7	Rice straw	S$_2$O$_8^{2-}$/ZrO$_2$–SiO$_2$–Sm$_2$O$_3$	H$_2$O	240	0.25	8.6	79
8	Wheat straw	H$_2$SO$_4$	–	210	0.6	19.9	77
9	Paper	H$_2$SO$_4$	–	< 240	–	59.8	80
10	Pulp residues	H$_2$SO$_4$		1st: 210–230 °C, 2nd: 195–215 °C	–	70–80	81
11	Sorghum grain	H$_2$SO$_4$		200		45.6	26
12	Bagasse	HCl		220		82.7	83

the last several decades. Heterogeneous acidic catalysts like acidic TiO$_2$ nanoparticles, zeolites (e.g., aluminosilicate) have also employed and display good activities. Suib et al. [50] recently reported the conversion of fructose to methyl levulinate with 80% yield through LA in methanol solvent was achieved in the presence of acidic TiO$_2$ nanoparticles. A biphasic reactor system consisting of an aqueous layer containing the acid catalyst, such as 1 M H$_2$SO$_4$ or ZSM-5, and an organic layer consisting of organic solvent (e.g., 2-sec-butylphenol (SBP), 4-n-hexyl phenol (NHP), or 4-propyl guaiacol) have been recently developed by Dumesic and coworkers [53–55].

A comprehensive overview of biomass based synthetic protocols for LA formation is compared in Table 2. In general, the mineral acid (e.g., HCl, H$_2$SO$_4$) catalyzed the production of LA from sugars often display higher yields. However, mineral acids (e.g., H$_2$SO$_4$, HCl) often associates with the environmental issues and the carbohydrate often competes with the food chain. Ongoing studies should devise a novel catalytic system whereby the renewable and non-edible feedstocks (e.g., hemicellulose) should be utilized and highly selectively transformed into LA, where the heterogeneous acidic and porous catalysts would be more promising.

3.2. From cellulose

Cellulose is an organic compound with the formula (C$_6$H$_{10}$O$_5$)$_n$, its structure is built up from linearly connected β(1→4) anhydroglucopyranose units that are covalently linked through acetal linkage between the equatorial hydroxyl groups on C4 and C1 carbon atoms as shown in Fig. 6 [18,19]. One cellulose molecule normally is composed of a few hundreds to thousands of glucoses. The unbranched cellulose chains are densely packed by inter-chain hydrogen bonds (Fig. 6). Cellulose is an important structural component of the primary cell wall of green plants, many forms of algae [32]. The cellulose content of cotton fiber is ~90%, that of wood is 40–50% and that of dried hemp is approximately 45%.

Hydrolysis of cellulose is very critical for the sustainable production of fuel and value-added chemicals, because it is abundant in nature, non-edible and not competing with the food chain [11]. Hydrolysis of cellulose is to initially break down cellulose into smaller polysaccharides or completely into glucose units, followed by the formation of LA under acidic or alkaline conditions [7,11,18,19]. However, hydrolysis of cellulose often faces many difficulties: (i) cellulose is very stable under many chemical conditions [11]. They are not soluble in water, many organic solvents, weak acids or bases [19]. (ii) The crystalline cellulose molecules bind strongly and packed densely to each other through the strong inter- and intermolecular hydrogen bond [11].

LA is normally formed through initial degradation of cellulose to glucose unit and then isomerised to fructose, where the fructose is further dehydrated to form LA as shown in Fig. 2. Peng et al. [56]

Table 5
Possible products from LA and potential LA markets demand [85].

Product	Use	Potential LA market (million lb/year)
MTHF	Fuel extender	10,000–100,000
DALA	Biodegradable herbicide	175–350
Diphenolic acid	Monomer	35
THF	Solvent	200

investigated the conversion of cellulose to LA by different metal chlorides including alkali metals (Li, Na and K), alkaline earth metals (Mg and Ca), transition metals (Cr, Mn, Fe, Co, Cu and Zn) and Al as a group IIIA metal. Among those metal chlorides, chromium chloride (CrCl$_3$) was found to be the most effective for the conversion of cellulose to LA, affording an optimum yield of 67 mol% at 200 °C for 3 h [56]. Efremov et al. [70] studied the conversion of cellulose into LA in water solvent using salt of CoSO$_4$, Fe$_2$(SO$_4$)$_3$ and Al$_2$(SO$_4$)$_3$ as catalysts. The most active among the studied catalysts was Al$_2$(SO$_4$)$_3$, which produced a LA yield of about 18 wt% at 250 °C. Hegner et al. [71] investigated the conversion of cellulose to glucose and LA with 5% yield via a solid catalyst system based on the catalyst like Nafion SAC 13 and FeCl$_3$/silica. More recently, Zuo et al. [72] studied a sulfonated chloromethyl polystyrene solid acid catalyst for catalytic conversion of cellulose into LA with 65.5%yield and perfect conversion under the conditions of 10 h and 90 wt% γ-valerolactone/10 wt% water as solvent. Yang et al. [73] reported Fe-resin (a modified Dowex 50 by cation exchange) solid catalyst for the selective decomposition of microcrystalline cellulose in 5 wt% NaCl solution under hydrothermal conditions. The conversion of microcrystalline cellulose was 90.9% with 33.3% yield LA under 200 °C for 5 h. Table 3 presented the key performance factors for the individual process steps. In spite of such progress, the dilute acid hydrolysis process still has shortcomings such as strong equipment corrosion, harsh operating conditions. The concentrated acid hydrolysis process usually operates at room temperature with concentrated mineral acid [77]. Its main problem is the strong equipment corrosion and the inadequate acid recovery. Although some methods have been taken to solve these problems some of extent, some crucial problems (e.g., complex procedure with low selectivity) still exist. A cost-effective and environment-friendly process in LA biorefinery is still largely needed.

3.3. From other biomass feedstocks

Common sources of lignocellulose include sawdust, corn stover, sugarcane bagasse, municipal waste and pulp sludge that are

currently thought as low-value waste [24,25,27]. However, energy crops dedicated to fuel and chemical production will need to be grown on a large scale to meet the vast demand for feedstock [28,32,33]. Various types of fast-growing grasses and trees have thus been identified as promising feedstocks with switchgrass, miscanthus, poplar and eucalyptus being prominent examples [18,32].

In 1940, the first commercial scale production of LA in an autoclave was started in United States by Stanley [43]. Some pioneered works have been in the groups of Hanna [26] and Heeres [78] using kernel grain sorghum and starch as starting material for the production of LA. Girisuta et al. [74,78] tried to convert water hyacinth to LA with 53 mol% (35 wt%) based on the amount of C6-sugars in the water hyacinth at the conditions of 175 °C, 1 M H_2SO_4 and 1 wt% water hyacinth intake. Recently, Chen et al. [79] reported the heterogeneous super-acidic catalyst named $S_2O_8^{2-}/ZrO_2–SiO_2–Sm_2O_3$ for the catalytic conversion of raw straw to LA, where 70% LA of the theoretical yield was obtained under the optimal conditions of 200 °C, 10 min, 13.3% of solid superacid to pretreated rice straw, and 1:15 of solid–liquid ratio. The key performance factors for individual process steps of LA formation are presented Table 4. Some studies have performed and investigated the production of LA using the above-mentioned biomass feedstocks, some good results have been obtained and some promising catalytic system has been designed. Due to the robust catalysts developed, many of these processes are progressively targeting to more complicate biomass substrates.

4. Transformation of levulinic acid to speciality chemicals and fuels

LA can be generated at least in principle from almost all C_6 sugars manufactured in the biorefinery [24,25,80,81]. For this reason, it has frequently been suggested as a starting material for a wide number of compounds [26,83,84]. Being a bifunctional gamma-keto-carboxylic acid, LA has a rich chemistry and can be converted into a wide range of fuel additives and commodity chemicals (as shown in Fig. 3). Some widely used chemicals and the amount of the market needed are depicted in Table 5. DuPont has also patented a number of LA derivatives with applications ranging from Nylon intermediates, ionic liquids, to biofuel additives [82].

4.1. Diphenolic acid

Diphenolic acid [also named 4,4-bis-(4′-hydroxyphenyl) pentanoic acid, often referred as DPA] is prepared by the condensation reaction of LA with two molecules of phenol [24,85–88] as shown in Fig. 7. DPA is expected as a promising substitute for bisphenol A, the primary raw material of epoxy resin and polycarbonates [87,88], which is widely used as a chemical intermediate in the paint formulation, protective and decorative coatings and finishes, lubricating oil additives, cosmetics, surfactants, plasticizers, and textile chemicals [89,90]. Besides, DPA contains multifunctional groups, which can be modified through chemical methods, potentially offering much more functionalized materials [85]. Extensive researches have been performed at the Rensselaer Polytechnic Institute in New York State on near-term applications for DPA to displace currently marketed BPA products [85]. In the longer term, DPA could be a viable alternative for the production of plastics [85].

Traditionally, the synthesis of DPA has been investigated using strong Brønsted mineral acids such as H_2SO_4 and HCl. These acids usually suffer from disadvantages such as corrosivity, difficulties in handling as well as separation, and waste treatment [86]. In recent years, the environmental and economic considerations have spurred the replacement of the toxic and corrosive reagents. Along this context, heterogeneous solid acid catalysts have played a key role in the synthesis of DPA. It has been reported that the production of DPA using mesoporous $H_3PW_{12}O_{40}/SBA$-15 composite as a heterogeneous catalyst, and excellent TOF over 50 h^{-1} was obtained at 100 °C [91–93]. In addition, sulfonated hyperbranched poly(arylene oxindole)s was synthesized to catalyze the condensation of phenol and LA with 1:1 M ratio of thiols as additive [94]. Although these more robust and greener catalysts were examined, the intrinsic drawbacks of solid heterogeneous catalysts including low catalytic active sites and their high susceptibility to leaching have given rise to moderate yields of DPA, and there is still a need for further improvement. Thiol-containing acid ionic liquids were prepared for the condensation of phenol and LA, which offered both a high yield of DPA (over 90 mol%) and the ratio exceeding 100 of p,p′–DPA to o,p′–DPA [95,96]. Albeit IL is a very advanced solvent, the synthesis cost as well as the thermal stability is still an issue. For this reason, the identification of less expensive catalyst may be a potentially valuable vein of future research. A series of supported propylsulfonic acid catalysts were studied in detail [93,95], including a commercial catalyst, an SBA-15 supported catalyst and two periodic mesoporous organosilane (PMO) based catalysts were shown to have significantly
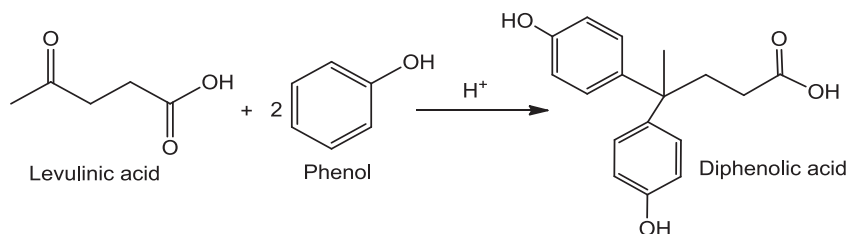

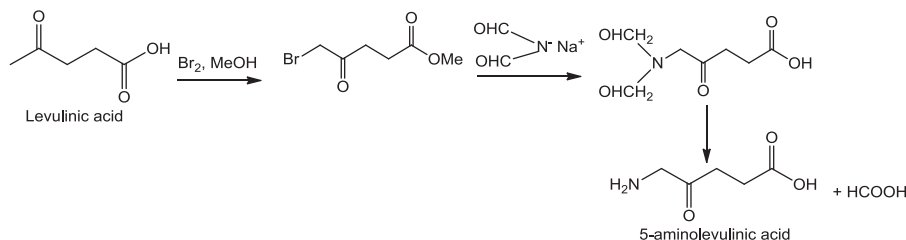Fig. 7. Production of diphenolic acid from the condensation of LA and phenol.

Fig. 8. NREL mechanism for the production of DALA from LA [24].

higher stability. The synthesis of supported propylsulfonic acid catalysts is still requiring improvements as well as novel methodology. The increased catalyst stability of the hydrophobic PMO catalysts led to the study of Nafion SAC-13 [95], a commercially available perflorinated resin-silica nanocomposite. Although Nafion SAC-13 has a significantly lower acid site density compared to the synthesized materials, the stability was significantly higher. Therefore, additional studies on the selective production of DPA can be expected to perform using heterogeneous catalysts and a separation friendly solvent in a single reactor.

4.2. Delta-aminolevulinic acid

Delta-aminolevulinic acid (DALA), also named as 5-aminolevulinic acid, is a naturally occurring substance present in all plant and animal cells [32,97,98]. It is the active ingredient in a range of environmentally benign, highly selective, broad-spectrum herbicides. It shows high activity towards dicotyledonous weeds and it has little activity towards monocotyledonous crops [99]. DALA has also been used as an insecticide [100] and for cancer treatment [101].

The synthesis of DALA from LA involves the selective introduction of an amino group at the C5-position of LA as shown in Fig. 8. The most widely used approach for activating the C5 position in the amination process is the bromination of LA in an alcohol solvent to produce mixtures of 5-bromoesters and 3-bromoesters that are separated by distillation [102]. The 5-bromolevulinate is then aminated using a nucleophilic nitrogen species [103]. A significant amount of research has been performed and carried out to synthesize DALA from LA. The complexity and low yields of conventional DALA synthesis techniques mean that it is currently a very expensive product, it's been used only for highly selective herbicidal treatments and for some cancer therapies. A number of methods have been reported to produce DALA [104–107]. One typical method often consists of a three-step synthesis including bromination of LA in methanol [103–105], reaction of methyl 5-bromolevulinic acid with potassium phthalimide and a subsequent hydrolysis of the resulting phthalimide derivative [103]. Another method is to convert the 5-bromo ester into ALA hydrochloride via an azide derivative [105]. Two routes have also been used to synthesize ALA hydrochloride from acidchloride of monomethyl and monoethyl butanedioates [106]. Ha et al. [103] reported the bromination of unsymmetrical ketones with Br_2 in methanol proceeded regioselectively in good yield at the less substituted methyl carbon. The bromination of LA was followed by azidation and amination to lead to an efficient three-step synthesis of DALA in 36% yield. Overall, the whole yield of DALA is still low, the identification of robust and selective catalyst is still largely needed. Lab-scale reactor experiments can be used in each case to identify important catalyst parameters that have determining effects on the selectivity. Ongoing studies are still need to focus on characterizing and optimizing the catalysts used in this process, on elucidating key mechanistic issues, and on evaluating how the reaction variables control the yields and selectivity.

4.3. γ-Valerolactone

It was recently proposed that γ-valerolactone (GVL), a frequently used food additive, exhibits promising characteristics of a sustainable platform chemical, including the possibility to use it for the production of either energy or carbon-based consumer products [108,109]. It is renewable, has low melting (-31 °C), high boiling (207 °C) and flash points (96 °C), a definitive but acceptable smell for easy recognition of leaks and spills, low toxicity, and high solubility in water to assist biodegradation. Moreover, GVL retains 97% of the energy of glucose and can be blended by itself in gasoline where it performs comparably to ethanol/gasoline mixtures as shown in Table 6 [110,111]. In addition, GVL does not form peroxides in a glass flask under air in weeks, making it a safe material for large scale use. Comparative evaluation of GVL and ethanol as fuel additives shows very similar properties [110]. Horváth and coworkers also show that the use of a single chemical entity, such as GVL, as a sustainable liquid instead of a mixture of compounds could significantly simplify its worldwide monitoring and regulation [111,112]. Another benefit of GVL to be a practical biofuel is that it is relatively inexpensive to produce. Using a cheap feedstock (e.g., glucose), this biofuel can be produced at prices between 2 and 3 US$/gallon [110].

Since GVL is important and promising fuel and also widely used commodity chemical, many studies have been performed to selectively produce GVL (Fig. 9) and it was shown that GVL can be selectively produced with good activities from LA using the Ru-derived homogeneous catalyst system [71,113]. Albeit the recycle and separation of catalyst from reaction residues later on remain a challenge, it offers great opportunities to understand the reaction pathway and better for us to design the catalyst as well as the catalytic system. Due to the easy recycle and environmentally benign property, heterogeneous catalytic system appeared more promising. Ru- and Cu-derived nanoparticles catalysts have been developed for this purpose [114–117]. Our previous studies also

Table 6
Selected properties of GVL, MTHF and EL [85,110,111].

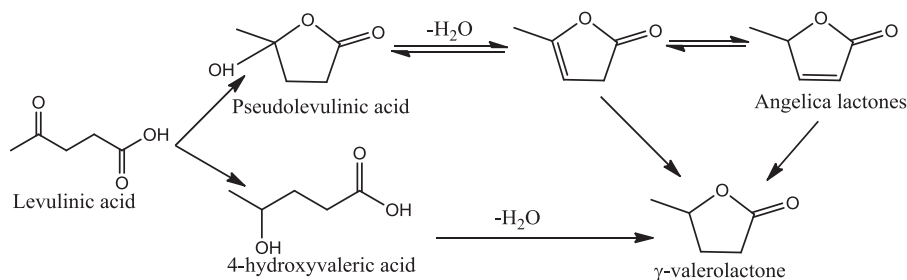| Terms	Ethanol	GVL	MTHF	EL
M (g mol^{-1})	46.07	100.12	86.13	144.17
Carbon (wt%)	52.2	60	69.7	58.7
Hydrogen (wt%)	13.1	8	11.6	7.7
Oxygen (wt%)	34.7	32	18.7	33.5
Boiling point (°C)	78	207	80	206.2
Melting point (°C)	-114	-31	-136	–
Flash Point (°C)	13	96.1	-11.1	195
Density (g mL^{-1})	0.789	1.0485	0.86	1.014
Solubility in water (mg mL^{-1})	Miscible	≥ 100	13	Soluble
Octane number [a]	108.6	–	80	–
Cetane number	5	–	23.5^c	< 10
Lubricity	–	–	–	287

[a] Research octane number.

Fig. 9. Reaction pathways for conversion of LA to γ-valeroclatone.
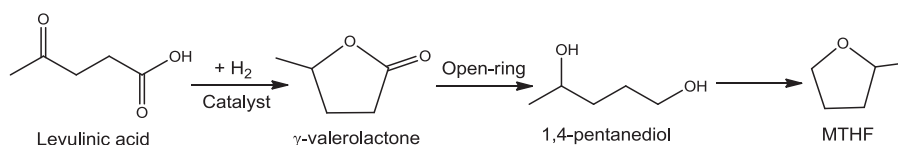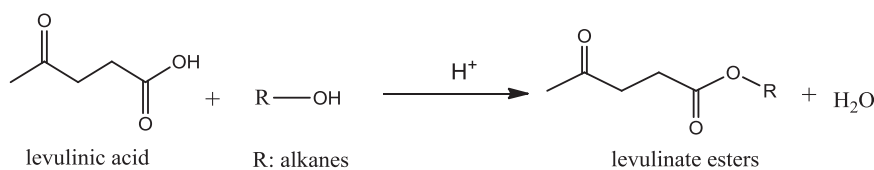
Fig. 10. Hydrogenation of LA to produce MTHF.

Fig. 11. Esterification synthesis of levulinate esters.

show that Cu-catalysts derived from hydrotalcite were highly selective for the production of GVL [118,119].

LA can be also transformed to hydrocarbon fuels by a number of catalytic routes involving deoxygenation reactions combined with C–C coupling reactions. However, the production of GVL intermediate is crucial, which is the starting material to produce both pentenoic and pentanoic acids, which are the precursors of hydrocarbons.

In this case, it is likely that the liquid phase would hinder the rate of LA hydrogenation reactions, and the catalyst may require a stronger hydrogenation function (or the use of higher H_2 pressure) than those used in the vapor phase studies. Future studies should offer a better understanding of how the catalyst functions and improving the ability of catalysts to deactivate specific classes of compounds, which are beneficial to design the catalytic system under realistic operating conditions.

4.4. 2-Methyltetrahydrofuran

2-Methyltetrahydrofuran (MTHF) is an organic compound with the molecular formula of $CH_3C_4H_7O$, which is a highly flammable mobile liquid. It has reported that the direct application of GVL as a fuel additive is not so ideal and still associates with several issues in the transportation sector, such as high water solubility, blending limits for use in conventional combustion engines, possible corrosiveness in storage and lower energy density compared to petroleum-derived fuels. These limitations spanned the reduction of GVL to MTHF [113,117], which can be blended up to 70% in gasoline and is considered as a more promising fuel. The production of fuel additives via renewable feedstocks offers perhaps the greatest potential for mass-market penetration of LA. It has been found that MTHF can be added up to 30% by volume with petroleum with no adverse effects on performance, and engine modifications are not required. Some important properties of MTHF are also listed in Table 6 to compare with other fuels. Although it has a lower heating value than regular petroleum, it has a higher specific gravity and hence mileage from MTHF blended fuel would be competitive. MTHF can greatly reduce the vapour pressure of ethanol when co-blended in gasoline. This has resulted in the development of "P-Series" fuels where MTHF acts as co-solvent for ethyl alcohol (high-octane) in "pentanes-plus" hydrocarbons obtained from natural gas [117].

Different homogenous Ru-derived catalysts [71,113], heterogeneous Cu-composites [117,120] and Noble-metal catalysts [121] have reported for the production of MTHF from LA (Fig. 10). For example, Fan et al. [120] reported a yield of MTHF as high as 91% based on GVL as a substrate dissolved in ethanol and Cu/ZrO_2 as a catalyst. The Ni-derived catalysts have also been reported to show good performance [122]. The hydrogenation can be performed in the liquid phase under the H_2 pressure or in the vapor phase at atmospheric pressure with the commonly supported Ni catalysts. The single-stage production of MTHF from LA with a Re/Pd on carbon catalyst has been reported in the patent [123].

At present, one of the biggest issues with the heterogeneous hydrogenation of LA for the production of MTHF is the high yield of coke produced during the process. Although this coke has some value as a source of process heat, it detracts from the total possible yield of MTHF and deactivates the catalyst like zeolite. The coke formed has high carbon content and is deficient in hydrogen, suggesting that the addition of a hydrogen donor could be useful in limiting the amount of coke produced during hydrogenation. There is still need for much research to be done for an effective, economical and efficient conversion process, especially for the optimization or improvement of these parameters through better design of catalyst and reaction system.

4.5. Levulinate esters

Levulinate esters produced using LA and the corresponding ethanol, methanol, butanol, or mixed alcohols—are certified viable additives for gasoline and diesel transportation fuels. These levulinate esters, like methyl levulinate, ethyl levulinate, and butyl levulinate, are the kind of short chain fatty esters displaying similar properties to the biodiesel fatty acid methyl esters (FAME) [124–126]. They cater for gasoline additives and diesel transportation fuels, which have manifold excellent performances, such as non-toxic, high lubricity, flashpoint stability and better flow properties under cold condition [127]. Besides, levulinate esters have also been recognized as important platform chemicals and have a wide range of applications. They can either be used in the flavoring and fragrance industries or as substrates for various kinds of condensation and addition reactions at the ester and keto groups in organic chemistry [128–130].

The most studied of the LA esters is a low-smoke diesel formulation developed by Biofine and Texaco that uses ethyl levulinate as an oxygenate additive [131]. The effects of adding ethyl levulinate, short-chain alcohols, and commercial additives have been determined by studying their influence on the acid value (AV), cloud point (CP), pour point (PP), cold filter plugging point (CFPP), induction period (IP), kinematic viscosity (KV) and the flash point (FP). The results showed the improved low temperature properties of the methyl esters compared to unblended samples of biodiesel. In summary, it was demonstrated that specific fuel properties such as low temperature operability could be improved through blending (ethyl levulinate and short-chain alcohols) and additive CFI strategies [132]. The 21:79 formulations consist of 20% ethyl levulinate, 1% co-additive and

79% diesel and can be used in regular diesel engines. The oxygen content of ethyl levulinate (EL) is 33 wt%, giving a 6.9 wt% oxygen content in the blend, resulting in a significantly cleaner burning diesel fuel [131].

The efficient production of levulinate esters (Fig. 11) through different routes have received numerous attention over the last several decades, the traditionally utilized catalysts for the production of esters are often on homogeneous mineral acids such as formic acid, H_3PO_4 and H_2SO_4 [133,134]. Due to its easy recycle and separation, heterogeneous catalysts have attracted more attention. Zeolite and heteroploy acid were the most often employed catalysts for the esterification because of their adjustable acidity, easy recycle, potential economic and environmentally benign benefits [135–137]. Recently, we have developed one-step synthesis of mesoporous $H_4SiW_{12}O_{40}$–SiO_2 catalyst for efficient synthesis of both methyl levulinate and ethyl levulinate with 73% and 67%, respectively. The biggiest advantage of the type of catalyst is highly stable, which offers stable activities over several runs [138]. Riisager et al. have reported the sulfonic acid functionalised SBA-15, sulfated zirconia and beta, Y, ZSM-5 and mordenite zeolite catalysts for the conversion of fructose to EL using ethanol as solvent and reactant. 57% yield of EL was obtained on sulfonic acid functionalised SBA-15 at 140 °C [139]. Recently, Baronetti et al. [140] studied a Wells–Dawson heteropoly acid supported on silicon gel for the synthesis of EL from LA and ethanol, whereas 76% yield was reported. The acidic nature and pore geometry are expected to be the most important properties of the microporous and mesoporous catalysts for the formation of levulinate esters.

5. Conclusions and outlook

The conversion of biomass and biomass-derived compounds into speciality chemicals and fuels can ameliorate many of the current issues associated with the use of fossil fuels. The production of LA from lignocellulosic biomass can be achieved from C5-sugars in hemicellulose and C6-sugars in cellulose through pretreatment and further acid catalyzed reactions. Many of these processes require the development of efficient catalysts able to selectively manipulate C–O bonds. The removal of different oxygen functional groups requires a variety of different catalytic active sites in the processing of cellulose or hemicellulose. The development of robust and solid acidic catalysts with specific functions will be highly desirable for this purpose.

1. Many of these processes for the highly selective production and separation of LA are still early in their development, and would benefit greatly from additional research on separation that is not covered in this review. Development of economically viable processes for converting more complicate biomass feedstocks to fuels and to chemical precursors for industrial products would be more attractive and has the potential for reducing the atmospheric CO_2 burden without compromising food supplies.
2. The solid catalysts developed for the hydrolysis should fully use a variety of catalytic functions, including acid sites, basic sites, and metal hydrogenation sites, to selectively remove oxygen functional groups.
3. At present, one of the biggest issues with the catalytic transformation of LA to fuels (e.g., MHTF) is the high yield of coke produced during the process. The coke formation pathway needs additional research and efforts. Efficiently addressing the formation of intractable coke in the procedure and efficient conversion of LA still require many future efforts from researchers and industry. Besides, understanding of the reaction mechanisms will be certainly beneficial for catalyst design.

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