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Catalytic valorisation of biomass levulinic acid into gamma valerolactone using formic acid as a H₂ donor: a critical review†

Ayman Hijazi, * Nidal Khalaf, Witold Kwapinski and J. J. Leahy*

This review sheds light on the catalytic valorisation of agroforestry biomass through levulinic acid and formic acid towards γ -valerolactone and other higher-value chemicals. γ -Valerolactone is produced by the hydrogenation of levulinic acid, which can be achieved through an internal hydrogen transfer reaction with formic acid in the presence of catalyst. By reviewing corresponding catalysts, the paper underlines the most efficient steps constituting an integrated sustainable process that eliminates the need for external H₂ sources while producing biofuels as an alternative energy source. Furthermore, the review emphasizes the role of catalysts in the hydrogenation of levulinic acid, with special focus on heterogeneous catalysts. The authors highlighted the dual role of different catalysts by comparing their activity, morphology, electronic structure, synergetic relation between support and doped species, as

Chemical and Environmental Science Department, University of Limerick, Limerick, V94 T9PX, Ireland. E-mail: j.j.leahy@ul.ie; Ayman.Hijazi@ul.ie; Tel: +353-83-3783841

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Ayman Hijazi is currently pursuing his postgraduate studies in the Bernal Institute, University of Limerick, Republic of Ireland. He is accommodated in Prof. James J. Leahy's lab, where his work focuses on developing novel heterogeneous catalysts for biomass hydrolysis processes along with developing robust analytical methods (HPLC, LC-MS, GC-MS, and GC-FID) for analysing organic acids

and furans products. Hijazi earned his BSc degree in chemical engineering from the Middle East Technical University, Turkey, in 2011. Afterwards, he held a process engineer job at a waste treatment plant, which receives municipal solid waste biomass feedstock and valorises it into biogas using anaerobic digestion technology. At the same time, he attended master's program at the American University of Beirut, where he received his MSc. in chemical engineering with a focus on developing waste to energy catalytic processes. The agenda of research was based on synthesizing heterogeneous catalysts capable of optimizing pyrolytic gas from the pyrolysis of scrap tires. In 2022, Hijazi joined Dairy Processing technology Centre (DPTC) in Ireland-Limerick where he conducts applied research on the valorisation of oil and grease from dairy industry into biofuels.



Nidal Khalaf is a PhD researcher in Chemical Engineering at the University of Limerick, Ireland. Nidal is a researcher in the REFLOW group, which is an interdisciplinary cross-sectoral European Training Network initiated by Marie Skłodowska-Curie Actions (MSCA) H2020. Nidal's main research interest revolves around the valorisation of dairy processing waste to produce valuable end products.

Nidal has earned his bachelor in Chemical Engineering from the American University of Beirut, followed by a job experience at ITCAN solutions working as a Chemical Engineering with the responsibility of designing and digitizing process flow diagrams for regional oil companies.



well as their deactivation and recyclability. Acknowledging the need for green and sustainable H₂ production, the review extends to cover the role of photo catalysis in dissociating H₂-donor solvents for reducing levulinic acid into γ -valerolactone under mild temperatures. To wrap up, the critical discussion presented enables readers to hone their knowledge about different schools and emphasizes research gaps emerging from experimental work. The review concludes with a comprehensive table summarizing the recent catalysts reported between the years 2017–2021.

1 Introduction

The reliance of the world on petroleum as a source of energy has been a subject of controversy for a while. It was previously reported that the oil peak expectations fall in 2020; however, an updated model expects that the fall of the oil age is not before 2040.¹ Moreover, the high dependence on non-renewable fossil fuels raises concerns about their fast depletion rate.^{2,3} Additionally, a continued concern is marked due to the extensive burning of fossil fuels for energy supply. This came out as a devastating blow, which is characterized by a drastic increase of CO₂ levels from 280 ppm before preindustrial to 409.5 ppm in 2017.⁴ Needless to say, finding a sustainable alternative to fossil fuels is an urgent need. Consequently, lignocellulosic biomass is pronounced as a prime candidate to be used directly as an energy source or to be valorised into added value chemicals as well as

gasoline blends that are compatible with current infrastructure.⁵ In that case, upgrading biomass generally requires a combination of O₂ removal reactions and molecular weight modifications *via* C–C coupling reactions.⁶ A wide variety of platform molecules are thereby produced, having distinctive properties and applications. To illustrate, levulinic acid (LA), functionalized by a ketone and a carbonyl group is involved in chemical industries such as resin precursors and polymers;⁷ formic acid (FA), known as methanoic acid, is an alternative direct source of energy in fuel cells;⁸ γ -valerolactone (GVL) is a famous fuel additive and an important monomer for polyester and bioplastic industries;^{7,9,10} methyltetrahydrofuran (MTHF) is also used as a gasoline blend.⁷

The derived biomass molecules are symbolized by their functional groups, which facilitate their use in producing chemicals compared to saturated alkanes.¹¹ LA is known for facilitating the production of added-value molecules. This can be achieved



Dr. Witold Kwapinski works as an Associate Professor at the University of Limerick in the Chemical Sciences Department. He is also Course Director of the IChemE-accredited Chemical & Biochemical Engineering (HonsBEng) programme. Witold is co-leader of the 'Carbolea' research group on biomass/biowaste thermochemical conversions at UL. Carbolea is a leading research group on advanced

biowaste strategies and technologies in Ireland and Europe. Work in his laboratory concentrates on pyrolysis, gasification, hydro-thermal processing of bio-waste, product upgrading and catalytic conversion. Witold has successfully supervised 14 PhD students. Currently (2021) he supervises 2 PhD students as main supervisor and 5 as co-supervisor. In Ireland he has participated in four EU projects and five national, publicly-funded projects. He is author of over ninety papers in ISI journals (h-index = 31), and more than 100 communications in international conferences. Witold graduated from Lodz Technical University and in his career worked in Germany and the UK. He also acted as a Visiting Lecturer at: Cambridge University (UK); Aalto University (Finland); American University of Beirut (Lebanon); Belarusian State Technological University; National Technical University of Ukraine. He is an Editorial Board member and occasional guest editor of three ISI journals.



J. J. Leahy is professor of process chemistry at the University of Limerick in Ireland. He has worked for 30 years on the valorisation of agri-waste as bio-fuels, fertilizers and intermediates for the production of chemicals. He currently coordinates two EU H2020 projects, (1) BIOWILL which aims to be a flagship for rural economies through a zero-waste biorefinery utilising all fractions of willow

trees for the production of high value pharmaceutically active ingredients and bio-based packaging materials, renewable energy in the form of bio-methane and natural fertilisers with potential for carbon offset; (2) REFLOW which is a collaboration between academic and industrial organisations in seven countries focused on the recycling of phosphorous from the wastewater from dairy factories and using it in CE approved fertilizers. Future common agricultural policy (CAP) recognises that it is essential to build stronger agricultural knowledge and innovation systems so that farmers and rural communities can benefit directly. EU analysis has shown that key to the success of links between the CAP Reform and the Green Deal are concrete examples such as BIOWILL and REFLOW. Nationally, JJ has forged links with major and small stakeholders with the agro-food and biofuels industry and is a principal researcher with the industry led Dairy Processing technology Centre (DPTC) based in Limerick as well as BIORBIC the Bio-economy research center Biorbic, where he leads several projects on biomass valorisation.



through its catalytic hydrogenation using secondary alcohols or FA as a H₂ donor.^{12,13} Therefore, FA is a promising biomass-derived compound that presents a potential pool of energy source of H₂.

Here in this review, we mainly focus on the valorisation of cellulosic food waste into LA and FA, as part of establishing sustainable production of higher-value chemicals and liquid fuels. The valorisation routes starting from cellulose and hemicellulose are defined in Section 2. Our approach is economic-oriented, and we seek to shed light on one-pot processes as presented in Section 3.2.1, wherein the *in situ* produced H₂ via FA decomposition provokes the hydrogenation of LA into further useful compounds, eliminating the need for an external source of H₂. The decomposition of FA into H₂ is highlighted in Section 3.1 (Table 1), while an overview of different H₂ sources is presented in Section 4, with an insight into the photocatalytic hydrogenation of LA into GVL using alcohol solvents presented in Section 4.1. To add, using H₂ for hydrogenation reactions remains a challenging step as it possesses low mass transfer in many organic solvents.¹⁴ Heterogeneous catalysts featuring a dual role of dehydrogenation/hydrogenation for driving the above process are also emphasized in Sections 3.1 and 3.2 Table 2. Moreover, insight into the nature of catalysts that have been used to date is gained by relating activity, deactivation, and recyclability to their morphological structure, as shown in Section 3.2.1.

Finally, in Section 5, we highlight recent studies that suggest promising catalysts, enabling simple down streaming and upgrading of GVL into significant compounds such as penta- noic acids (PA). Ultimately, bio-solvents are the candidate final product to which further analysis could be done to substitute petroleum-derived solvents involved in pharmaceutical industries. Nevertheless, this review provides attention on gaps and challenges to shift individual catalytic reaction steps into a process that extends from upstream treatment of lignocellu- losic biomass to higher value end products.

2 Valorisation of lignocellulosic biomass into levulinic acid and formic acid

The valorisation of lignocellulosic biomass feedstock offers a sustainable approach that combines the low-cost production

of LA-FA mixture with energy recovery, where the end products are a variety of liquid compounds including biofuels and bio solvents. It is reported in literature that LA and FA are obtained in equimolar quantities by the fermentation of cellulosic biomass.^{15–17} The aqueous solution of LA and FA is achieved by acidic hydrolysis of the cellulose.³ Moreover, LA and FA can also be formed from the hemicellulose fraction of biomass. In either case, liberating carbohydrates polymers from the rigid structure of lignin is a crucial preliminary step before any subsequent reaction.¹⁸

2.1 Route from cellulose

As mentioned previously, FA and LA are obtained in equimolar ratios by acid hydrolysis of cellulose, which constitutes 40–50% of the whole biomass. This route comprises the dehydration of hexoses (C6 sugars) to obtain 5-hydroxymethylfurfural (HMF). Further hydration of HMF results in the acid mixture (LA& FA).³ The reaction mechanism of the hydrolysis of C6 sugars, in which FA is formed along with LA, takes place in the presence of a strong acid catalyst, *e.g.*, H₂SO₄, HCl, and HNO₃.^{19–21} Heeres *et al.* made a breakthrough by using trifluoroacetic acid (TFA) as an acid catalyst to hydrolyse D-glucose and D-fructose sugars. The results signified TFA with high potential in attaining competitive yields of acids compared to using conventional H₂SO₄.²² The authors had previously examined the role of TFA as an acid catalyst for hydrolysis of D-glucose. At 180 °C, the aforementioned reaction yielded 57 mol% of LA. Furthermore, the hydrolysis of D-fructose in the presence of TFA acid catalyst under the same conditions resulted in a higher yield (70 mol%) of LA than D-glucose substrate.^{20,23} These results came in agreement with the literature²⁴ and proved that LA is produced in higher yields from D-fructose-rich feeds than from D-glucose ones. Before proceeding, it is worth noting that humins, the insoluble by-products, are formed by acid hydrolysis side reaction of the intermediate HMF. However, Heeres *et al.*²² experienced minor formation of humins due to fast conversion of D-fructose using TFA into LA along with FA.

2.2 Route from hemicellulose

LA is also produced from the hemicellulose constituent, which composes 25–35% of biomass. This route is typically performed in aqueous acidic medium. The reaction includes the formation

Table 1 Heterogeneous catalysts for FA decomposition into H₂ & CO₂

Catalyst	TOF (H ₂)	Solvent	Temp. (°C)	Ref.
Pd-P-SiO ₂	719 h ⁻¹	Formate salts HCOONa	85	36
Pd-S-SiO ₂	959 h ⁻¹	K ₂ SO ₄	85	36
Pd shell@Ag core	252 h ⁻¹	H ₂ O	50	40
Pd-Au/C	27 h ⁻¹	Formate salts HCOONa	90	45
Pd-Au/C-CeO	832 h ⁻¹	Formate salts HCOONa	102	38
Pd/γ-Al ₂ O ₃	600 h ⁻¹	NaOH, 0.1 vol% O ₂	20	52
1 wt% Pd/C	255 h ⁻¹	Gaseous phase	100	46
Au/TiO ₂	201 h ⁻¹	Gaseous phase	100	50
Au/SiO ₂	7023 h ⁻¹	Gaseous phase	100–300	51

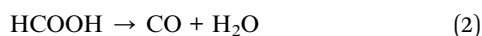
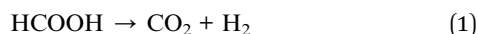
^a TOF: Turn over frequency (s⁻¹).



of furfural by the dehydration of pentoses (xylose C5 sugars), the building blocks of hemicellulose.^{3,20} Therefore, furfural is formed as an intermediate, representing an excellent platform molecule which can be converted into valuable chemicals or fuel additives blended with currently used fuels.^{25,26} Furthermore, the produced furfural is hydrogenated into furfuryl alcohol, which is readily hydrolysed under acidic medium into LA.³ However, hemicellulose might experience acid hydrolysis to obtain xylose oligomers that undergo acid hydrolysis side reaction to obtain FA and acetic acid. That being said, both carboxylic acids are obtained from xylose formulated and acetylated oligomers, respectively.²⁷ The latter reaction chemistry was proposed to take place *via* side acidic reaction inside a continuous biphasic reactor, where feedstocks are mainly xylose oligomers derived from hardwood chips biomass.⁶³ Further research can be devoted to investigating the separation of the co-produced FA to be utilized as a H₂ donor. This suggests an integrated process in which LA streamline, produced from furfural is mixed with a streamline of the separated FA for hydrogenation into further biomass platform compounds.

3 Formic acid decomposition

It is essential to understand the mechanism of FA decomposition to design a robust catalytic process for hydrogenating LA in the presence of FA as H₂ donor. FA decomposition follows two competitive routes. In detail, FA is disintegrated either by dehydrogenation (eqn (1)) or dehydration (eqn (2)).



It was reported that both pathways are thermodynamically favoured. Indeed, both reactions are easily shifted forward due to negative Gibbs free energy of $-32.9 \text{ kJ mol}^{-1}$ and $-20.7 \text{ kJ mol}^{-1}$, respectively.²⁸ The slight difference in Gibbs free energy as well as enthalpy results in competitive production of CO as a by-product, when H₂ is targeted.²⁹ Selective production of CO-free H₂ is the ultimate goal to obtain an enhanced overall catalytic performance of LA hydrogenation *via* internal H₂ transfer using FA. Therefore, designing a heterogeneous catalyst that favours dehydrogenation of HCOOH (eqn (1)) on the expense of the dehydration step (eqn (2)) is a key approach for LA/FA system to avoid unfavourable CO by-product, which leads to the poisoning of heterogeneous catalyst.^{30,31}

3.1 Formic acid decomposition into free hydrogen using heterogeneous catalysis

In this section, we herein report a variety of heterogeneous catalysis that are engaged in FA decomposition, starting with heterogeneous catalysts for aqueous FA decomposition. Afterwards, we will emphasize on heterogeneous catalysts that are involved in gas phase FA decomposition.

FA decomposition in the presence of metals, alloys, and oxides heterogeneous catalysis dates back as far as the 1950s and 1960s.³² Heterogeneous catalytic systems were developed to

seek appreciable reaction kinetics of FA decomposition while saving energy demand for the reaction. Generally speaking, noble metal heterogeneous catalysts favour dehydrogenation decomposition of FA (eqn (1)), whilst oxides and base metals catalysts are engaged in the dehydration route (eqn (2)).^{33–35} Zhao Y. *et al.* synthesized a group of immobilized catalysts by anchoring Ru and Pd metals using functionalized groups onto silica supports. Amongst, Pd-P-SiO₂ attained the highest activity of TOF of 719 h^{-1} at 85°C followed by Ru-S-SiO₂ with TOF of 344 h^{-1} . Decreasing temperature resulted in lower activity, which reached TOF of 16 h^{-1} for Pd-S-SiO₂ at 45°C . It was found that the inclusion of sulfates by using Na₂SO₄, MgSO₄, and K₂SO₄, boosted the catalytic activity to exceed 940 h^{-1} with sulphur functionalized catalysts.³⁶ These results bear Pd^(II) as an active species, which is stabilized by mercaptopropyl groups.³⁶ Nevertheless, performing FA decomposition in the presence of heterogeneous catalysts suffers from drawbacks owing to the presence of CO contamination, water vapour formation, and therefore catalyst deactivation.^{37,38} To illustrate, elevated temperature favoured decarbonylation reaction, generating CO gas despite using active Pd-Au/C core-shell catalyst.^{38,39} For this reason, Tedsree K *et al.* optimized a core-shell catalyst by the inclusion of core metal Ag into Pd shell metal to be active for FA decomposition at low temperatures. The attractive activity of TOF = 252 h^{-1} at 50°C was observed for Ag@Pd (1 : 1) core-shell catalyst. This trait is attributed to altering Pd active sites *via* direct charge transfer from Ag core metal, which thereby stimulates the bridging adsorption of FA to promote hydrogen production.⁴⁰ Further on bimetallic catalysts, the morphology is influenced by the followed preparation method. Bimetallic Pd-Au can be constructed as a mixture, clusters to clusters, random alloy, and core-shell.^{41,42} These options can be achieved through calcination. For instance, Pd is detected in the outer framework of the particle surface, resulting in a rich Pd shell on top of an Au rich core. This structure could be flipped by further calcination that leads to Pd rich core and Au rich shell morphology.⁴³ Additionally, the application of subsequent calcination processes yields further structural changes signified by three shell layers of core-shell catalyst: Pd-Au alloy as the inner core, Au as intermediate layer, and a rich Pd outer shell.⁴⁴ Haung Y. *et al.* prepared a core-shell Pd/Au@Au/C catalyst, which showed a high anti-poisoning activity *versus* CO and an attractive activity represented by 90% conversion of FA and only 30 ppm CO after 6 h at a temperature of 92°C .³⁹ Moreover, they proposed the crystallization process for making Pd/Au@Au/C system (Fig. 1).

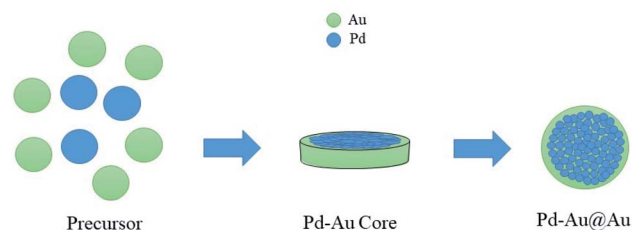
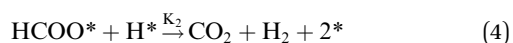


Fig. 1 Crystallization process of Pd/Au@Au/C system.³⁹



Another bimetallic catalytic system was studied by Zhou X. *et al.* in which they discovered that the highest FA dehydrogenation was attributed to Pd–Au alloy system as well as Pd–Ag alloy on a carbon support. Considering the loading ratio, reaction temperature and HCOOH/HCOONa ratio, Pd–Au/C showed the highest TOF of 27 h^{−1} followed by Pd–Ag/C with a value of 17 h^{−1} at 365 K. An attractive catalyst stability for 240 h^{−1} with only 80 ppm of CO formation is attributed to the basicity of HCOONa solution. The resulting reforming gas qualifies for PEMFC standard as it doesn't exceed 100 ppm CO.⁴⁵ The inclusion of CeO into both catalysts improved their activity further due to the formation of more oxidized Pd that can oxidize adsorbed CO. Indeed, the TON attained was 227 h^{−1} and 76 h^{−1} for Pd–Au/C–CeO and Pd–Ag/C–CeO, respectively.³⁸ The improved catalytic activity of TON of 832 h^{−1} was observed at a higher temperature of 375 K using Pd–Au/C–CeO alloy catalyst.

Bulushev *et al.* compared the activity of Pd and Au active sites over carbon and TiO₂ supports in gaseous phase FA decomposition at 373 K. The highest TOF of 255 h^{−1} was attributed to 1 wt% Pd/C followed by 10 wt% Pd/C with a TOF of 180 h^{−1}. The higher decomposition rate of FA was due to the higher dispersion of Pd nanoparticles. On the other hand, lower activities were observed for 1 wt% Au/TiO₂ and 0.8 wt% Au/C at TOFs of 57 h^{−1} and 21 h^{−1}, respectively. Despite the higher activity of Au/TiO₂ catalyst in decomposing FA, a lower selectivity of H₂ was noticed,⁴⁶ which comes in agreement with TiO₂ support engaged in favouring FA decomposition through decarbonylation route (eqn (1)).^{47,48} It was reported elsewhere in literature that Au comprises low areal rates in comparison with other noble metals, which is represented by first-order kinetic of FA decomposition,⁴⁹ whereas well-dispersed Au is capable of decomposing FA.⁵⁰ It is worthy to note that Pd particles were inhibited by CO which exhibits strong adsorption. Whereas, Au showed weaker CO adsorption and improved WGS reaction, producing additional H₂.⁴⁶ Further interesting work was done on investigating the role of Au species in FA decomposition. The thermal treatment of Au/Al₂O₃ caused Au cluster size to increase (sintering effect) accompanied by a drastic decrease in HCOOH decomposition rate. Consequently, FA dissociation is favoured by well spread Au species only. Despite similar cluster size of Au/TiO₂ and Au/Al₂O₃ of 3–4 nm, the TOF for HCOOH decomposition were 201 mol h^{−1} g^{−1} and 7 mol h^{−1} g^{−1}, respectively. In this context, Au is less dispersive over TiO₂ than on Al₂O₃ support. It is worth noting that none of the used catalysts; Au/TiO₂, Au/Al₂O₃, and Pt/Al₂O₃ yielded CO and H₂O, indicating the absence of dehydration of HCOOH and reverse WGS reaction.⁵⁰ On another end, the authors proposed that the irreversible production of H₂ is achieved by the adsorbed H produced by the preceding step as shown below.⁵⁰



Eqn (3) and (4) further studies investigated the catalytic performance of Au species over different oxide supports. Gazsi

A. *et al.* found that Au/SiO₂, Au/CeO₂, and Au/Norit favoured FA decomposition through dehydrogenation route (eqn (1)). Whilst dehydration of FA (eqn (2)) was dominated in the presence of Au/Al₂O₃, Au/ZSM-5, and Au/TiO₂. The most active catalyst regarding FA conversion was Au/SiO₂ with a TOF 7023 h^{−1} of 100% H₂ selectivity between 373 K and 523 K. They also reported that the FA rate of decomposition is not dependent on Au particle size.⁵¹ However, their results came in contrary to conclusions about the Au cluster size effect investigated by Manuel Ojeda and Enrique Iglesia as mentioned previously.⁵⁰

Regarding reaction kinetics, FA decomposition follows a zero-order pattern over Au/SiO₂, which depends on formate intermediates instead of HCOOH substrate initial quantities.⁵¹ This comes in harmony with the suggested kinetics by Ojeda M. *et al.* who also recognized that changing HCOOH partial pressure did not affect FA decomposition.⁵⁰ In both studies, the proposed mechanisms involve the cleavage of C–H bond of formate, which falls in the rate-determining step.^{50,51} Another contradiction arises regarding H₂ selectivity. A very low yield of H₂ (TOF_{H₂} = 18 h^{−1}) was observed for Au/Al₂O₃ at 473 K,⁵¹ whereas much higher H₂ was produced with only 10 ppm of CO traces detected in the presence of Au/Al₂O₃ at ambient temperatures.⁵⁰ In both cases, Au inhibited catalyst deactivation due to weak CO–Au_x complex formation.

A very recent breakthrough was achieved by Xu P. *et al.* on removal of adsorbed CO over Pd/γ-Al₂O₃ by adding traces of oxygen. The effect of the concentration of O₂ on the conversion and selectivity of the FA decomposition was also investigated. The optimal concentration of O₂ of 0.1 vol% yielded an activity of TOF_{H₂} = 600 h^{−1} beyond which the selectivity of H₂ drops down, while conversion was preserved at 60%. The yield of H₂ dropped to 500 h^{−1} at O₂ concentration of 2 vol% due to the consequent oxidation of H₂ into H₂O on the expense of CO oxidation.⁵² Sneka-Platek O. *et al.* used another approach to inhibit CO poisoning in which tuning the alloy ratio of Ag : Pd at 4% Ag–1% Pd resulted in isolated Pd atoms and thereby in the highest conversion of HCOOH at 34%.⁵³

3.2 Formic acid: a hydrogen donor for hydrogenation of levulinic acid into higher value platform compounds

Here in this section, we emphasize heterogeneous catalytic routes that govern the transformation of levulinic acid into higher-value compounds in the presence of FA as a hydrogen donor. As mentioned earlier in this paper, FA comprising 4.4 wt% H₂ and a volumetric capacity of 53 g H₂ L^{−1}, is produced in equimolar stoichiometry with LA.⁵⁴ Hydrogenation is a key factor that is involved in upgrading biomass into higher-value chemicals and fuel additives. For instance, LA (4-oxypentanoic acid) represents an attractive platform molecule, which is produced easily and inexpensively from biomass, undergoes sequential deoxygenating steps to yield higher value liquid alkanes.^{3,55} To add, hydrogenation of LA yields several compounds, having distinctive properties and applications. To list, γ-valerolactone (GVL) is a valuable polyester monomer, 1,4-pentanediol is also used in polyester production, methyltetrahydrofuran (MTHF) is a valuable liquid hydrocarbon that can



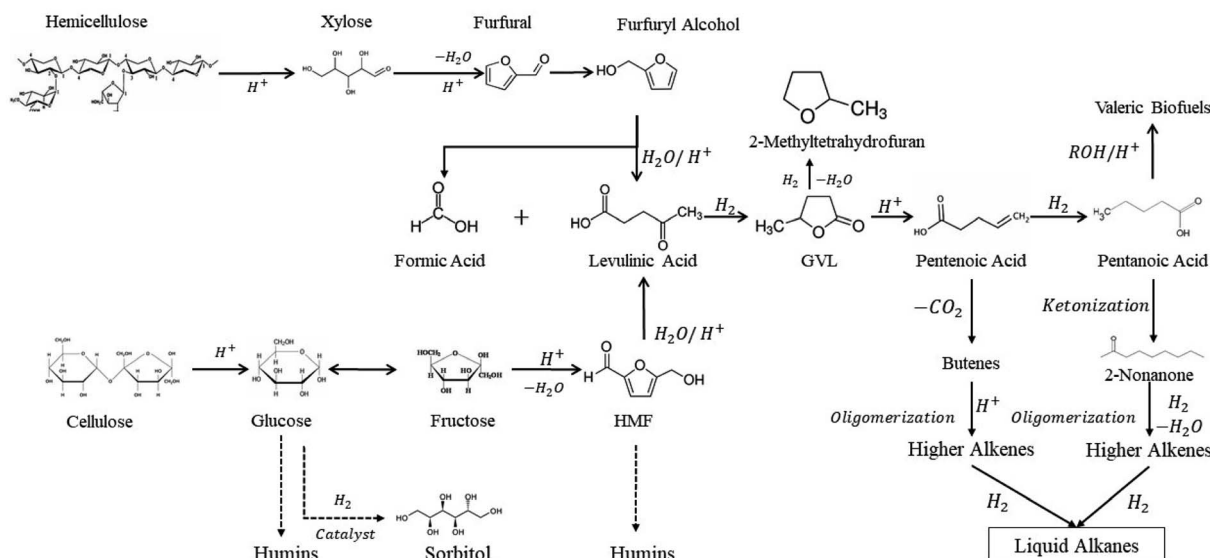


Fig. 2 Biomass platform molecules upgrade into valuable products and fuel additives.³

be used as a gasoline blend, and diphenolic acid which is involved in polycarbonate production,⁷ and pentanoic acid (PA).^{56–58}

Owing to the difficulty of handling conventional storage systems as an external source of hydrogen, shifting towards the *in situ* production of hydrogen from FA for hydrogenating reactions has become crucial.^{59,60}

Biomass compounds processing has been well discussed in literature from different perspectives. A good review was published elsewhere about upgrading biomass-derived compounds from different cellulosic biomass fractions, *e.g.* cellulose, hemicellulose, and lignin through C–C coupling reactions (Fig. 2).³

Another review focuses on the conversion of carbohydrates using heterogeneous catalysts. For instance, hexoses and pentoses, the building rocks of carbohydrates, undergo dehydrogenation and dehydration catalytic reactions to yield HMF and furfural (Fig. 3), respectively, which are subsequently upgraded into fine chemicals.⁶¹

Huber W. G. *et al.* wrapped up all known routes to produce bio-oils from lignocellulosic biomass. They reported a wide range of liquid fuels and gasoline additives that are formed through molecular weight adjustments.⁶²

Levulinic acid has been widely reported as an attractive platform chemical from which higher-value chemicals are produced, including levulinate esters, GVL, HMF, and MTHF.

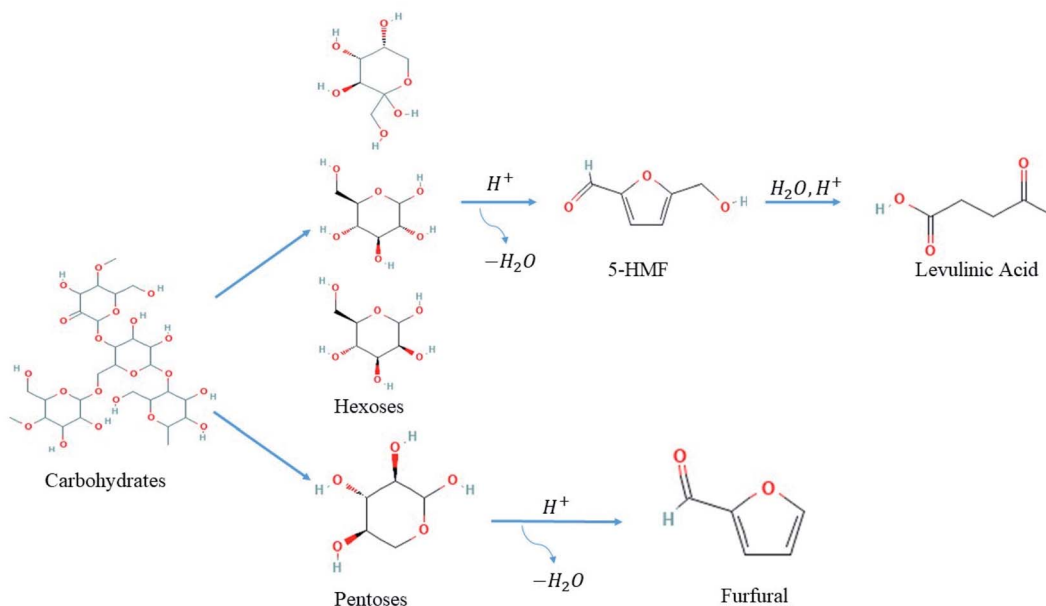


Fig. 3 Possible routes for dehydration of carbohydrates into levulinic acid and furfural platform compounds.⁶¹



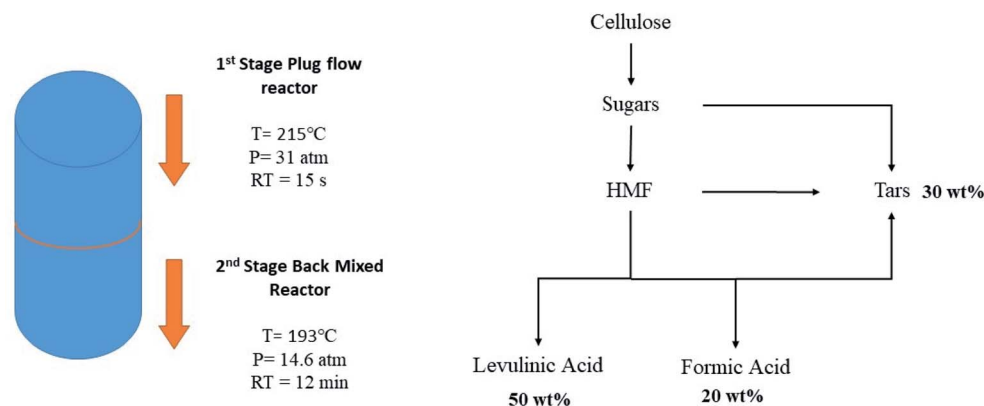


Fig. 4 Two-stage production of levulinic acid and formic acid from cellulose.⁶³

Noteworthy, designing a process with the least number of deoxygenating steps as one-pot transformation is shifting to a more economic route. As an added advantage for a cost-effective biomass process, replacing the external source of hydrogen by *in situ* molecular H₂ produced from FA is applied in addition to designing a catalyst capable of performing dehydrogenation and hydrogenation.

LA platform chemical along with FA is produced commercially from sugars that are produced subsequently from cellulose (Fig. 4). The production cost is estimated to be 0.09–0.11 \$ per kg for a throughput of 1000–2000 dry tons per day.⁶³

LA comprises distinctive properties due to the presence of carbonyl and ketone functional groups. Consequently, LA can undergo different reactions, mainly at its carbonyl group to yield cyclic compounds. Owing to its distinct products including but not limited to GVL, levulinate esters, 2-methyl-tetrahydrofuran, valeric biofuels, and pentanoic acid.⁶⁴

Deng Li *et al.* developed a catalytic route that comprises the production of GVL from biomass carbohydrates with a yield of 93 mol% by using RuCl₃·3H₂O/PPh₃ with pyridine base at 423 K. The novelty is pronounced by eliminating the need to separate levulinic acid from FA in the intermediate mixture. Noteworthy, it was found that introducing CO₂ to the reaction medium boosted the catalytic activity of Ru catalyst to reach a yield of 100 mol% GVL, whilst H₂O did not have any effect.⁶⁵

Sequential production of deoxygenated compounds is achieved by Ru/C catalyst followed by a dual catalytic bed containing Pd/Nb₂O₅ & Ce–Zr. The former catalyst completely converted LA and FA into GVL at 423 K. In the second reaction stage, Pd/Nb₂O₅ catalyst resulted in 100% conversion of GVL with 78% selectivity of pentanoic acid. Further on, they observed that the addition of zirconia led to further improvements. Indeed, the dual catalyst system Pd/Nb₂O₅ & Ce–Zr produced 89% selectivity of nonanone (C₉) from GVL.⁶⁶ Even though sulphuric acid was reported as a major inhibitor for catalysts, Ru/C catalyst showed good activity in the presence of H₂SO₄ medium.^{67,68} The authors explained this by emphasizing the importance of using optimum H₂SO₄ proportions for cellulose pretreatment during the upstream process.⁶⁶

In another study done by Deng Li *et al.*, their previous work including one-step process using RuCl₃/PPh₃ catalyst is

substituted by two-step processes using immobilized Ru–P/SiO₂ catalyst for FA dehydrogenation and Ru/TiO₂ for intramolecular hydrogenation of LA into GVL. The immobilized Ru–P/SiO₂ catalyst showed highest TOF of LA of 447 h^{–1} at 423 K (GVL yield 96%).⁶⁹ However, the team encountered contradictory results with Ruiz *et al.*⁶⁶ regarding the activity of Ru/C catalyst. According to Deng Li *et al.*,⁶⁹ the Ru/C catalyst did not show promising results in FA decomposition and *in situ* hydrogenation of LA into GVL (TOF 69 h^{–1}, 7% GVL yield). Instead, Ru/TiO₂ catalyst exhibited 63% GVL yield from LA at 4 MPa H₂ at 423 K.⁶⁹ An important aspect of the effect of CO₂ on Ru-catalysed hydrogenation of LA arose from this research; reinjecting the CO₂ produced from FA did not show any improvement of Ru/C in catalysing LA hydrogenation.⁶⁹ Dongmei H *et al.* (2017) also evaluated the activity of immobilized Shvo's catalyst over SiO₂ surface as well as covalently grafted catalyst in reducing LA into GVL using FA while avoiding the external use of H₂. The highest activity of 504 TON, 21 TOF(h^{–1}) and 88% GVL yield was attributed to immobilized Shvo's catalyst over SiO₂ surface. The reaction was held in the presence of 1,4-dioxane solvent under nitrogen gas for 24 h at 90 °C.⁷⁰

Feng J. *et al.*⁷¹ proposed a new reaction pathway for the production of GVL from LA using FA solely as H₂ source. A blend of Ru/C catalyst and trimethylamine accelerated LA hydrogenation and resulted in considerable activity at 87.26% as LA conversion and 80.75% as GVL yield. The XRD pattern showed an overlap between the characteristic peaks of Ru and graphite at 2θ = 44.6°, implying the high dispersion of Ru over carbon support. The proposed reaction route was exhibited using experiment probe of HPLC, ¹H NMR & ¹³C NMR by which LA, triethylamine, GVL, ethanol, 4-hydroxyvaleric acid, and ethyl levulinate are the compounds present at the end of the reaction. This features two important observations, the first of which is that FA was completely consumed, and that the esterification reaction is possible due to some produced ethanol that reacts with LA. The postulated mechanism is a good tool that helps researchers in investigating for the possible production of CO on the expense of CO₂ from FA decomposition (Fig. 5).

Due to the continued concern over the inhibiting effect of H₂SO₄ on heterogeneous catalysts,^{68,72} Heeres H. *et al.*²² proposed the use of TFA instead. It was reported that TFA has

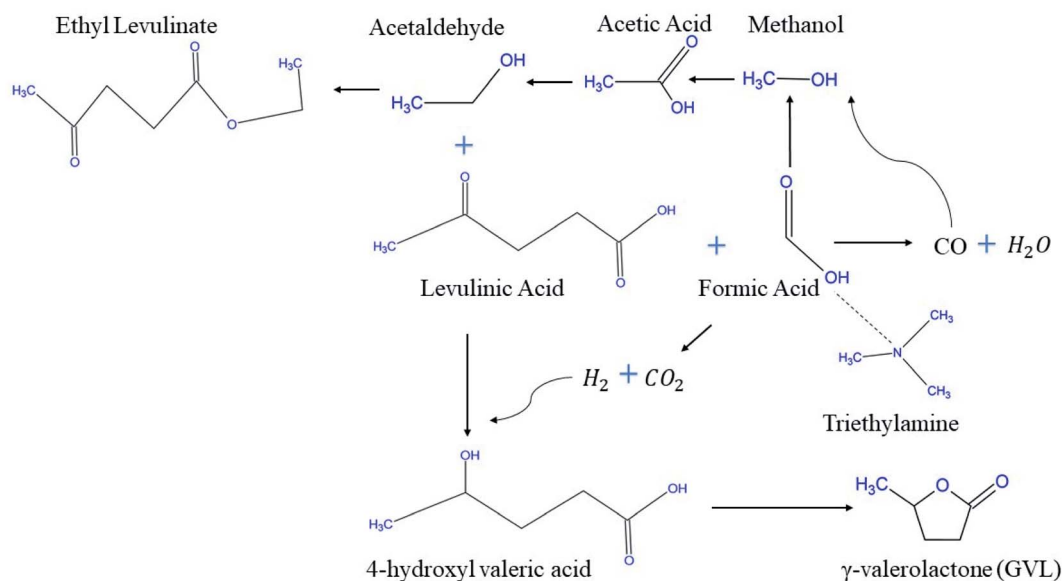


Fig. 5 Proposed reaction pathway of LA into GVL and ethyl levulinate using FA.⁷¹

a pK_a value of 0.5.⁷³ Indeed, TFA resulted by a yield of 57 mol% of GVL²² slightly higher than the yield of GVL of 55 mol% in the presence of H_2SO_4 .²⁰ The team studied extensively the conditions of conducting a one-pot process starting from C6-sugars to yield GVL. It was found that Ru/C catalyst resulted in 11 mol% LA yield and 52 mol% yield of GVL.²² On another note, the authors also shed light on further improvement of GVL yield% while minimizing hydrogenation side reactions, which can be achieved by tuning reactor parameters; temperature and mixing.²² An alternative strategy to avoid catalyst inhibition by the acidic medium is using reactive extraction in which butene is added to LA, FA, and H_2SO_4 aqueous solution to yield formate esters and levulinate esters. The aforesaid aqueous solution is separated easily into an organic phase (hydrophobic esters) and pure H_2SO_4 upon its contact with water. The group proposed a dual catalytic system containing Pd/C followed by Ru/C catalysts. H_2 is generated *in situ* from FA and formate esters over Pd/C hydrogenate LA and its ester over Ru/C catalyst.⁷⁴ This comes in harmony with sulphur tolerant Pd support material used for catalysts.^{75,76}

Interestingly, $SnCl_4$ catalyst was used as a substitute for H_2SO_4 in breaking down furfural biomass carbohydrates into LA and FA, which subsequently undergo catalytic transfer hydrogenation over Au–Ni/ZrO₂.⁷⁷

Kopetzki D *et al.* suggested the use of Na_2SO_4 salt in reducing LA into GVL using H_2 produced from FA. The salt catalyst activity relies on its dissociation constant in which SO_4^{2-} ions switch into a weak base at elevated temperatures (548 K) and eventually deprotonate FA. Hence, the use of a conventional base was avoided.⁷⁸ It was reported elsewhere that salt additives induce autocatalysis in aqueous solutions.⁷⁹ Accordingly, this approach should be given more attention towards either improving its activity further or blending it with other heterogeneous catalysts to boost up the GVL yield.

The high sensitivity of Ru/C catalyst amid acidic conditions inspired Demesic *et al.* to synthesize 15 wt% RuRe (3 : 4)/C catalyst for the hydrogenation of LA by FA in the presence of H_2SO_4 , with no observed deactivation. Indeed, the utilized catalyst resulted in a GVL yield of more than 95% at 423 K and higher stability, which is demonstrated by the increased TOF from 50 h^{-1} to 150 h^{-1} for Ru/C and RuRe/C catalysts, respectively.⁶ Likewise, the concept of Ru/C catalyst deactivation due to presence of acids drove Cao *et al.* to study the catalytic hydrogenation of LA by consuming FA as a reducing agent using Au nanoparticles on different catalyst supports. Their results presented ZrO₂ doped with Au as an attractive catalyst in comparison with Pd, Pt, Ru, and Pd as well as Au/C, Au/SiO₂, and immobilized Au/TiO₂.⁸⁰ The activity of Au nanoparticles was linked to its particle size (1.2–2.5 nm). Both studies come in agreement regarding the particle size effect of Au particles; larger particle size has limited the activity of Au catalyst.^{50,80} Therefore, the good catalytic activity of Au nanoparticles over ZrO₂ could be attributed to its value-added activity in HCOOH decomposition step.⁸¹ The high dispersion of Au nanoparticles of size 2.4 nm in their metallic state (Au^0) was found to be improved by the inclusion of Ce into Au doped ZrO₂ catalyst. These improvements play a key role in enhancing the decomposition of FA and thereby the hydrogenation of LA. The addition of Ce facilitated the formation of tetragonal phase of Zr along with the increase of weak and medium acidic sites, thus the formation of GVL was considerable at yield 83.5% due to upgraded dehydration reaction of the intermediate derived from LA hydrogenation reaction at conversion 90.8%. Despite the use of a high reaction temperature of 240 °C, the catalyst showed robustness with a limited decrease in its activity after 5 consecutive runs.⁸² Another study performed by Zhou C. *et al.*⁷⁷ confirmed the improvement of Au/ZrO₂ activity in hydrogenating LA by means of FA in the presence of highly dispersed Au^0 due to the incorporation of Ni metal. The role of Ni comes



in agreement with the above-mentioned Ce¹⁰⁶ in reducing Au particles to provide highly dispersed doped Au⁰ with less aggregation.

A strong relation between the method of preparation of nano-alloy Ni-based Au doped catalyst and its activity in hydrogenating LA into GVL in the presence of FA was demonstrated by M. Ruppert A. *et al.* It was found that highest LA conversion and highest GVL yield at 89% and 86%, respectively, were attributed to co-impregnation method of both metal precursors which are then thermally reduced under H₂. The group utilized DFT calculations and thorough characterization for the nano-alloy surface and concluded that selective FA decomposition is due to high energetic span of FA adsorption was favoured by Ni atoms incorporated within Au nanoparticles.⁸³

The effect of Au nanoparticles on different oxidic supports was studied thoroughly on LA decomposition into GVL using hydrogen transfer reaction in the presence of FA. Different Au@oxides catalysts were synthesized using co-precipitation and conventional impregnation techniques. Various oxide supports including ZrO₂, Al₂O₃, SiO₂, TiO₂, MgO were used for fabricating Au doped catalysts by which Au/ZrO₂ achieved highest GVL yield of 85% and LA conversion of 93% at 210 °C after 5 h.⁸⁴ Unlike Au–Ce/ZrO₂ catalyst reported above,⁸² the presence of Au³⁺ species improved the activity of the catalyst. XPS analysis elucidated the decrease in Au³⁺ species from 49.2% in fresh catalyst to 10% in spent one due to reducing agent FA. The Au/ZrO₂ catalyst synthesized by co-precipitation experienced a slight drop in GVL yield to 69% after 3 reaction runs.⁸⁴

The activity of Ru/C showed the highest conversion values of LA into GVL, and the highest selectivity compared with Pd/C, RANEY® Ni, and Urushibara Ni. Nevertheless, Ru/C exhibited

low stability which necessitates adding a portion of fresh catalyst for further runs. LA conversion and GVL selectivity dropped from 92% and 99% on its first run to 61% and 70% after the second run, respectively. Above all, the authors emphasized the hydrogenation mechanisms over Ru/C catalyst (Fig. 6).

Both LA and H₂ are chemisorbed on Ru/C before H–H bond cleavage step takes place, where one H atom will be transferred onto the carboxyl oxygen in LA and consequently an intermediate is produced. Thereafter, a second H atom transfers to the carbonyl carbon produces γ -hydroxyvaleric acid which undergoes subsequent dehydration into γ -valerolactone.¹¹

Recently, Al Naji M. *et al.* made a breakthrough in the field of LA hydrogenation in the presence of FA as a reducing agent in aqueous solution. The novelty of their work was pronounced by synthesizing a robust catalyst, comprising high thermal stability and can withstand low pH conditions (pH = 2). The most active catalyst, 1.6 wt% Pt/MP-ZrO₂ achieved a LA conversion of 84% and a GVL yield of 82% at 493 K after 24 h reaction time. Noteworthy, pentanoic acid of 22% wt was discovered at a higher temperature (533 K).⁸⁵ On a different note, the authors confirmed that FA acid decomposition into H₂ and CO₂ is a rate-limiting step which precedes LA hydrogenation over the same Pt active sites (Fig. 7).

Their findings come in line with Gazsi *et al.*⁵¹ and Ojeda *et al.*⁵⁰ as it proved that C–H bond cleavage contained by formate intermediates controls the overall reaction. To add, the reaction follows zero-order kinetics, same as mentioned in the literature, which can be attributed to the desorption of CO₂ & H₂ to the liberation of Pt active sites for LA hydrogenation (Fig. 7). This suggests a competitive adsorption between LA and FA on the active sites that provoke hydrogenation,³¹ featuring FA decomposition the rate limiting step of the overall reaction.

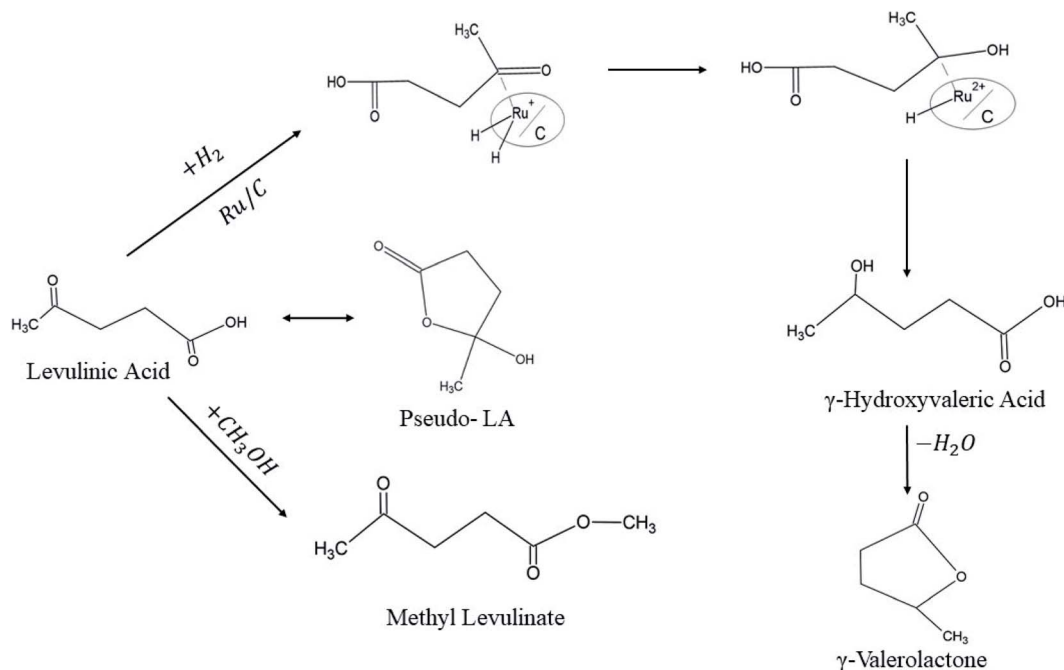


Fig. 6 Levulinic acid hydrogenation mechanism over Ru/C catalyst.¹¹

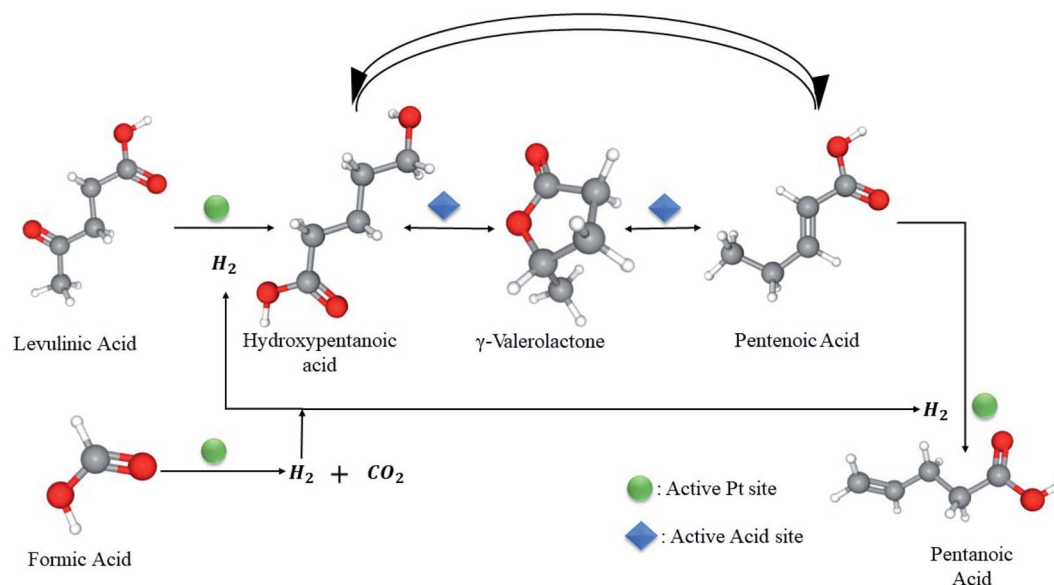


Fig. 7 Competitive FA dehydrogenation and LA hydrogenation over Pt active sites to GVL and PA.⁸⁵

It was previously emphasized that TiO₂ and ZrO₂ supports resulted in good activity regarding LA conversion to GVL using external molecular H₂ at 473 K.⁸⁶ Whereas, ZrO₂ exhibited higher activity and stability in comparison with TiO₂ support when doped with Ru active sites.^{11,87} In this context, Al Naji *et al.* also synthesized a bifunctional catalyst by way of doping noble metal Pt on zeolite support. The discovered catalyst was characterized by its acidic property, which thereupon permitted its ability to convert GVL into pentanoic acid. Briefly, this conversion was accomplished *via* a moderate number of acidic sites of zeolite, on which GVL ring-opening into pentanoic esters is favoured. At the same time, PEAs are hydrogenated using H₂ produced from FA decomposition, where both reactions (PEAs hydrogenation and FA decomposition) occurred over dual Pt active sites. The enhanced activity of hydrogenation/dehydrogenation reactions using dual active noble Pd metal supported on acidic zeolite catalyst were also demonstrated in pyrolysis of waste rubber, cracking down complex hydrocarbons into simpler compounds.⁸⁸ The conversion of LA achieved *via* the dehydration of 4-hydroxypentanoic acid intermediate, which is considered as a rate determining step, was reportedly enhanced by tuning Zr/Al ratio of Ru/(AlO)(ZrO)_n catalyst. The improved activity was characterized by enhanced strength and distribution of Lewis acidic sites of (AlO)(ZrO)_{0.1} and calcination temperature of 400 °C.⁸⁹

Designing an economic LA hydrogenation system is shifting from using sustainable FA as a hydrogen donor alone to the use of inexpensive metal catalysts. For instance, non-noble metals were tested in LA hydrogenation in the presence of catalytic transfer hydrogenation using nickel, zirconium, and iron.^{90–93} Amongst, Zr comprises the required acidity that stimulates LA hydrogenation into GVL.^{94,95} This was characterized by the high LA conversion due to high acidic density sites (136 μmol g^{−1}) when Zr was used as a support in 1.6 Pt/MP-ZrO₂.⁸⁵

Non-noble metals heterogeneous catalysts have always been an attractive topic for researchers as they seek cost-effective biomass hydrogenation processes. A recent study investigated the relation between the catalyst performance of MnCo oxide catalyst and its crystal structure. Series experiments were made using several MnCo oxide catalysts using different Mn : Co ratios. The highest activity corresponded to Mn₂Co_{0.1}O_x of 83.4% LA conversion and 70% GVL selectivity achieved at 230 °C. The improved activity was attributed to the structural distortion induced at MnCoO₃ and MnO_x interface, which facilitated the adsorption of FA by H–H formation and π–π interaction with ketone group of LA simultaneously. Previous attempts for applying non-noble metals in hydrogenating LA into GVL using FA in vapour phase^{96–101} and in aqueous phase^{102–108} are published elsewhere. Amongst, deactivation was studied by Hussain Sk *et al.*¹⁰¹ who found that using pure MgO catalyst exhibited good activity at the start-up before it declines due to deactivation. However, using calcined Mg–Al hydrotalcite catalysts yielded complete conversion of LA for 10 h and appreciable selectivity of GVL of 98%. The catalyst showed a good extent of stability conveyed by the reusability under same reaction conditions. The conversion of LA dropped to 86% while GVL selectivity was preserved near 98% after 4th cycle of the reaction.¹⁰⁹

A recent study also aimed at designing cost-efficient catalyst that is effective in hydrogenating LA into GVL at mild reaction conditions. The group used hard-soft template-assisted electro-deposition method to engineer Ni₇₈Pt₂₂ nanowires based on polycarbonate membranes that accommodate Ni–Pt mesoporous wires. Experiments showed that a TOF of 74 h^{−1} (100% conversion) and GVL selectivity near 99% were achieved at 140 °C during 120 min¹¹⁰. Ni and Cu cheap metals showed an excellent dispersion over SiO₂ support, featuring good catalytic activity in terms of hydrogenation of LA into GVL at a yield of



96% along with 4% Angelina lactone at 285 °C. The bimetallic Ni-Cu/SiO₂ catalyst characterized good stability for prolonged runs of 200 h. This robustness is attributed to nanocomposite morphology nature of Cu-Si, which prevents metallic sintering. Indeed, the highest H₂-uptake chemisorption of 0.039 mmol g⁻¹ corresponds to the optimal catalyst loading of 20% Ni & 60% Cu-SiO₂, which proved a homogeneous dispersion of metallic nanoparticles.⁹⁹ In another study, doping Ni metal on RANEY® catalyst resulted in a complete conversion of LA (100%) and a yield of GVL at 68.5% using a ratio FA/LA of 4 : 1 under 200 °C for 48 h. The RANEY® Ni catalyst was able to catalyse cellulose under same conditions into GVL at yield 23.3%.¹¹¹

Considering the synergetic relation between Cu & SiO₂ and the improved catalytic activity obtained, Lomate S. *et al.* (2017)⁹⁶ characterized the SiO₂ supports and Cu-doped SiO₂ catalysts, thereby studying the relation between the morphology and its activity. The physio-chemical properties of the catalyst were investigated and found to affect its activity. For instance, the highest TOF of 0.0707 moles LA h⁻¹ g⁻¹ corresponds to Cu-SiO₂ catalyst with larger CuO clusters with stronger interaction with SiO₂ surface. The strong interaction was also confirmed by the existence of the partial oxidation of Cu species represented as Cu^{δ+} with a binding energy 933.25 ± 0.35 eV located between Cu⁺ and Cu²⁺. Indeed, the higher activity of Cu-SiO₂ catalyst was attributed to its morphology, having narrow pore diameter distribution that plays a role in confinement of smaller Cu clusters inside pore walls, thus easily accessible for LA hydrogenation into GVL. Indeed, this work has thoroughly investigated the complex role of acid nature of the catalyst surface and its redox properties have on its activity and product selectivity. The use of characterization tools provided solid details about the catalyst nature including its electronic structure, which facilitated drawing a conclusion that Lewis acid sites of medium acid strength played a key role in the conversion of LA into GVL. Whilst Brønsted acid sites provoked hydrogenolysis of GVL into further hydrocarbons over metal sites and thus, increasing the yield of pentanoic acid and angelica lactone (AL) on the expense

of GVL. The presence of mononuclear Cu²⁺ over oligomeric (Cu-O-Cu)ⁿ⁺ led to higher activity of Cu/SiO₂ catalyst at 66% LA conversion and 81% GVL yield (Fig. 8).⁹⁶

Designing a cost-effective route for hydrogenating LA into GVL using FA put it forward for considering the use of non-noble metal supported on oxides surfaces. For instance, ZnAl oxides were tested using different temperatures and LA/FA ratios, where it exhibited considerable GVL yield of 90% and LA conversion near 85% after 6 h reaction time at 140 °C and 5 : 1 FA/LA ratio.¹¹² The work also featured kinetic modelling for proposed FA decomposition, LA hydrogenation as well as reversible formation of angelica lactone (AL) intermediates. The inhibitory effect of side reactions lies in the formation of lactones oligomers strongly adsorbed over basic sites of catalysts. Moreover, dehydrogenation of FA and hydrogenation of AL are key factors that establish the bounds within which LA dehydration reversible reaction is promoted in the forward direction without allowing the accumulation of intermediates (AL) (Fig. 8).¹¹²

From all the aforementioned information, LA can be transformed into its building blocks, which serve as valuable chemicals and biofuels additives. Together with GVL, LA can also be converted into other platform compounds such as pentanoic acid (valeric acid)^{57,113,114} or pentenoic acid^{115–118} (Fig. 3). In detail, GVL yielded from LA experiences ring opening to produce PA and pentanoic esters that undergo subsequent catalytic deoxygenating reactions to produce higher alkanes. As an illustration, Bond *et al.* established a dual catalytic system that comprises SiO₂/Al₂O₃ followed by HZSM-5/Amberlyst acid catalysts, producing higher alkenes from butene and pentenoic acid intermediates.^{13,119} Likewise, pentanoic acid is also produced from GVL *via* hydrogenation/ring-opening before it experiences a consequent transformation into liquid alkanes, having distinctive properties which qualify it as a good diesel fuel blend.⁶⁶ Lately, Zixiao Yi *et al.* introduced a comparative study of doping acidic catalyst by different metals; Ni and Ru. The two metals showed different reaction routes by which 3 wt% Ni/HZSM-5 catalyst resulted by limited hydrogenation of

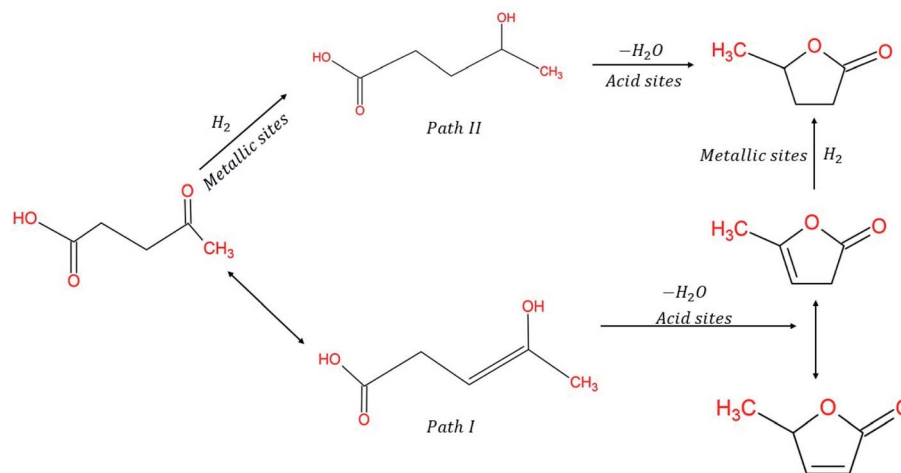


Fig. 8 Conversion routes of LA into GVL.⁹⁶

LA into GVL, whilst 3 wt% Ru/HZSM-5 catalyst facilitated further hydrogenation reaction, resulting in PA and pentanoic esters.¹²⁰ Identically, the increase in acidic density due to Ru inclusion as well as 1.6 Pt MP⁻¹-ZrO₂ gave rise to PA production *via* GVL ring-opening mechanism.⁸⁵ This comes in agreement with the findings of P. Sun *et al.* who reported that excessive acidity leads to decreasing GVL yields due to further ring opening reactions.¹¹⁷ Similarly, the dispersion of metal and the strong interaction between the metal and the doped acidic support MCM-49 can be adjusted by which a mesoporous Ru/MCM-49 can achieve LA conversion into GVL. This high conversion expressed by a TOF value of 3000 h⁻¹ was attributed to the high amounts of lewis acid sites on which lactonization of 4-hydroxypentanoic acid into GVL is achieved.¹²¹ Metal active sites incorporated in heterogeneous catalysts experience some inhibitory factors that retard its activity, one of which is metal leaching due to the presence of the organic levulinic acid substrate. Interestingly, Bai X. *et al.* have developed a robust catalyst based on Ag-ZrO₂-graphene oxide nanocomposite.¹²² In this perspective, Li J. *et al.* developed an attractive ternary catalyst Cu/ZrO₂-Al₂O₃ for converting LA into GVL while avoiding the leaching of Cu. This was attributed to the existence of oxygen vacancies in the extra framework of the catalyst on which LA is adsorbed before it subsequently transforms into GVL.¹²³ In the same context, it was reported that sol-gel entrapment of Ru in ZrO₂ minimizes leaching of Ru/ZrO₂ catalyst when used under acidic conditions (pH = 3.4). A conversion near 73% of LA and a complete decomposition of FA/HCOO⁻ (100% conversion) were attained using only 2.5% wt Ru over ZrO₂. Additionally, the authors tested the catalyst stability by incorporating 0.1 wt% SiO₂, which eventually hindered any change of the tetragonal crystalline phase into monoclinic one.¹²⁴

Generally speaking, designing non-noble metal-based catalysts has been an attractive material for researchers owing to its low cost and abundance that adds to the sustainability of the process. To demonstrate, Ni was one of the most used active metal species.^{91,125-127} With this in mind, Ni/NiO showed a quantitative LA conversion and GVL yield of 100% and 99.9%, respectively, at a relatively low temperature of 120 °C and 20 bar H₂.¹²⁶ Other research groups considered the acidity of catalyst support as a key factor in altering the conversion and yield of LA and GVL, respectively. In this context, acid supports, SiO₂, Al₂O₃, Y-Al₂O₃ doped by Ni showed promising conversions of LA in the presence of external molecular H₂.¹²⁸⁻¹³⁴ A complete conversion of LA and a GVL yield of 99.2% as well as a selectivity near 99.2% were exhibited using (40 wt%) Ni/Y-Al₂O₃ catalyst under dioxane solvent.¹³² In particular (15 wt%) Ni/Al₂O₃ showed high conversion without using a solvent.¹³¹ It is worth mentioning that active Ni species exist in the metallic state (Ni⁰), which comes in agreement with XPS results governing Ni⁰ (2p_{3/2}) peaks,¹²⁰ proving reduced catalyst improved activity.

Equally important, Cu non-noble metal is also doped on alumina and silica supports^{58,97,128,135} while other groups used zirconium oxide (ZrO₂) supports.^{58,102,136} Amongst, Cu/SiO₂ catalyzed intramolecular hydrogenation of LA by utilizing FA as an H₂ donor with 28 : 22 wt% (LA : FA) ratio despite its low LA

conversion of 48% and acceptable level of GVL selectivity of 80%.⁹⁷ Nevertheless, Cu/ZrO₂ catalyst outperformed Cu/SiO₂ and achieved 60% LA conversion and 100% GVL selectivity by consuming FA. Furthermore, the former attained complete decomposition of LA at elevated temperatures of 200 °C for 5 h.¹⁰² Zirconium active species exist in both oxide states and Zr⁴⁺ on which LA hydrogenation takes place by using alcohol as solvents as well as H₂ donor (2-propanol, 2-butanol, and 2-pentanol).^{94,95,137-141} The synergetic effect between Ni and Cu non-noble metals over SiO₂ support was investigated in the vapour phase selective hydrogenation of LA into GVL using FA. The addition of Ni into Cu/SiO₂ improved the hydrogenation of LA further compared to Cu/SiO₂. The highest LA conversion of 99% and GVL selectivity of 96% was attributed to the optimal loading of 1 : 3 Ni to Cu at 285 °C. The temperature effect was demonstrated as both LA conversion and GVL selectivity increased with the increase of temperature. The good stability of the catalyst under high temperatures near Tamman temperature of Cu and for prolonged reactions up to 200 h was due to the presence of Ni. Interestingly, the excellent catalytic activity of nanocomposite was attributed to the excellent dispersion of the metallic nanoparticles and the absence of solid solution between Ni and Cu proved by the XRD and XPS.⁹⁹

Based on the information mentioned above, two mechanisms characterize the hydrogenation of LA by means of *in situ* H₂ donated by FA. The difference between the proposed mechanisms lies in different mode of adsorption of LA over the heterogeneous catalyst, resulting in a different intermediate compound. The first approach is outlined by forming 4-hydroxyvaleric acid intermediate as a result of LA hydrogenation over the metal active sites doped onto support. Thereafter, the 4-hydroxyvaleric acid undergoes dehydration step (lactonization) over acidic sites, for instance MP-ZrO₂, to form GVL.⁸⁵ Whereas the alternative route comprises the inverse order, where LA experiences dehydration step first over acidic sites to produce angelina lactone, which is readily hydrogenated into GVL over metal sites later.^{12,142,143} A conclusive table that sums the recent work in heterogeneous catalysis reported between 2017–2021 (Table 2).

3.2.1 Production of GVL from biomass in one-pot processes. One-pot conversion of glucose, which is derived from cellulose biomass, into GVL, has been an attractive topic for biorefineries. This approach avoids the costs incurred by the industry for LA separation. Rather, the hydrogenation of LA is performed along with hydrolysis of hexoses oligomers in one-pot. In this context, a recent attractive study by Liu Y. *et al.* investigated the production of GVL from glucose using heteropolyacids and Ru-based catalysts. The group investigated the optimal reaction conditions including time, temperature, and solvent. The highest GVL yield reached near 39% when two-steps reaction was carried out using H₃PW₁₂O₄₀ and Ru/TiO₂ rutile catalysts at optimal temperature of 190 °C and butyrolactone-H₂O solvent for 2 h run time. Interestingly, performing the reaction under H₂ gas only as a one-step procedure resulted in 36.26% of sorbitol and only 2.13% yield of GVL since hydrogenation of glucose is more favoured than the hydration of glucose.¹⁴⁴ A similar study was performed by Cui J. *et al.*, who tested various solvents of different



Table 2 List of heterogeneous catalysts (2017–2021) for conversion of levulinic acid in presence of FA as sole source of H₂^a

Year	Substrate	H ₂ Donor	Catalyst	T (°C)	t (h)	X ^a /Y ^b /TOF ^c	Recyclability	S% GVL ^d /AL ^e /VA ^f	Ref.
2017	LA	FA	Cu–SiO ₂	230	1	53% ^a		82% ^d	96
			Cu–SiO ₂	270	1	66% ^a		81% ^d	
			Cu–SiO ₂	290	1	68% ^a		75% ^d	
2017	LA	FA	Triethoxy-silylpropoxy-Shvo's catalysts	90	12	90.93% ^a 28% ^c		99.90% ^d	70
2018	LA	FA	Au–Ni/γ-Al ₂ O ₃	190	2	89% ^a , 86% ^b			83
2018	LA	FA	2 wt% Au/Ce _{0.4} Zr _{0.6} O ₂	240	2	90.8% ^a 83.5% ^b	• Recovery of catalyst by centrifugation, then washing with pure water and ethanol and dry at room temperature	100% ^d	82
			Au/ZrO ₂	240	2	40.7% ^a 36.4% ^b		89.5% ^d	
			0.6 wt% Au/Ce _{0.4} Zr _{0.6} O ₂	240	2	63.5% ^a 49.7% ^b		77.3% ^d	
				240	2	13.1% ^a	• Good stability due to tetragonal phase attributing to strong metal–support interaction	70.2% ^d	
			Au/CeO ₂			9.2% ^b	• Limited decrease in activity after 5 runs		
2018	LA	FA	Calcined hydrotalcite Mg/Al (3 : 1)	270	5	100% ^a	• Cycle I TOS = 30 h Cycle II TOS = 22 h Cycle III TOS = 14 h Cycle IV TOS = 9 h • Regeneration of active sites under flowing air after each cycle • After cycle IV, LA conversion slightly decreased to 86% • After cycle IV, GVL selectivity was constant at 98%	98% ^d 1% ^e	101
2018	LA	FA (1 : 1)	RANEY® Ni catalyst	200	24	52.6% ^a 20.4% ^b			111
		FA (1 : 1)	RANEY® Ni catalyst	200	48	62.6% ^a 24.4% ^b			
		FA (1 : 2)	RANEY® Ni catalyst	200	48	90.9% ^a 60.5% ^b			
		FA (1 : 4)	RANEY® Ni catalyst	200	48	100% ^a 68.5% ^b			
2018	LA	FA	0.2 g Ru/C + 3 mL triethyl-amine	160	3	87.26% ^a 80.75% ^b			71
2018	LA	FA	2.5% Ru/ZrO ₂	150	12	73% ^a	• Catalyst washed with water	>99% ^d	124
			2.5% Ru/ZrO ₂ (WI)	150	12	63% ^a	• Activity significantly from 73% to 54% in the second run • XRD showed transformation from tetragonal to the thermodynamically stable monoclinic structure	>99% ^d	
2018	LA	FA	Cu–SiO ₂	250	1	48% ^a	• Deactivation of Cu–SiO ₂ catalyst studied at 250 °C with LA : FA ratio = 1 : 2	80% ^d 17% ^e	97
			Cu–TiO ₂	250	1	8% ^a	• Consistent conversion of LA (48%) and selectivity of GVL	25% ^d 55% ^e	
			Cu–ZSM-5	250	1	38% ^a	• Strong interaction between Cu with SiO ₂ support	4% ^d 82% ^e	



Table 2 (Contd.)

Year	Substrate	H ₂ Donor	Catalyst	<i>T</i> (°C)	<i>t</i> (h)	<i>X</i> ^a / <i>Y</i> ^b /TOF ^c	Recyclability	<i>S</i> % GVL ^d /AL ^e /VA ^f	Ref.
2019	LA	FA	Cu–Al ₂ O ₃	250	1	24% ^a	<ul style="list-style-type: none"> • Insignificant coke formation of Cu–SiO₂ and Cu–TiO₂ catalysts • Catalyst washed by acetone 5 times and dried at 100 °C for 2 h • Stable after 3 cycles with 69% yield of GVL • Selectivity of catalyst was not affected 	77% ^d 15% ^e	84
			6 wt% Au/ZrO ₂	210	5	93.3% ^a		91.1% ^d	
			4 wt% Au/ZrO ₂	210	5	85% ^b 80.8% ^a 70.4% ^b		87.1% ^d	
2019	LA	FA	1 wt% Au/ZrO ₂	210	5	13.6% ^a 13.4% ^b	<ul style="list-style-type: none"> • Mn₂CoO_x catalyst showed durable performance after 5 cycles • Conversion of LA fluctuated slightly around 60% from the 1st to the 5th cycle • GVL yield fluctuated between 84% and 87% from the 1st to the 5th cycle • Selectivity of VA did not change dramatically from the 1st to the 5th cycle • Recyclability of 1Au–2Ni/ZrO₂ catalyst • Spent catalyst was recovered by simple filtration • Calcined at 300 °C for 4 h. & reduced in H₂ flow at 300 °C for 1h • GVL yield showed a slight decrease after 3 cycles • Good recyclability of Au–Ni/ZrO₂ • Continuous but slight decrease in LA conversion during first 4 cycles • LA is being directly or indirectly deposited on catalytic surface • After 4th cycle, used catalyst was calcined at 600 °C, and TPO results were similar to the fresh catalyst 	98.5% ^d	85
			1.6 Pt/MP-ZrO ₂	220	24	82% ^a 84% ^b			
			1.5 Pt/MP-ZrO ₂	220	24	53% ^a 52% ^b			
2020	LA	FA	CoO _x	230	20	37.3% ^a	<ul style="list-style-type: none"> • Mn₂CoO_x catalyst showed durable performance after 5 cycles • Conversion of LA fluctuated slightly around 60% from the 1st to the 5th cycle • GVL yield fluctuated between 84% and 87% from the 1st to the 5th cycle • Selectivity of VA did not change dramatically from the 1st to the 5th cycle • Recyclability of 1Au–2Ni/ZrO₂ catalyst • Spent catalyst was recovered by simple filtration • Calcined at 300 °C for 4 h. & reduced in H₂ flow at 300 °C for 1h • GVL yield showed a slight decrease after 3 cycles • Good recyclability of Au–Ni/ZrO₂ • Continuous but slight decrease in LA conversion during first 4 cycles • LA is being directly or indirectly deposited on catalytic surface • After 4th cycle, used catalyst was calcined at 600 °C, and TPO results were similar to the fresh catalyst 	85.2% ^d 10% ^f	109
2020	LA	FA	MnO _x	230	20	76.7% ^a		74.7% ^d 12% ^f	
			Mn ₂ Co _{0.1} O _x	230	20	78.9% ^a		76.7% ^d 11.8% ^f	
			Mn ₂ Co _{0.1} O _x + 0.1 mol L ^{−1} Na ₂ SO ₄	230	20	83.4% ^a		70% ^d 14.1% ^f	
			1Au/ZrO ₂	240	1	66.7% ^a 73.4 % ^b		90.9% ^d	77
			1Au–2Ni/ZrO ₂	240	1	87.9% ^a 89.1% ^b		98.7% ^d	
2020	LA	FA	0.5Au–2Ni/ZrO ₂	240	1	62.2% ^a 63% ^b	<ul style="list-style-type: none"> • Calcined at 300 °C for 4 h. & reduced in H₂ flow at 300 °C for 1h • GVL yield showed a slight decrease after 3 cycles • Good recyclability of Au–Ni/ZrO₂ • Continuous but slight decrease in LA conversion during first 4 cycles • LA is being directly or indirectly deposited on catalytic surface • After 4th cycle, used catalyst was calcined at 600 °C, and TPO results were similar to the fresh catalyst 	98.4% ^d	77
			2Ni/ZrO ₂	240	1	1.2% ^b			
			ZnAl oxide	140	<6	87% ^a 90% ^b		90% ^d	112
2021	Glucose	FA	Ru/TiO ₂	190	2	38.98% ^a			144

^a *X* = conversion (%); *Y* = yield (%); TOF = turnover frequency (s^{−1}) *S* = selectivity (%); LA = levulinic acid; GVL = γ-valerolactone; AL = angelica lactone; VA = valeric acid.

concentrations to valorise biomass, mainly polysaccharides into GVL using a blend of Brønsted acidic catalyst and Ru/TiO₂.¹⁴⁵ Most research output have focused on developing heterogeneous catalysts for improving LA substrate

hydrogenation into GVL step. Nevertheless, biomass valorisation upstream processes usually result in bulk mixtures. For instance, fructose alcoholysis produces LA along with alkyl levulinates. This issue inspired Delgado J. *et al.* to investigate



Ru/C catalyst activity to produce GVL from a mixture of LA and butyl levulinate (BL). They proposed that this transformation takes place through two steps; hydrogenation step of LA & BL into 4-hydroxypentanoic acid and butyl 4-hydroxypentanoate intermediates, which are then readily lactonized into GVL over Ru/C catalyst. Moreover, they provided a comprehensive kinetic model to validate that non-competitive Langmuir–Hinshelwood with no dissociation of H₂ and non-competitive Langmuir–Hinshelwood with H₂ dissociation model are best approach of the reaction mechanism.¹⁴⁶

The challenging task of valorisation of renewable biomass into its constituents, for example biofuels, places emphasis on synthesizing heterogeneous catalysis. Ultimately, researchers aim at developing a heterogeneous catalytic system where the conversion of hemicellulose part of biomass into biofuels such as GVL in a one-pot process is achieved, while avoiding the use of liquid acid. It was reported elsewhere that a catalyst blend of ZSM-5 and Au/ZrO₂ achieved a complete conversion of xylose and hemicellulose into furfural, followed by a subsequent hydrogenation into GVL at a yield of 80% in the presence of 2-propanol and without the need of external H₂. The reaction was performed at 120 °C for 30 h which therefore resulted in a maintained a GVL yield not less than 65% after 4 reaction cycles of 24 h each.¹⁴⁷

4 Catalytic hydrogenation of LA using different H₂ sources

Up until this point we have put a special emphasis on FA as a sole source of H₂ for hydrogenating LA over heterogeneous catalyst. A concise overview on solvents, published in literature other than FA, is presented in this section. For instance, various alcohols such as methanol,¹⁴⁸ isopropyl alcohol,^{10,149} 2-butanol,^{94,150} and ethanol¹⁵⁰ are used as H₂ sources for LA hydrogenation. The use of isopropyl alcohol marked appreciated levels of LA conversion near 99% and an attractive selectivity of GVL at 99% in the presence of 50-Ni-MMT catalyst.⁹¹ In a different study, 2-butanol and 2-isopropyl alcohol were examined using F–ZrF and UiO-66-SO₃H catalysts, respectively.¹⁵¹ For F–ZrF, high LA conversion and GVL selectivity were obtained by 2-isopropyl alcohol in the presence of DMF, which comes in agreement with Hengne A. M. *et al.*⁹¹ Despite achieving a complete conversion of LA and high GVL selectivity, the addition of solvents like DMF proposes additional environmental concerns. However, exploiting the presence of FA offers a greener process by avoiding the use of hazardous solvents. In addition, the complication of using conventional high pressure H₂ puts a risk when shifting into large-scale applications, making FA a safer and a cost-saving substitute.

4.1 Photocatalytic hydrogenation of LA into γ -valerolactone using alcohol solvents H₂ donor

On another end, the use of photo catalysis is emerging as researchers are seeking to supplement catalytic processes with sustainable green energy. That being said, exploiting light

energy has shown, for example, a promising role in catalytic pyrolysis of waste rubber tires.¹⁵² Photo catalysis are of vital importance to the degradation of contaminants and antibiotics traces in waste water.¹⁵³ Interestingly, higher value solvents derived from biomass such as GVL can be successfully produced from LA using niobic acid photo catalyst using UV-assisted accumulated electron transfer technique.¹⁵⁴ Moreover, TiO₂ doped with Pt is suggested as a promising catalyst that features a dual role in the production of GVL from LA and levulinate esters using alcohol as H₂ source and under mild reaction conditions. In brief, the catalyst showed a high GVL yield of 93% for thermocatalytic route using 2-propanol solvent but lower yields for photocatalytic one. Nevertheless, the addition of NaOH base promoted GVL yield up to 95% using ethanol as a green solvent.¹⁵⁵ Noble metals Pt, Pd, & Au-loaded TiO₂ photo catalyst were screened by Zhang H. *et al.* for hydrogenation of LA into GVL in presence of isopropanol. The corresponding order of LA conversion was Pt/TiO₂ < Pd/TiO₂ < Au/TiO₂ of 69% (69.5% GVL yield), 71% (76.4% GVL yield), and 79% (85.3% GVL yield), respectively.¹⁵⁶ The carboxyl functionalized Zn-porphyrin on polymer support yielded 72% GVL after 16 hours under visible light.¹⁵⁷ The list of photo catalysts used for LA hydrogenation are tabulated in Table S1 (ESI document†).

5 Discussion and further research recommendations

As mentioned earlier in this paper, FA is a major key factor in many applications as it houses valuable gases; H₂ and CO. Therefore, HCOOH is treated as a hydrogen or CO storage system to be used for further purposes. Two methods define explicitly how both gases are charged into FA, particularly, CO₂/CO and bicarbonate approaches.^{158,159} Additionally, heterogeneous and homogeneous catalysts are employed to drive the reaction towards the production of HCOOH.^{160–162} Charged FA readily liberates either H₂ or CO. In fact, HCOOH decomposition is catalytically favoured by a variety of heterogeneous catalysts. Whenever FA is accounted as H₂ donor, designing a catalyst capable of maximizing dehydrogenation reaction on the expense of dehydration is preferred. Even though homogeneous catalysts favour the decomposition of FA at relatively mild conditions, its separation, and the use of solvents pronounce major setbacks. It is of high significance that possible traces of CO, as a result of FA dehydration, react with catalyst precursor, producing further active species.¹⁶³ Further research could be done on this concept, which would permit the presence of CO traces in the product stream. This provides the opportunity to operate at more cost-effective conditions with no need for producing pure H₂. The inclusion of benzene into the catalyst led remarkably to further improvements due to its light dissociation under light irradiation. This suggests the use of photoactive catalysts along with benzene or other dissociative compounds that would assist in FA dehydrogenation. Photoactive catalysts using Pd & Pt@TiO₂ support have shown a promising activity under harsh reactions represented by waste rubber cracking.¹⁵² A comprehensive literature review about



approaches for designing photoactive catalysts based on TiO_2 , CdS , and C_3N_4 for HCOOH decomposition into H_2 was published elsewhere.¹⁶⁴ Photo catalysts reported in literature were evaluated using isopropanol, ethanol, and 2-propanol as H_2 donor.^{155–157,165} These studies should direct toward testing FA decomposition for *in situ* H_2 production in the presence of photo catalyst.

On another end, the use of heterogeneous catalysts facilitates its separation from the yielded product, and thereby the reuse of the catalyst is possible. Besides, heterogeneous catalysts suffer deactivation due to CO poisoning yielded by dehydration reaction^{37,38} due to elevated temperatures. For that reason, some research groups tended to manipulate the crystalline frameworks by calcination processes, which allow the synthesis of alloy, core-shell, and bimetallic structures. As shown above, an increase in Au cluster size due to thermal treatment decreased catalyst activity thereupon. Unfortunately, few studies were reported regarding the sintering effect on the active sites of heterogeneous catalysts as a result of elevated temperatures. Morphology and dispersion analysis of the active sites must be further performed using *in situ* SEM & TEM at different temperatures to inspect sintering and contamination deposition.

Coupled with its ability to accommodate massive energy content (5.3 MJ kg^{-1}) as well as its low cost of production, making it an ideal fuel substitute, FA is a key compound for catalytic hydrogenation reactions. Specifically, FA is a key factor in LA hydrogenation into GVL, which undergoes successive deoxygenating reactions to yield higher alkanes (Section 3). In real applications, a pretreatment cracking step using strong acid (H_2SO_4 , HCl) is carried out for lignocellulosic biomass and therefore heterogeneous catalysts are prone to deactivation. Different catalyst structures experience different effects of metal leaching on catalyst activity. For Cu catalysts, the leaching of metals detected through ICP-OES of the liquid products can lead to a significant reduction in catalyst activity down to 70%. Copper metal leaching was confirmed using FT-IR for investigating soluble copper complex.⁵⁸ In other studies, ICP analysis showed that metals such as Fe, Ni, Cr, Co and Mo leach into the liquid product upon the hydrogenation of LA in the aqueous phase.⁶

Owing to the setback of metal leaching, designing a robust support is essential for improved metal-support interaction. Catalysts with carbon supports have been proved overcome the issue of leaching on the expense of catalyst regeneration.¹⁶⁶ On the other hand, stable ZrO_2 support of tetragonal phase demonstrated a stronger binding to the active Cu species (<2 ppm) than Al_2O_3 (174 ppm), avoiding metal leaching into the solvent.⁵⁸

Further research should be employed on using either alternative acids²⁰ or using conventional acids in appropriate quantities to avoid catalytic inhibition.⁶⁶ Hence, it would be essential to perform LA catalytic hydrogenation by using FA as an H_2 donor but under acidic conditions. Separating acids from the reaction mixture is a costly process. Alternatively, more attention should be given to solvents such as butene that yield immiscible levulinate esters.⁷⁴ Findings achieved by Deng Li

et al. suggested a promising effect of the addition of CO_2 on the catalytic activity which should be investigated further as it exists as a major by-product as a result of FA dehydrogenation reaction.⁶⁵ Likewise, studying the possibility of optimizing WGS reaction by injecting CO paves the road for utilizing the traces of CO existing in the product.¹⁶⁷

Generally speaking, executing an optimized catalytic hydrogenation of LA through intramolecular H_2 necessitates designing a catalytic reactor that accounts for engineering perspectives. Particularly, the assessment of heterogeneous catalysts must take into consideration heat and mass transfer as well as mass transfer limitations between the inner pore surface and the bulk biomass. That being said, designing different mixing systems is useful to obtain benchmark values of potential conversions range instead of just one conversion value for the studied catalyst. Furthermore, the produced gas could be continuously bubbled throughout the reactor in which better mixing and higher catalytic activity could be achieved. Equally important, further studies that integrate experimental results and simulations should be implemented, aiming to optimize reactor design and operating conditions. Continuous processes from engineering perspective are hardly found in literature and more efforts should be devoted to bringing pilot scale applications on table such as the work performed by Zhou *et al.*⁷⁷ Scaling-up the process of production of valuable biomass-derived chemicals and biofuels from lignocellulosic derived LA requires considering its economic feasibility. A comprehensive techno-economic analysis performed by Patel A. *et al.* (2010) addresses the feasibility of producing 5-nonanone from LA and also evaluates the relative purification costs, both of which are based on discounted cash flow analysis.¹⁶⁸ The model uses molecular H_2 raw material input at $1736.07 \text{ kg h}^{-1}$ of a market value $0.116 \$ \text{ per kg}$. Indeed, shifting towards using stored H_2 in FA disregards near $201 \$ \text{ per h}$ of the running cost of hydrogenation processes.¹⁶⁸

All things considered, the most active heterogeneous catalysts comprise noble metals, which are expensive and less abundant in nature. However, some findings exhibited promising LA + FA conversion into GVL by using cheaper metals doped over acidic catalysts.¹²⁰ Establishing less number of deoxygenating steps that yields valuable chemicals and/or higher liquid alkanes render them as a cost-effective catalytic route. In this regard, some developed catalysts^{85,120} produced higher alkanes bio-solvents beyond GVL despite the fact that they contain noble metals, putting a whole new set of development options on the table.

6 Conclusion

The interest in GVL production has been increasing not only for its distinctive properties, but also for its potential as a feedstock to produce higher-value compounds. Heterogeneous catalysts lie at the heart of biomass deoxygenating mechanisms allowing efficient LA conversion, promoted GVL yield, and competent recyclability. It has been noticed that oxides were extensively used as supports for noble metals to hydrogenate LA into GVL through FA decomposition as a sole H_2 source. Nevertheless,



other authors shifted their focus to non-noble metals, for example, Ni and Cu to establish more economic processes. We have seen in the last 2 years that photo catalysis has been overarching the need to exploit light energy for fulfilling the production of GVL at mild conditions, which obviously is worth further investigations.

Conflicts of interest

There are no conflicts of interest to declare.

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