
Review

A Review on the conversion of levulinic acid and its esters to various useful chemicals

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Abstract: Levulinic acid (LA), an important chemical produced from a bio-based resource for current petrochemical operation, the details of hydrogenation to gamma (γ)-valerolactone (GVL) is reviewed. Levulinic acid (LA) was listed among one of the top value-added chemicals by U.S. Department of Energy and also been identified as a promising sustainable material for the synthesis of other important chemicals. It can be synthesized via a process known as hydrolysis. Its synthetic hydrolysis can be carried out employing some kinds of saccharides (e.g. glucose), the major constituent unit composed in cellulose. Its production from cellulose, the most abundant and renewable natural resource on earth is advantageous; however, recalcitrance nature that holds components together in biomass prevents the easy accessibility to the utilization of cellulose therefore as a result of this, considerable pretreatment is required. This review elucidates the details of levulinic acid (LA) synthesis starting from γ -valerolactone (GVL), its derivatives and their useful applications in various fields, most especially in the biorefinery. We concentrate on derivatives such as methyltetrahydrofuran (MTHF) as gasoline additives, ethyl levulinate as a diesel additive, succinic acid, 2-Butanol (2-BO) and 2-pentanol (2-PO) mainly synthesized from Levulinic acid (LA).

Likewise, catalysts and Catalytic system for the synthesis were also reviewed. Finally, Baeyer-Villiger (BV) oxidation of levulinates into succinates was also given brief consideration in this mini review.

Keywords: Lignocellulose; levulinic acid (LA); Gamma-valerolactone (GVL); Baeyer-Villiger (BV) oxidation; methyltetrahydrofuran (MTHF); hydrogenation

Abbreviations: Acac: Acetylacetonate; LA: Levulinic acid; LE: Levulinic esters; MTHF: Methyltetrahydrofuran; HMF: Hydroxymethylfurfural; 2-BO: 2-Butanol; 2-PO: 2-Pentanol; GVL: γ -valerolactone; BTU: British thermal unit (Btu); PDO: 1,4-pentadiol; TPPMS: Monosulfonated Triphenylphosphine; TPPTS: Trisodium 3,3',3'-phosphinetriyltribenzenesulfonate; BVO: Baeyer-Villiger Oxidation

1. Introduction

The present energy system is unsustainable as a result of equity issues as well as environmental, economic, increase in global populations and geopolitical concerns that have implications far into the future complemented by the finite and depletion of petroleum based resources on earth. At present, fossil fuels still remain key player contributing greater percent to energy supply of the entire world [1]. Recent reports have it that, greenhouse gas emission that emerges from the use of petroleum-based resources is one of the alarming challenges confronting the human society [2]. The world energy demand is predicted to rise up to 48% by the year 2040, as reported by the U.S. Department of energy, representing a projection from 549 to 815 quadrillion Btu consumption [3]. Petroleum-based resources are undoubtedly the culprit of the world's major energy demand since the mid-20th century; this has further increased in recent years, owing to the meteoric growth in technology. Also, the nonrenewable nature of fossil fuels, and the environmental concern associated with its use have prompt the search for eco-friendly and sustainable alternative energy sources, in order to shift from the sole dependence on fossils resources, and meet the global energy demand alongside, without conflicting the ecosystem. A promising substitute that can reduce the high dependence on fossil fuel is the use of biomass, a renewable organic and abundant resources, to ensure a sustainable future [4]. Lignocellulose, the most abundant form of biomass, is composed of three primary components; cellulose (40–50 wt%), hemicellulose (25–30 wt%), and lignin (15–30 wt%), a phenolic polymer. Woody, herbaceous plants, and other crop residues like sugarcane bagasse, wheat straw, are suitable lignocellulosic feedstocks applied in the biorefinery process, to proffer valuable applications that can be derived from the petroleum-based source. Approximately, 170 billion metric tons of lignocellulosics production are made available yearly, a little amount of this has been used for chemicals and energy syntheses, due to the complexity of lignocellulosic biomass, it is relatively not viable to chemical transformation [5]. But, due to the great advantages associated with the utilization of biomass, serious scientific research attention has been put in this field by modern chemists. There are various available methods, through which biomass can be converted to different viable products. The choice of method is dependent on the nature and application of the end product desired. Power/heat, transport fuels, and fine chemicals (or their precursors) are the three

major derivable products from biomass (Figure 1). The utilization of biomass products is possible in other to reduce the alarming consumption of non-renewable based sources, and to combat the deteriorating effects of fossil consumption on the environment. Biomass is considered as a potential substitute, in order to reduce the societal dependence on fossil resources. The use of biomass as a fuel produces an insignificant amount of CO₂, which is equivalent to the amount consumed by plants during photosynthesis, a natural process during which plants that make up the biomass reconverts CO₂ to carbohydrates. Hence, if biomass is continuously used as the resources for subsequent conversion, there will be relative, no increment in the amount of natural CO₂ in the atmosphere, this uncommon attribute of biomass is termed ‘carbon neutrality’. Biomass can be seen as a suitable replacement for fossil resources with the benefits of reducing CO₂ emission. Hence, research on the utilization of biomass very necessary, and have attracted most researchers around the globe, due to rising environmental concern. In addition, comparison with fossil fuels, which are one-way in CO₂ emissions, biomass is applicable for its short span of growth, which makes it crucial in a recycling-based society [3,4].

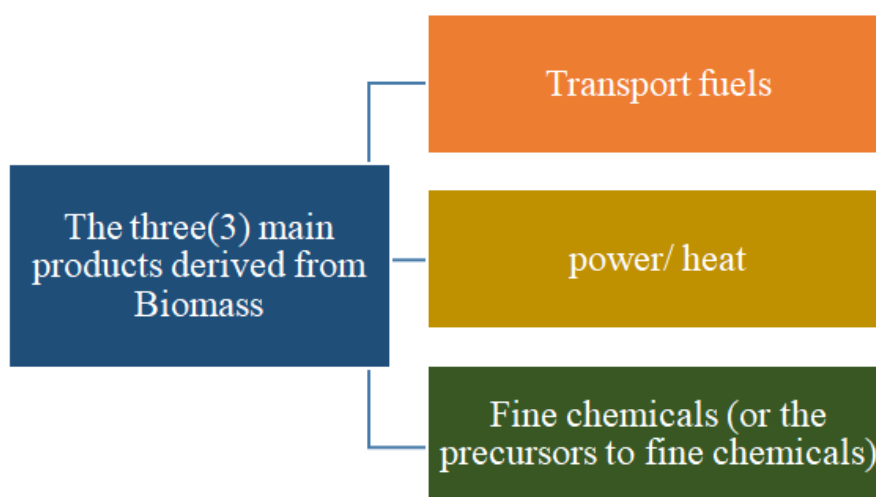


Figure 1. Major products from Biomass.

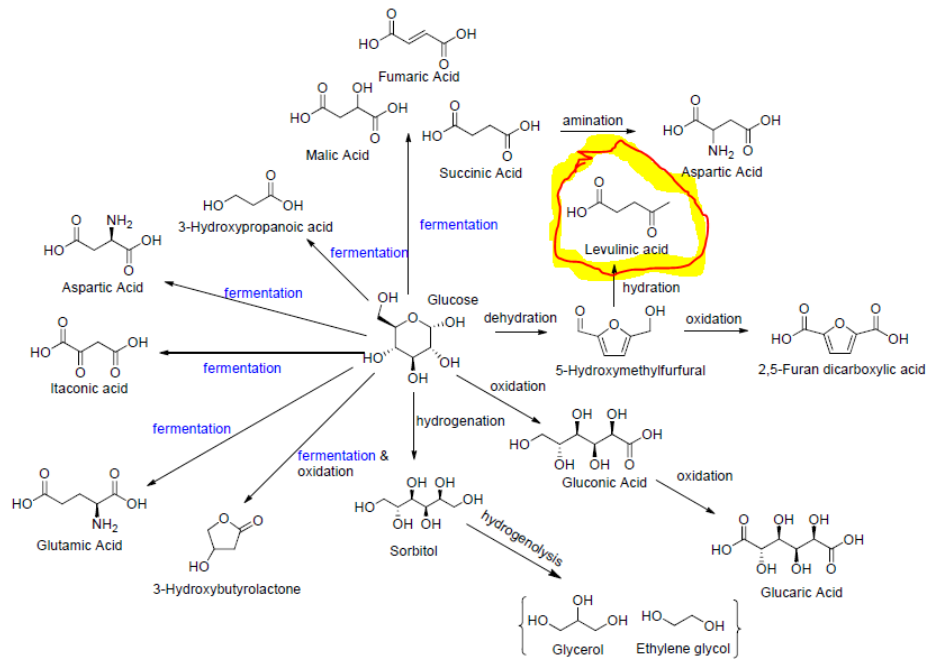
2. Synthesis of platform molecules from biomass: cellulose

A wide range of chemicals has their precursor compounds (building blocks) made from biomass. There is great possibility associated with the synthesis of these chemicals using biomass, as compared to those available from petroleum-based resources. Furthermore, the synthesis of high-value chemicals can be achieved through the modification of certain species of plants via biotechnology [6]. The difference between the building blocks derived from petroleum and bio-obtained feedstocks is that bio-compounds are highly oxygenated. This offers an added advantage in the use of biomass, because, many end products of petroleum-based industry are oxygenated, but the economic feasibility of various oxygenation process for hydrocarbon is low. Besides, the reagents required for the few available methods are considered toxic, like lead (Pb), chromium (Cr), etc. which causes serious hazard when disposed into the environment [7]. However, highly functionalized bio-derived feedstock is required to be converted to higher energy density-based

molecules, or easily applicable precursors that are obtainable synthetically [8–10]. ‘Building block chemicals’ from biomass are referred to as ‘platform molecules’, they contain several functional groups that could be processed into various useful molecules/value-added products, which could arrest the market in the nearest future, provided other synthetic chemicals can be derived from it. A suitable platform must have a source that is economically stable in other for its derivatives to be cheap. The processes employed in the synthesis of fuels and chemicals mostly involves the complete cracking process, which entails the breakdown of complex petrochemical molecules before the subsequent build up to desired products, this happens with syngas production during the synthesis of alkanes and alcohols. This same process is employed in the conversion of biomass to syngas. The transformation of biomass into chemical building blocks which retains features (like electrophilic and nucleophilic properties) can follow an alternative and exhaustive productive process; this could be employed in subsequent transformations, such that the desired end products are achieved. Such platform chemicals can be processed through chemical or biological methods. Lignocellulosic biomass consists about 40–50% of cellulose, this value is relatively high, coupled with the fact that cellulose is not edible. Hence, its usage does not compete with food supply. Designing processes that can effectively utilize biomass to produce useful chemicals are of economic importance. Besides all other chemicals that are achievable from biomass transformations, ‘levulinic acid’ is of great importance, hence, the focus of this review. This review is focused on the synthesis of levulinic acid (LA) from γ -valerolactone (GVL), its derivatives and their applications in the various field, with sole attention on the biorefinery. Much attention will be on derivatives like methyltetrahydrofuran (MTHF), a gasoline additive, ethyl levulinate as a diesel additive, succinic acid, 2-Butanol (2-BO) and 2-pentanol (2-PO) which are mainly synthesized from levulinic acid (LA). Also, catalysts and catalytic systems for the process would be treated, then, Baeyer-Villiger (BV) oxidation of levulinates will be briefly considered.

3. Levulinic acid (LA)

The National Renewable Energy Laboratory of the U.S. Department of Energy revealed 12 chemicals in 2004, which is obtainable through biomass transformation. The list of top value-added chemicals which are practically obtainable during biomass transformation is shown in Scheme 1. Different compounds can be derived through the chemo-catalysis of glucose, the product derived is dependent on the catalyst selected and reaction conditions. Gluconic acid is gotten via oxidation, sorbitol through hydrogenation, fructose through isomerization, and 5-hydroxymethylfurfural via dehydration, this can be further transformed into levulinic acid (LA) and formic acid (FA) by hydrolysis. Glucose can be alternatively subjected to bio-catalysis directly, and be enzymatically transformed into other valuable products, e.g., itaconic acid, succinic acid, and 3-hydroxypropionic acid, etc. Scheme 1 [8]. The chemicals which are potentially suitable precursors for finished products enable biomass to be a crucial resource, which could be applied in the synthesis of chemical products that are currently obtainable from petroleum-based source today. Some years ago, the Biofine Corporation designed a technique for the conversion of cellulose into levulinic acid (4-oxopentanoic acid), a potential ‘platform chemical’. Levulinic acid can be derived from the oxidation of simple sugars (glucose or fructose) [9,10].



Scheme 1. Top value-added chemicals from glucose identified by the U.S. Department of Energy [8].

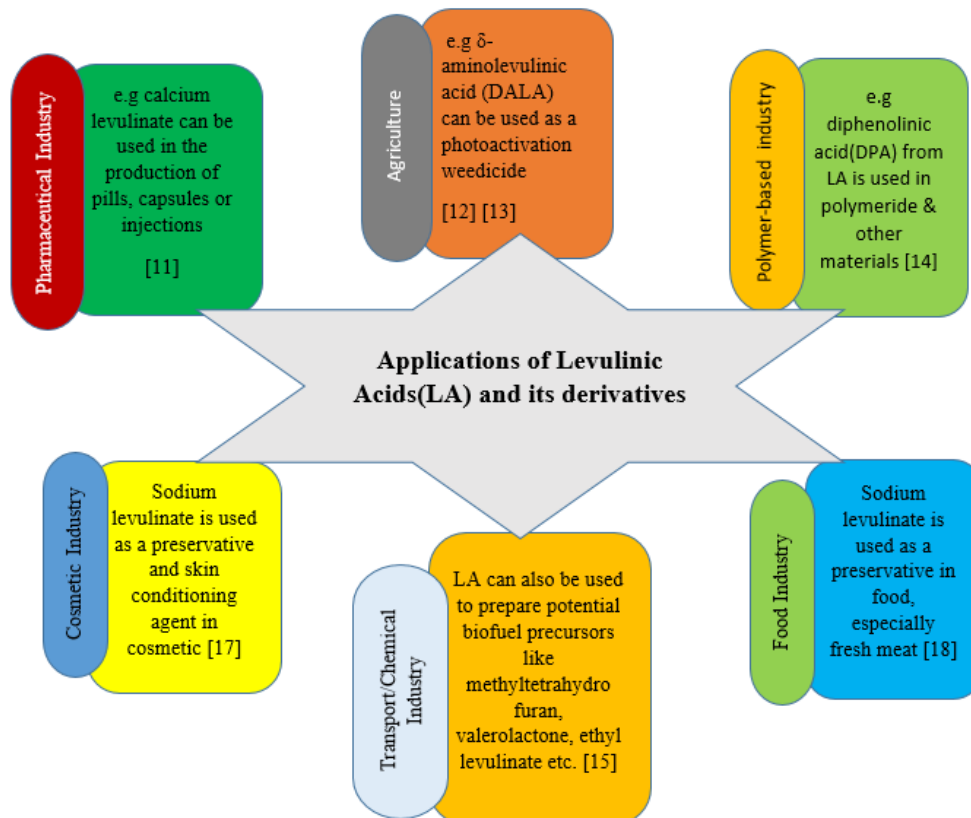
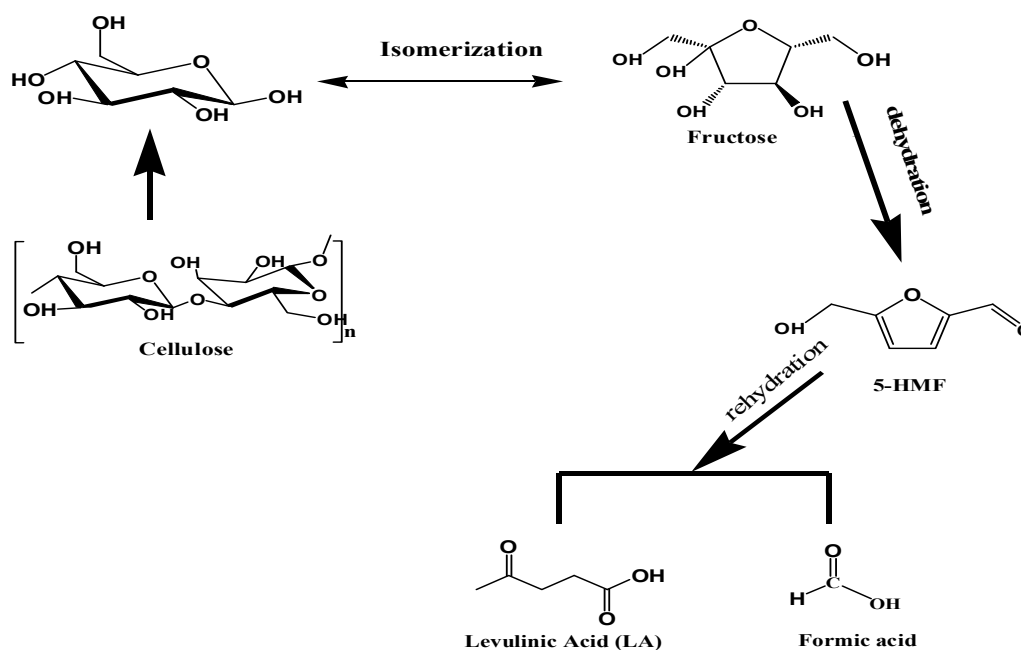
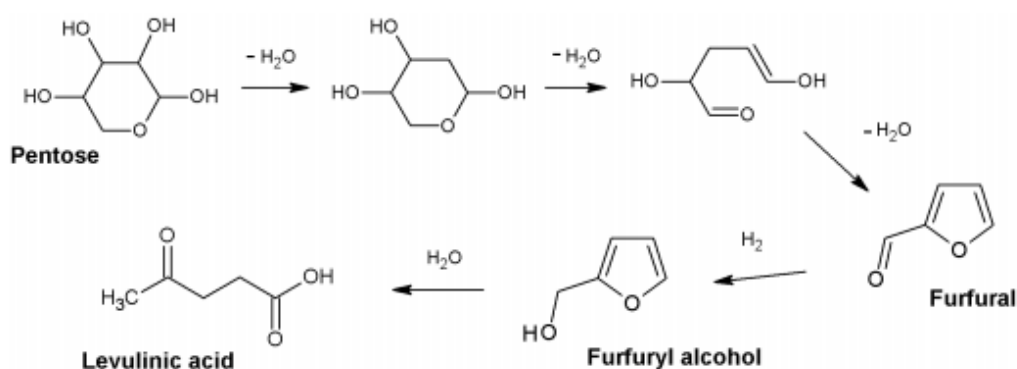


Figure 2. Applications of Levulinic acids(LA) and its derivatives, corresponding references in the bracket.

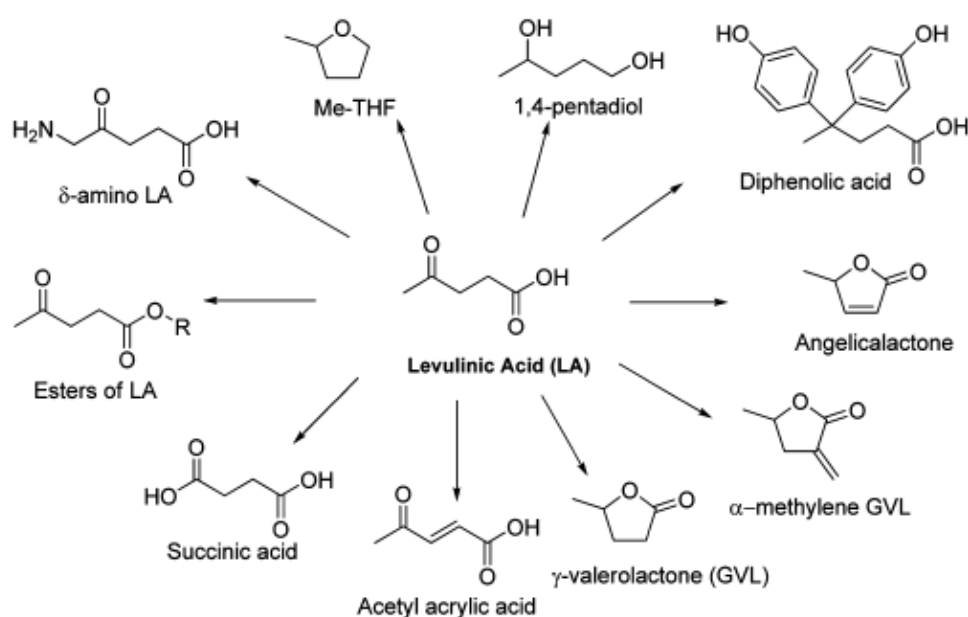
Levulinic acid (LA) has several important applications. Levulinic esters (LE), which is obtained through esterification of LA is applicable as oxygenated fuel. Hydrogenation of LA gives methyltetrahydrofuran (MTHF), which is an additive in gasoline. 2-Methyltetrahydrofuran (2-MTHF), which is an alternative fuel, also finds a great application as the electrolyte for lithium rechargeable batteries, 2-MTHF is derived from levulinic acid. γ -valerolactone and ethyl levulinate are other valuable chemicals that are derived from levulinic acid [13]. There are five carbon atoms in the molecule structure of levulinic acid (LA). 1 mol of levulinic acid can be produced from 1 mol of hexose stoichiometrically. Cellulose, which is one of the major components of biomass passes through degradation, on the course of transformation to levulinic acid (LA). The degradation pathway from cellulose to LA is illustrated in Scheme 2. Firstly, cellulose is hydrolyzed to glucose, and then glucose undergoes isomerization to give fructose, fructose is then dehydrated to give 5-hydroxymethylfurfural (HMF), an intermediate product. Levulinic acid (LA) is then obtained through hydrolysis of HMF in an acidic condition, with the formation of formic acid alongside. Formic acid is applicable in the synthesis of formalin, plasticizers, pharmaceuticals, textiles, and rubber. Formic acid is currently a low-priced commodity, but there are high potentials of its utilization in fuel cells, and also as a starting material for hydrogen synthesis in future. Scheme 3 illustrates the reaction flow for the conversion of pentose sugar to furfural and levulinic acid (LA). LA is potentially a beneficial platform chemical in the biorefinery today [13].



Scheme 2. Shows the pathway for the degradation of cellulose to levulinic acid.



Scheme 3. Reaction pathway for the conversion of pentose sugars to furfural and levulinic acid.



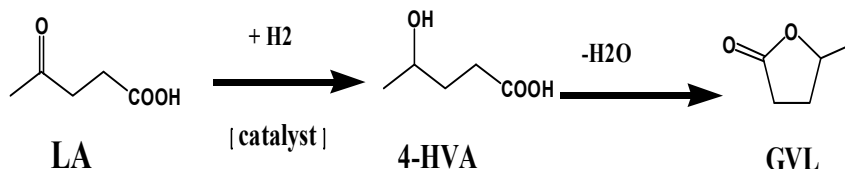
Scheme 4. Derivatives of Levulinic Acid (LA) [8].

Levulinic acid (LA) reacts with variety of compounds to give products that are applicable in pharmaceutical, biological active material, corrosion inhibitors, adsorbents, personal care products, batteries, coatings, polymers, anti-freeze agents, electronics, photography, plasticizers, flavoring agents, antifouling compounds, fuels, herbicides and solvents [15–17]. Some possible routes, through which LA can be transformed are summarized in Scheme 4. Figure 2 upshots the applications of LA and its derivatives.

4. Synthesis of GVL from LA: evaluation of catalysts and catalytic system

Gamma-valerolactone (GVL) has been predicted as a major sustainable liquid which could be useful in the production of renewable hydrocarbon, which is applied to both homogeneous and heterogeneous catalytic systems. GVL, which is a major precursor in a biorefinery, can be obtained from LA through selective transformation. Gamma-valerolactone (GVL) can be synthesized from

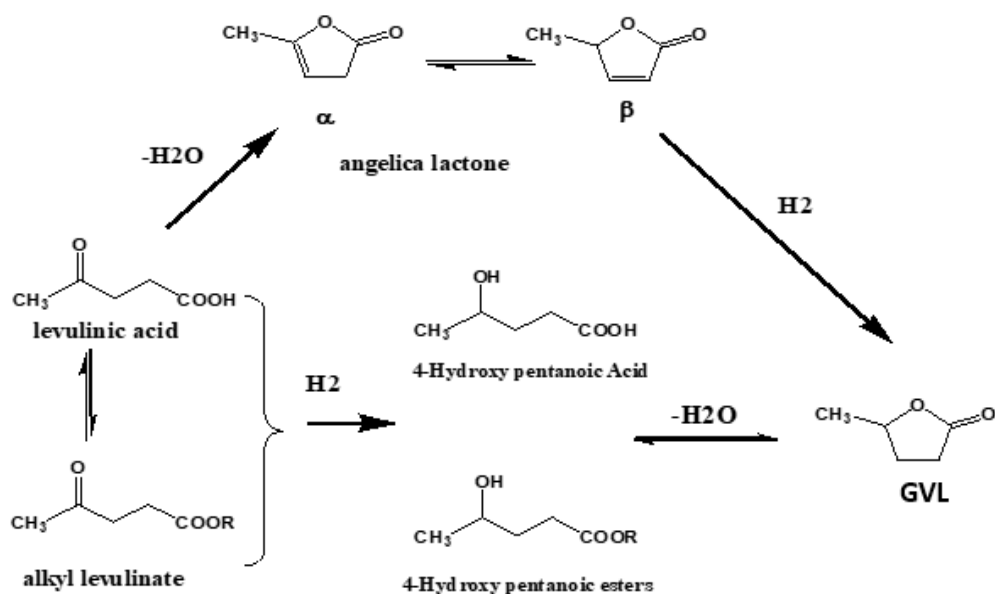
LA by two main methods. The first involves the hydrogenation of LA or its esters to gamma-hydroxyvaleric acid (or ester), which through intramolecular esterification yields GVL as the product [19,20]. Another route through which GVL can be obtained from LA is the catalytic hydrogenation through 4-hydroxyvaleric acid (4-HVA) as shown in Scheme 5. GVL, which is a platform molecule with sustainable qualities, suitable for the synthesis of fuel, production of solvent, and find useful application as a feedstock in alkenes and transportation fuels production [21–23].



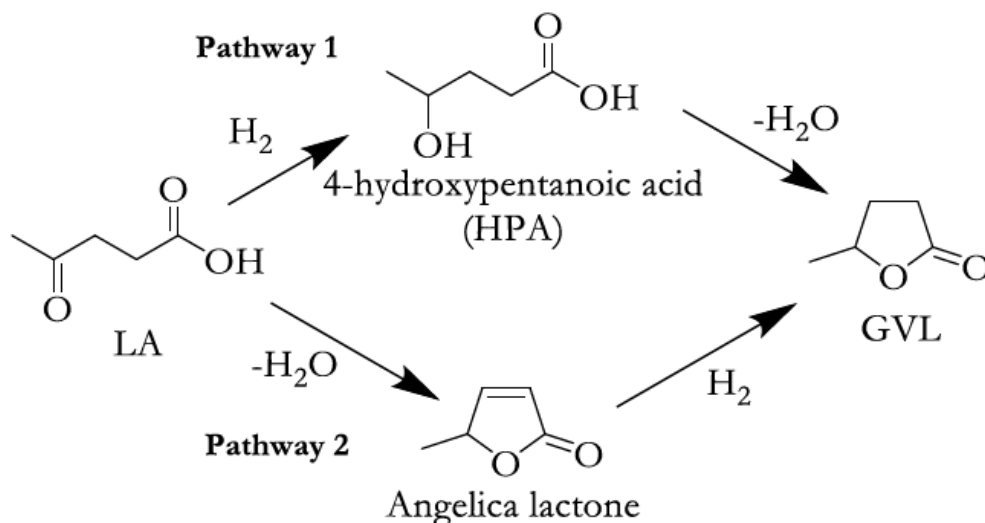
Scheme 5. Synthesis of GVL from LA.

The reduction which is carried out in a heterogeneous environment leading to the formation of GVL is usually selective; it occurs in an interesting manner as yield ranges from good to excellent status [24]. A complete conversion of LA with > 97% GVL selectivity, using 5% Ru/SiO₂ or Ru/C catalyst has been reported [25]. A ruthenium-based homogeneous catalytic system where formic acid of molecular hydrogen was applied as the hydrogen source have shown a high level of activity [26–28]. Joó et al. recorded the first application of water-soluble homogeneous HRuCl(TPPMS)₃ for the reduction of the oxo- and keto- acids several years ago before other reports [29]. Though, the turnover frequency obtained (TOF = 13 h⁻¹) at pH = 1, depicts a very low catalytic activity. According to reports, GVL can be obtained from LA with Ru/TPPTS catalyst in an aqueous solution with 95% good yield of GVL [30]. The application of TPPTS modified Ru catalyst in biphasic hydrogenation of LA in CH₂Cl₂/H₂O was reported by Heeres et al., an excellent yield was achieved under a relatively mild condition [31]. The activity of Ruthenium catalyst can be step up by using better electron-donating phosphine ligands such as PBu₃. Ru/1,1,1-tris-(diphenylphosphinomethyl) ethane (Ru/TriPhos), chlorine free active catalysts have been confirmed for the reduction of LA to give GVL, 1,4-pentanediol, and methyl-tetrahydrofurans (MTHF) [32,33]. For environmental conservation purpose, it is necessary to note that oxygenates, like 2-Metetrahydrofuran easily lead to the formation of peroxide. The fact that peroxides are threats to the environment should be put into consideration [34]. Despite the beneficial applications of alkylphosphines in transition metal catalysis, in terms of high activity and stability, they have shortcomings in their toxicity, unpleasant smell, and are usually oxygen and water sensitive. Introduction of ionic moieties such as—SO₃Na into ligand structure can lower their vapor pressure, and as well accelerate their solubility and stability in polar solutions. Tukacs et al. investigated the electronic and steric characterization of novel electron-donating sulfonated phosphines, and also their application in the Ru catalyzed reduction of LA including its IR and NMR studies. In their work, they claimed that γ -valerolactone could be derived from the levulinic acid gotten from biomass, via reduction, in the presence of a catalyst. It was reported that the catalyst was generated from Ru(Acac)₃ and various sulfonated phosphine RnP(C₆H₄-m-SO₃Na)_{3-n} (n = 1,2; R = Me, Pr, iPr, nBu, Cp) ligands in a reaction environment devoid of solvent and promoters. The introduction of a sulfonato group into ligand structure does not significantly affect the electronic and steric properties, this was established

through the characterization of sulfonated and non-sulfonated ligands. It was confirmed that the activity of electron-donating sulfonated phosphine modified catalysts hugely surpassed the activity of Ru/TPPTS system attaining turnover number up to 6370 and maintained this activity after complete transformation of LA to GVL. They claimed that there was no sign of formation of by-product during the conversion in the IR and NMR studies. The catalyst recovery was successfully demonstrated. The volatile compound was removed at the end of the process through a vacuum, while the catalyst compounds left behind was dissolved in LA, and this showed similar activities like before distillation. A second method is acid-catalyzed dehydration of levulinic acid (LA) to angelica lactone, followed by hydrogenation (Scheme 6), though, GVL yield is lower since acidic media promote coke formation and angelica lactone polymerization [35]. Scheme 7 summarizes the pathways of LA hydrogenation to GVL. (1) hydrogenation followed by dehydration; (2) dehydration followed by hydrogenation.



Scheme 6. Routes for the production of gamma-valerolactone (GVL) (modified).



Scheme 7. Mechanistic pathways of LA hydrogenation to GVL. (1) hydrogenation followed by dehydration; (2) dehydration followed by hydrogenation [35].

A recent study by Piskun et al. shows the presence of HPA during the hydrogenation reaction and not angelica lactone, which would also suggest the dominance of pathway 1 [36]. However, there is no absolute consensus, with recent studies claiming that the reaction proceeds *via* pathway 2 [37,38]. γ -Valerolactone (GVL) is suitable as a promising solvent considering its non-toxic nature and as well find a useful application for the synthesis of a fuel additive or fuel precursor as a result of its functionality or reactivity characteristic feature [39]. Putting its sustainability and renewability to keen consideration, GVL is suitable to provide new avenues where petroleum-based products and fuels could be substituted with biomass-based resources. Alonso DM et al. in their critical review highlighted four major key opportunities for the synthesis of GVL from biomass-derived sources. As described in their work the opportunities we set to derive from production of GVL biomass are as follows: (1) Purification of LA from mineral acids. The issues raised by the use of mineral acids could be addressed by replacing them with heterogeneous catalysts for the production of levulinic acid (LA). This is considered as the most suitable approach means for solving the mineral acids related issues; (2) Choosing stable catalysts in the presence of mineral acids. Recently remarkable development has been recorded as far as this aspect is concerned, using real biomass derived feed is necessary for catalyst stability; (3) Alternative catalysts to noble metal catalysts. The usage of non-precious metal catalysts or solid acid catalysts in the recent work with GVL as a solvent could as well open way for non-precious metals to be used in the hydrogenation process of LA. This would allow the overall system to be more economically feasible; (4) Techno economic analyses of different pathways will be important factor to address the relative challenges attached (e.g., product yields, solvent selection, catalyst metal, etc.) in these GVL processes [39]. Using homogeneous catalyst in the synthesis of levulinic acid poses a major bottleneck of isolation and separation of the product from the aqueous phase containing the mineral acids. In view of this organic solvent extraction is needed for the isolation of LA from the product stream, for instance methyl isobutyl ketone (MIBK) could be a suitable candidate in this regard [40]. The properties of the GVL make it an excellent solvent as it is able to solubilize lignocellulosic biomass and achieve

high yields of LA using solid catalysts. Dumesic et al. in their recent works give interesting account of GVL, where novel options to valorize biomass in GVL/water/H₂SO₄ medium were highlighted as follows:

Synthesis of monomeric carbohydrates using corn stover fractionation in a ternary mixture of GVL, water and another organic solvent, (benzene, toluene, phenol, etc.) [41].

Synthesis of maleic acid via oxidation of furfural synthesized from corncobs fractionation in aqueous GVL solution [42].

High-yield production of furfural by dehydration of xylose obtained from maple wood fractionation in aqueous GVL solution [43].

Recently a lot of researchers have focused their attention on the continuous-flow upgrading of levulinic acid to GVL. Considering the recent research work carried out by Moreno-Marrodan and Barbaro where a sulfonated resin embedded with Ru nanoparticles was developed as a bifunctional heterogeneous catalyst for the hydrogen-mediated reduction of levulinic acid (LA) to GVL. About 90–95% excellent conversion and quantitative selectivity were recorded at mild reaction conditions; 70 °C reaction temperature and 5 bar pressure with feedstock of levulinic acid and a stream of H₂ to the reactor. The activity of catalyst was intact for the period of 32 h reaction operation time [44]. Palladium and silver nanoparticles supported on a graphitic carbon nitride surface was employed by Tadele et al. in their recent work for the production of GVL from levulinic acid (LA) where formic acid was adopted as the H donor. With the reaction conditions of 50 min and 70 °C reaction time and temperature respectively the catalyst in suspension nature was pumped in a feedstock solution of levulinic acid (LA) and formic acid leading to formation of a quantitative yield of GVL in a coil reactor [45]. Gerardy et al. recently reported a cascade process where a single bifunctional Ni-K/HZSM-5 catalyst was applied for the conversion of levulinic acid (LA) directly into a mixture of valeric acid and ethyl valerate. In their work a three-step process for the production of valeric biofuels from levulinic acid was reported including hydrogenation to γ -valerolactone (GVL), hydrogenation of GVL to valeric acid, and a final esterification to give alkyl valerates [46].

5. Levulinic acid (LA): synthesis of 2-butanol (2-BO) and 2-pentanol (2-PO) from LA

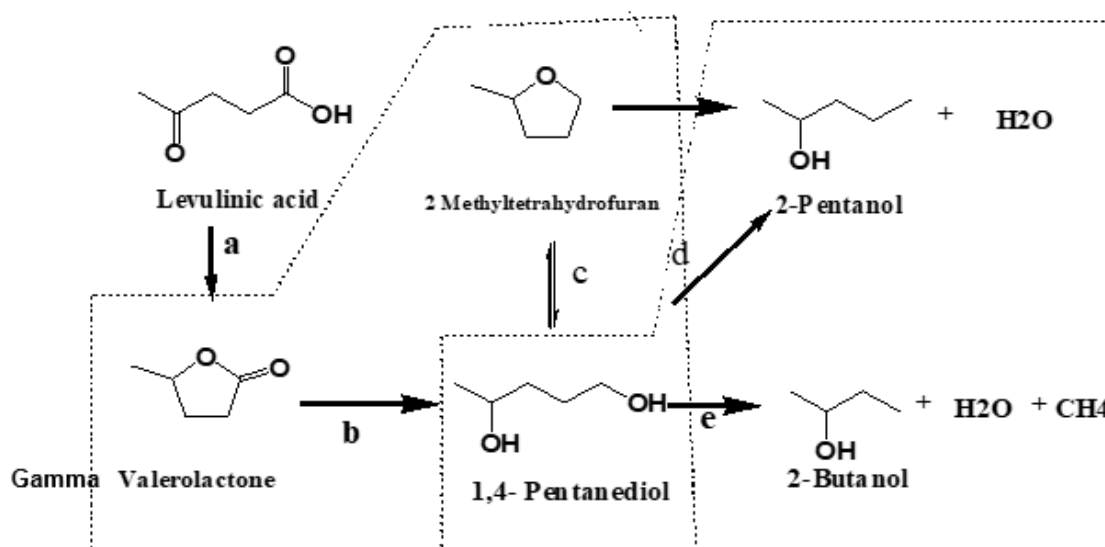
2-Butanol and 2-pentanol are monohydric alcohols that can be derived from LA in the pilot scale production. Levulinic acid (LA), an important platform chemical gotten from lignocellulosic biomass, has the potentials of being transformed to other value-added chemicals. 2-BO/2-PO are formed by the removal of the extra oxygen atoms present in the LA molecule. 2-BO/2-PO are tenable to transformation into fuel, fuel additives and solvents [47–49]. Scheme 8 shows the overall reaction that leads LA to the production of 2-BO and 2-PO.

Step-a: LA is firstly hydrogenated, then subjected to cyclization to form γ -valerolactone (GVL) [50,51].

Step-b, c: GVL is transformed into 1,4-pentadiol (PDO) and 2-Methyltetrahydrofuran (MTHF) via a ring opening and dehydration reactions, respectively. PDO and MTHF can be reconverted through dehydration or hydrolysis reactions [52,53].

Step-d, e: A two parallel pathways is unleashed on PDO to cause a C-C bond scission, leading to the formation of 2-BO, and C-O bond scission to produce 2-PO. 2-PO is formed on the hydrogenation of MTHF [54,55]. Due to the multiple role that the catalyst employed in LA transformation ought to play, its highly selective, considering the multiple steps involved in lactone activation, ether, and C-C/C-O bonds. The catalyst directive role on the reaction thus expands the selectivity of PDO, 2-BO,

and 2-PO. Cao et al. reported the transformation of GVL to PDO at 200 °C and 6 MPa initial pressure, using Cu/ZrO₂ as a catalyst, in their work. Kaneda worked with Pt-Mo catalyst, this increased the selectivity of LA hydrogenation with 93% yield of PDO under a milder situation of 130 °C and 3 MPa, in comparison with the earlier work by Cao et al. [56]. Palkovits et al. reported the hydrogenation of LA using Ru/C catalyst, it gave a 75% total yield, the best yield so far recorded for 2-BO & 2-PO with such catalyst. Though the process was carried out in a severe condition of 190 °C and 10 MPa H₂ pressure; hence a general limitation on the process [57]. A yield of 57% of 2-BO & 2-PO was obtained by Arias, using Ru/C catalyst for the transformation of MTHF (an LA hydrogenation intermediate) at a temperature of 250 °C and 4 MPa initial pressure [58]. Rh-MoOx/SiO₂ catalyst was employed by Li et al., in the hydrogenation of LA at 80 °C and 6 MPa (a mild condition), yet the achieved selectivity of 1-pentanol and 2-PO was only 15.8% [59]. We can conclude from the results obtained from previous researches, that elevated temperature and high H₂ pressure are indispensable conditions for these supported metal catalysts in order to promote 2-BO & 2-PO yields.



Scheme 8. Analysis of reaction network for LA hydrogenation [60].

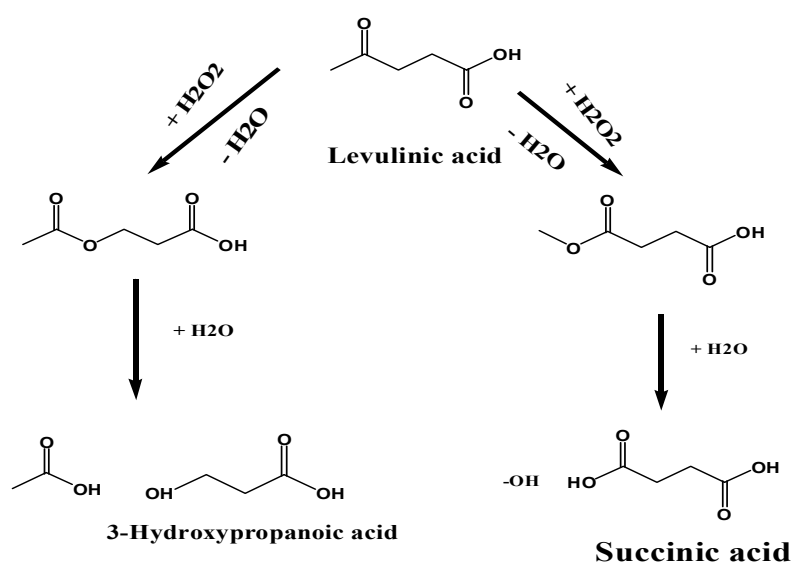
Lircus et al. in their recent work, reported on the use of nanoporous metals for the hydrogenation of LA, nanoporous ruthenium (NP-Ru) displayed good catalytic performance for the synthesis of alcohols. The overall yield of 2-butanol and 2-pentanol was 78.8%, and the yield of 1,4-pentanediol was recorded to be 74.6%, these were obtained at a reaction temperature of 140 °C and 100 °C respectively, where water is the solvent [60]. Nanoporous metals are phenomena materials which have high surface-area to volume ratio, and a large proportion of low coordinated surface-active sites. These metals have exhibited excellent catalytic performance in hydrogenation, dehydrogenation and dehydration reactions, even under very mild conditions [61]. They initially studied several Ru-based catalysts using the same conditions for the hydrogenation of LA. 100% conversion of LA was obviously reported using these catalysts, though a different selectivity was observed. γ -valerolactone is the main product derived with powder Ru, Ru/C, and Ru/Al₂O₃ catalyst;

it was still 2-BO & 2-PO. The disparity shows that NP-Ru possess more affinity for the lactone group of GVL, and hence activates better than other Ru catalysts. Several other nanoporous metals (e.g., Ni, Fe, Co, Cu) catalysts were investigated, in order to verify the major desired product(s) formed during the hydrogenation of LA under same conditions, GVL was still the major product obtained, with little amount of 2-BO and 2-PO followed by observation of an accompanied leaching of catalyst [62,63]. Velisoju et al. in their recent work gave account of single step production of pentanoic acid (PA) from levulinic acid (LA) employed Ni-W/SiO₂, Ni-W/Al₂O₃, Ni/HZSM-5 and Ni-W/H-ZSM-5 catalysts at 270 °C reaction temperature. Among the investigated catalysts Ni-W/H-ZSM-5 demonstrated high levulinic acid (LA) conversion and pentanoic acid (PA) selectivity compared to other catalysts. This higher PA formation rate over Ni-W/H-ZSM-5 was attributed to high proportion of Brønsted acid sites available on Ni-W/H-ZSM-5 surface compared to other supports. In this report they claimed that the major role of Brønsted acid sites in levulinic acid (LA) conversion to pentanoic acid (PA) was to initiate subsequent conversion of the intermediate GVL [62].

6. Synthesis of succinic acid from LA

6.1. Baeyer-Villiger (BV) oxidation of levulinates into succinates

Levulinic acid is one of the important compounds that are easily derived from cellulose; it is useful platform chemical in the chemical industry, a significant progress has been made in its production from cellulose-containing biomass [63,64]. A continuous process that converts biomass into LA has been developed by Biofine Renewables, LLC. This implies that new reaction schemes that will improve the industrial consumption of levulinic acid as raw material should be developed [65–67].



Scheme 9. A complementary reaction scheme for Baeyer-Villiger oxidation of levulinic acid with hydrogen peroxide [68].

The presence of the carbonyl group in the molecular structure of levulinic acid provides different possible reaction pathways to levulinic acid transformation. Several high valued compounds are achievable via Baeyer-Villiger (BV) oxidation of levulinic acid, as shown in Scheme 9. The BV oxidation is generally a two-step reaction, during which a peroxide is added to a C=O group through a nucleophilic attack to form a Criegee intermediate, this is succeeded by the migration of H or alkyl group that is vicinal to the C=O group and the insertion of an oxygen atom into the C-C bond or C-H bond. As displayed in Scheme 9, the insertion of oxygen between the δ -carbon and the γ -carbon is followed by hydrolysis, which gives succinic acid and methanol. In another instance, if the insertion occurs between the γ -carbon and the β -carbon, 3-acetoxypropanoic acid is produced [68]. 3-acetoxypropanoic acid is readily hydrolyzed into acetic acid and 3-hydroxypropanoic acid. The U.S. Department of Energy listed both succinic acid and 3-hydroxypropanoic acid among the top 12 platform molecules, as shown in Scheme 1. Succinic acid is employed in the production of biodegradable polymers, food additives, pharmaceuticals, and detergents, etc. It is also a starting material in the synthesis of 1,4-butanediol, gamma-butyrolactones, and tetrahydrofuran, etc. Likewise, 3-hydroxypropanoic acid is a potential monomer for the synthesis of biodegradable polymers. Acrylic acid and its derivatives could be derived from the dehydration of 3-hydroxypropanoic acid; this has contributed to its expanded market. It has also been utilized in the synthesis of other useful chemicals, like 1,3-propanediol [13,69]. But the available technologies applied in their production mainly depend on biological pathways, so, suffer from usual limitations that affect biological production, such as difficult pH control, difficulty in the separation of constituents (e.g., products from fermentation broth), deactivation of enzymes, etc. [70–74]. Hence, the chemocatalytic conversion is a better substitute to achieve these important chemicals. There are two folds of challenges for BV oxidation of levulinic acid; the first is the difficulty in designing an active catalytic system for the oxidation, since LA is a linear ketone with a carboxylic group, and its generally more challenging to convert linear ketones using BV oxidation, this is partly due to the absence of ring strain [75]. Secondly, there is the possibility of insertion of oxygen on either side of the carbonyl (C=O) group, hence, to direct the location of insertion is very necessary and reaction selectivity must be instated. Fermentation is a synthetic pathway from edible biomass (sugar) to succinic acid that has recently been commercialized [76]. Though the use of non-edible lignocellulosic biomass as raw material for valuable chemicals would be better required and preferable, and to secure low cost and sustainability [77,78]. A simple treatment of lignocellulose with Brønsted/Lewis acid catalyst in water or methanol will efficiently result in formation of levulinic acid or its methyl ester in a single step [79–81]. Hence, a simple, direct chemical transformation from levulinic acid to succinic acid is needed, because succinic acid is an important four-carbon feedstock applicable for conversions to a number of value-added products, like 1,4-butanediol, γ -butyrolactone, and 2-pyrrolidone, it also functions as a raw material in the synthesis of bio-based polymers and green, sustainable plastics [82–86]. Hence, a direct and feasible chemical method for the conversion of non-edible lignocellulose to succinic acid through levulinic acid is really desired to achieve a real industrial application. However, the existing chemical methods available for the conversion of levulinic acid to succinic acid involves critical multiple step synthetic route [87,88]. The method also required corrosive reaction conditions and toxic heavy metals in the process and a poor yield is achieved on the course of reaction [89–91]. For instance, vanadium catalyst is needed for the gas-phase oxidation of levulinic acid, an appreciable yield of succinic acid is achieved with high temperature (375 °C) [92]. Silica-coated magnetic nanoparticle-supported

Ru(III) catalyst when applied in the oxidation at a lower temperature (150 °C), however, a pressure of 10bar of O₂ is demanded. A more convenient method was reported by the use of aq. 30% H₂O₂ in acidic media, which was based on the application of an unusual terminal Baeyer-Villiger oxidation (BVO) of levulinic acid to produce succinic acid, a net yield of 62% was achieved [93–95]. A large amount of acetic acid and 3-hydroxypropionic acid are formed simultaneously through normal BVO (ca. 6:4 selectivity). This shows that the development of a kinetically controlled conversion of levulinic acid to succinic acid under a mild reaction condition is yet needed. Figure 3 shows a recent method reported by Kawasumi et al., it directly converts levulinic to succinic acid at room temperature with high yield. It involved the customization of haloform reaction to enable a one-step, regioselective oxidative demethylation of levulinic acid under a very mild condition. There was a successful investigation of the procedure of the process on the range of methyl ketones and secondary ethanol derivatives for verification [88]. Kong, X. et. al., reported the silicotungstic acid supported on commercially silica-gel sphere supports as catalyst for the esterification of levulinic acid for the first time by modification as alternative inorganic acid for the production of ethyl levulinate (EL). The synthesis was carried out with ethanol and ethyl levulinate (EL) yield obtained was 97% with 20% silicotungstic acid [96].

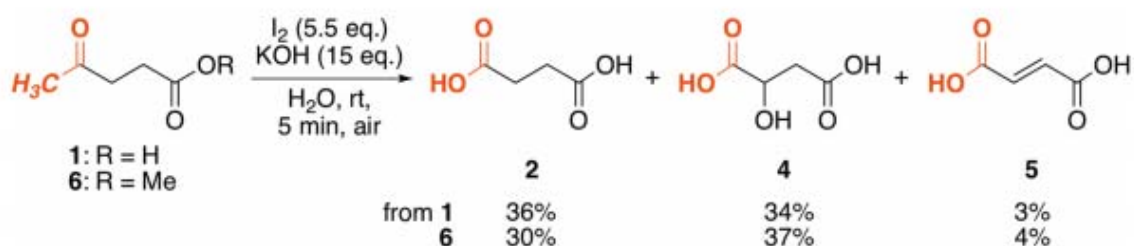


Figure 3. ‘Classical’ iodofrom reaction of 1 and 6 to afford succinic acid 2 [88].

7. Conclusion

A numerous number of research activities is currently embarked on globally exploring potential chemical transformations of biomass into value-added chemicals and fuels. Levulinic acid (LA) is a very useful building block for the production of chemicals which find useful applications like in the synthesis of additives, polymer and as a resin precursor. LA is still a promising substrate not only for biocomponents production but also for other chemicals. In the course of searching for new LA sources, wasted parts of raw materials used in food, agricultural, wood industry, etc. should be considered for full exploration in order to alleviate environmental degradation experienced due to the usage of petroleum-based products, and to make the production cost effective. This action would not only allow us to find new LA sources but also could upgrade the value of some waste and could enable new, effective utilization, bringing us more advantages. Increasing energy, fuel, chemicals demand causes the need to turn attention to renewable, unconventional, alternative raw materials, which include biomass. The biorefinery sector, who are currently receiving full support from the European Union is boosting the research strength, as this can be seen in sustainable and bio-based research programs based on the pieces of evidence around the globe. New biomass sources which are

cheap, easy in processing and have the ability for rapid renewal at any time are desired to achieve sustainable development. Looking for alternative fuel and energy sources comes down to searching for the new production methods and technological solutions and to the upgrading of existing ones for process efficiency, selectivity and economy increase, with the least possible negative impact on the environment in terms of harmful substances emission. Taking this type of actions is very important because coal, crude oil, and natural gas, are depleting resources and the existence of biomass waste, which lay on landfills and their potential is not used. Further work should be embarked on to improve catalysts and catalytic systems for the synthesis of levulinic acid (LA), to develop environmentally friendly catalysts in line with principles of ‘Green Chemistry’ in order to salvage our environment from present environmental degradation.

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Conflict of Interest

All authors declare no competing conflicts of interest.

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