

# An Overview of the Obtaining of Biomass-derived Gamma-valerolactone from Levulinic Acid or Esters without H<sub>2</sub> Supply

Giselle González \* and María C. Area

Gamma-valerolactone (GVL) is a highly reactive keto-lactone and a promising platform biomolecule, used as an additive for food and fuels, green solvent, and fuels precursor, among others. Its production from biomass usually involves hydrogenation and subsequent cyclization of levulinic acid or its esters. The process of conventional hydrogenation requires high pressures and temperatures, an external hydrogen source, and scarce noble/precious materials as catalysts. However, it could be produced under mild conditions, using bifunctional metal-acid catalysts with high metal dispersion and meso or microporosity, high surface area, temperatures lower than 200 °C, pressures ≤ 1MPa, and secondary alcohols (such as isopropanol) as hydrogen donors. The catalytic transfer hydrogenation followed by cyclization (CTHC) of levulinic acid (LA) and its esters (LE) to produce GVL using secondary alcohols as H donor is a great alternative. Variables involved in CTHC such as raw material, time, temperature, and type of catalyst, mainly transition metals and their combinations, are reviewed in this work.

*Keywords:* Biorefinery; Catalytic transfer hydrogenation; Gamma-valerolactone; Heterogeneous catalysis; Transition metals; Levulinic acid; Levulinic esters

*Contact information:* Instituto de Materiales de Misiones (IMAM), Universidad Nacional de Misiones - Consejo Nacional de Investigaciones Científicas y Técnicas (UNaM – CONICET), Félix de Azara 1552 (3300), Posadas, Misiones, Argentina. \*Corresponding author: gi.gonzalez.93@gmail.com

## INTRODUCTION

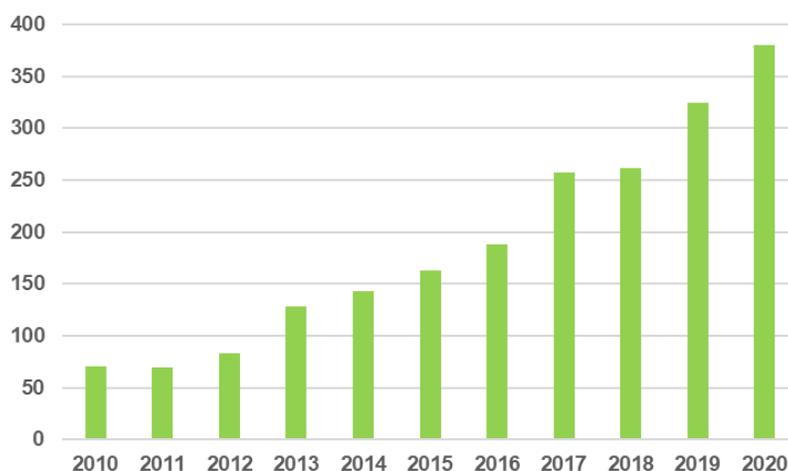
Anthropic development has an overwhelming dependence on fossil resources, increasing their depletion over the years and generating a critical concern in the scientific society, which has strongly mobilized the search for alternatives (Chu and Majumdar 2012; Dechambre *et al.* 2017). Biomass in the frame of the biorefinery concept seems to be the best option for oil replacement in refinery schemes because of its abundance and renewable characteristics (Jakob and Hilaire 2015). Moreover, biomass processing can be neutral in greenhouse gases if efficient production methods are applied (Albanese and Ruiz 2015). Besides, small to insignificant additional CO<sub>2</sub> emissions occur during the production and use of bioenergy, reducing or even eliminating the negative impact on the carbon balance of our biosphere (Saxena *et al.* 2009). It has been predicted that for 2030, 20% of the fuel for transport and 25% of the chemicals will be produced from lignocellulosic biomass, since they are the only renewable carbon source suitable to replace fossil fuels with a minimal carbon footprint (Yan *et al.* 2015). Currently, fossil sources are the source of most of the chemicals (De Jong *et al.* 2020).

According to the IEA Bioenergy Task 42, biorefineries platforms (*e.g.*, sugars, biogas, syngas) link feedstocks with final products, applying different processes. The sugar

platform using lignocellulosic biomass as feedstock harnesses cellulose and hemicelluloses C5/C6 sugar fractions (Cherubini *et al.* 2009). By using a set of concatenated reactions, they can then be transformed into valuable compounds with industrial applications such as 5-hydroxymethylfurfural (HMF) (Antonetti *et al.* 2016, 2017; Licursi *et al.* 2017), furfural (FUR) (Mariscal *et al.* 2016), levulinic acid (LA) (Antonetti *et al.* 2015; Licursi *et al.* 2018b; Rivas *et al.* 2015, 2018), gamma-valerolactone (GVL) (Alonso *et al.* 2013), and others (Heeres *et al.* 2009; Lange *et al.* 2010; Fábos *et al.* 2014; Cen *et al.* 2018; Kang *et al.* 2018; Kasar *et al.* 2018; Kim *et al.* 2020a; Lilga *et al.* 2018).

GVL has been identified as a promising platform bioproduct (Tang *et al.* 2019b) to produce value-added chemicals from biomass, for example, gasoline-range and liquid hydrocarbon fuels (Braden *et al.* 2011; Wang *et al.* 2020a). Green chemistry is a global trending topic, and gamma-valerolactone is a great candidate as a solvent to make successful eco-friendly processes. Some examples are the production of the 2,5-furandicarboxylic acid (FDCA) that can replace oil-based terephthalic acid in polyethylene terephthalate (PET), high yield biomass fractionation and subsequent production of higher value products, replacement of NMP (N-methyl-2-pyrrolidone) in polyurethane dispersions (Germán *et al.* 2021), an alternative for dimethylformamide (DMF) and  $\gamma$ -butyrolactone (GBL) in carbon-based lead halide perovskite solar cells (CPSCs) (Worsley *et al.* 2021), and efficient polyethylene terephthalate (PET) swelling and dissolving agent for plastic recycling (Chen *et al.* 2021), among others (Quang *et al.* 2016; Li *et al.* 2018b; Zhang *et al.* 2018; Chen *et al.* 2019; Ahmed *et al.* 2020; Kim *et al.* 2020a,b; Al Ghatta *et al.* 2021; Wang *et al.* 2021; Yang *et al.* 2021).

The expectations generated by GVL are high, which is reflected in the number of publications involving its different aspects (Fig. 1).



**Fig. 1.** Number of publications per year when searching the word "valerolactone" in ScienceDirect (<https://www.sciencedirect.com/search?q=valerolactone>)

Extensive reviews about GVL can be found in the literature, focusing on its potential uses (Tang *et al.* 2014b), its production from different chemical sources (Alonso *et al.* 2013), and the hydrogenation of LA and its esters to obtain GVL (Zhang *et al.* 2017). Besides, some reviews include the use of different catalysts (Wright and Palkovits 2012), such as noble metals (Luo *et al.* 2013; Maumela *et al.* 2021), non-noble metals (Dutta *et al.* 2019), and bimetallic ones (Alonso *et al.* 2012). Also, GVL production through catalytic

transfer hydrogenation (CTH) starting from biomass-derived feedstocks (Osatiashiani *et al.* 2017). On the contrary, this article focuses on heterogeneous catalytic processes to obtain GVL by CTH and cyclization (CTHC) from biomass-derived LA and LE using achievable catalysts, mild conditions, and simple technologies with relatively low investment costs, reducing process requirements, and safety cautions.

At present, the production of GVL at laboratory scale involves the use of molecular hydrogen at high pressures (Ding *et al.* 2014; Yan and Chen 2014; Li *et al.* 2017a; Dutta *et al.* 2019), which needs careful handling and robust reactors, thus increasing the capital costs. In addition, usual catalysts are noble or scarce materials. Implementing lower-cost processes by using milder conditions will encourage GVL production. This work is an up-to-date review that aims to find data that allows foreseeing more economical combinations of variables to reach the highest conversion of LA (or LE) with the highest selectivity for GVL production by CTHC. The collected data include previous successful experiences and results of GVL production from LA and its esters using the CTHC pathway. Cases with conversions and selectivity equal to or higher than 85% and with not-extreme reaction conditions, such as pressures less than 2 MPa, temperatures lower than 250 °C, and catalysts composed of non-noble transition metals (excepting zirconia, for economic reasons), were considered.

Scopus and ScienceDirect databases were used, which are open access for the National Council for Scientific and Technical Research of Argentina (CONICET). The keywords employed were gamma-valerolactone, levulinic acid, levulinic ester, biomass, and catalytic transfer hydrogenation. The considered time-lapse was last 10 years, including older articles containing relevant information.

## GAMMA-VALEROLACTONE FROM BIOMASS

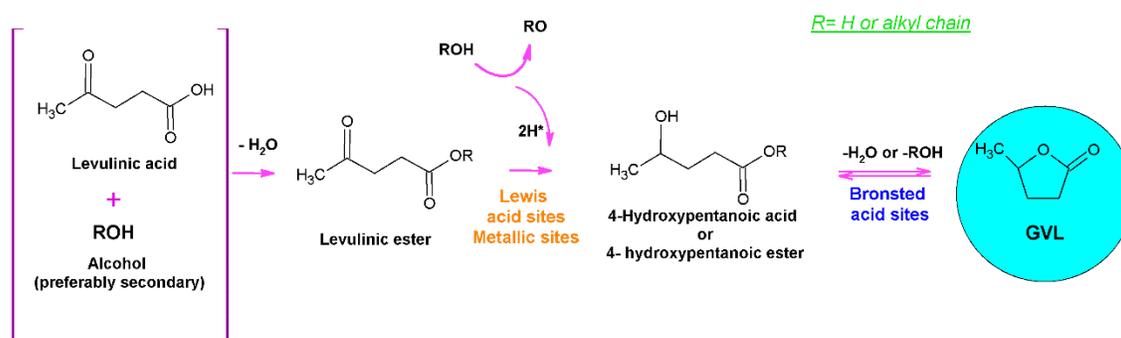
Cellulose, hemicelluloses, and lignin are the principal components of biomass. They are linked in a complex matrix and must be fractionated to produce derivatives, such as chemical products (Area *et al.* 2012; Ribechini *et al.* 2012; Galia *et al.* 2015; Licursi *et al.* 2015; Vallejos *et al.* 2017). The resulting polysaccharides must be hydrolyzed (Tsigie and Ju 2012) to release the hexoses and pentoses.

Numerous researchers have studied the obtaining of GVL from biomass (Han 2017; Metzker and Burtoloso 2015; Putro *et al.* 2015), cellulose, glucose, and fructose (Heeres *et al.* 2009; Li *et al.* 2020; Zhao *et al.* 2020). However, there are several challenges to overcome in these one-pot procedures, such as minimizing humins production, finding a multistage catalyst, and scalable reaction conditions, among others.

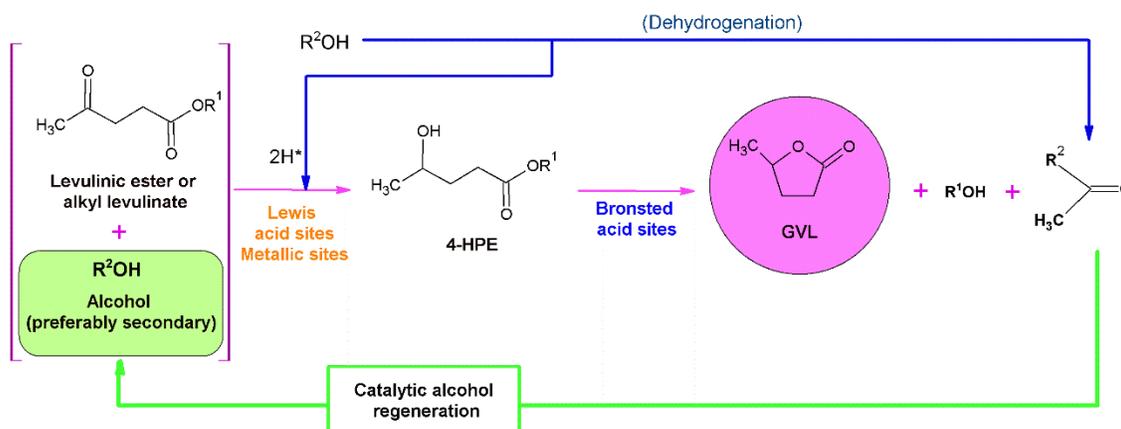
Biomass precursors of GVL are levulinic acid or levulinic ester (Antonetti *et al.* 2016; Kapanji *et al.* 2021; Putro *et al.* 2015; Rivas *et al.* 2018). Levulinic acid/ester production from biomass involves several stages (Covinich *et al.* 2020). First, the fractionation separates lignin from hemicelluloses and cellulose, with these last two molecules serving as the precursors of the subsequent processes. Later, hydrolysis in aqueous or alcohol media catalyzed by Brønsted acid sites produces hexoses/pentoses from cellulose and hemicelluloses. In the case of hexoses, glucose (GLU) isomerizes with fructose (FRU), and both isomerize to mannose to a minor extent (Moliner *et al.* 2010). Subsequently, these sugars are dehydrated to produce hydroxy-methyl-furfural (C6) or furfural (C5). Finally, to reach the levulinic acid, HMF is dehydrated, whereas FUR is first hydrogenated and then dehydrated. Considering hexoses, the conversion of fructose tends

to be higher than that of glucose (Liu *et al.* 2020). In particular, the fructofuranose gives a higher selectivity to HMF due to its high reactivity and the presence of a five-membered ring (Assary *et al.* 2012). Nevertheless, the fructopyranose is the dominant form in fructose in an aqueous solution (near 68%), and in the acid-catalyzed decomposition, it is less selective to HMF (Assary *et al.* 2012). Thus, isomerization is an important step. Effective catalysts for dehydration of FRU to HMF have low activity when starting from GLU (Qi *et al.* 2008). This multi-stage process generates high amounts of solid by-products by intermediates of polymerization called humins, which are one major obstacle for the sugar platform biorefineries (Alonso *et al.* 2013; Licursi *et al.* 2017; Rackemann and Doherty 2011; Wettstein *et al.* 2012).

Producing GVL from LA or levulinic esters (LE) in a liquid phase under mild conditions involves two stages: hydrogenation, and cyclization. Hydrogenation uses molecular hydrogen or alcohol as H-donor. If the process is catalyzed, then the first case is called direct or conventional catalytic hydrogenation (CDH), and the second, catalytic transfer hydrogenation (CTH) (Wang and Astruc 2015). First, the LA (or LE) is hydrogenated to reach 4-hydroxy-pentanoic acid (4-HPA) or ester (4-HPE). Then, GVL produced by intraesterification releases water or alcohol as a byproduct (Hengne *et al.* 2016), generated by the C-OH or C-OR bond (respectively) scission at the  $\alpha$ -carbon (Mamun *et al.* 2019) of the 4-HPA/4-HPE (Fig. 2).



**Fig. 2.** The mechanism for catalytic transfer hydrogenation and cyclization (CTHC) of levulinic acid to produce gamma-valerolactone (Hengne *et al.* 2016; Gong *et al.* 2018)



**Fig. 3.** Catalytic transfer hydrogenation and cyclization (CTHC) mechanism proposed by Chia and Dumesic when the alkyl chain of the alcohol used as donor and the levulinic ester are not the same (adapted from Chia and Dumesic 2011)

In the hydrogenation reaction, when molecular hydrogen is the H-donor, no byproducts are produced. However, when alcohol is the H-donor, it goes through a dehydrogenation to produce hydrogen atoms, and the byproducts are an aldehyde or a ketone (ROH to RO in Fig. 2), (Wang *et al.* 2020b). The regeneration of the solvent can restore it, as in the case of alcohol (Geboers *et al.* 2014), which can be reused (Fig. 3). Hydrogenation is exothermic and depends on the catalyst activity, whereas cyclization is endothermic (Wang *et al.* 2020b). The C-H formation in the  $\gamma$ -carbon to form the alkoxy intermediate is rate-controlling (Mamun *et al.* 2019), whereas the ring closure is easy (Chia and Dumesic 2011; Mamun *et al.* 2019). Strongly acidic conditions favor the two-step process (Hengne *et al.* 2016).

Risks involved in the direct hydrogenation reactions comprise fire or explosion due to the possible pyrophoric nature of the catalysts or substrates, flammable solvents, hydrogen pressure, or unstable intermediates (Chandra and Zebrowski 2016). Current industrial hydrogen production involves natural gas or fossil hydrocarbons reforming (Yu *et al.* 2020b). Thus, the use of a renewable H-donor is an interesting alternative. Alcohols are also products from a conventional refinery, but their use requires fewer precautions and lower equipment costs since the reactors require less complexity because of the lower pressures. In the future, it is expected that both molecular hydrogen and alcohols can be obtained in biorefineries (Campos 2018; Schubert 2020). LA or LE CTH involves Meerwein-Ponndorf-Verley (MPV) reduction (Johnstone *et al.* 1985). If used together with non-precious metal heterogeneous catalysts, MPV gives selective results, and the solvent used can be recycled after being used (Chia and Dumesic 2011).

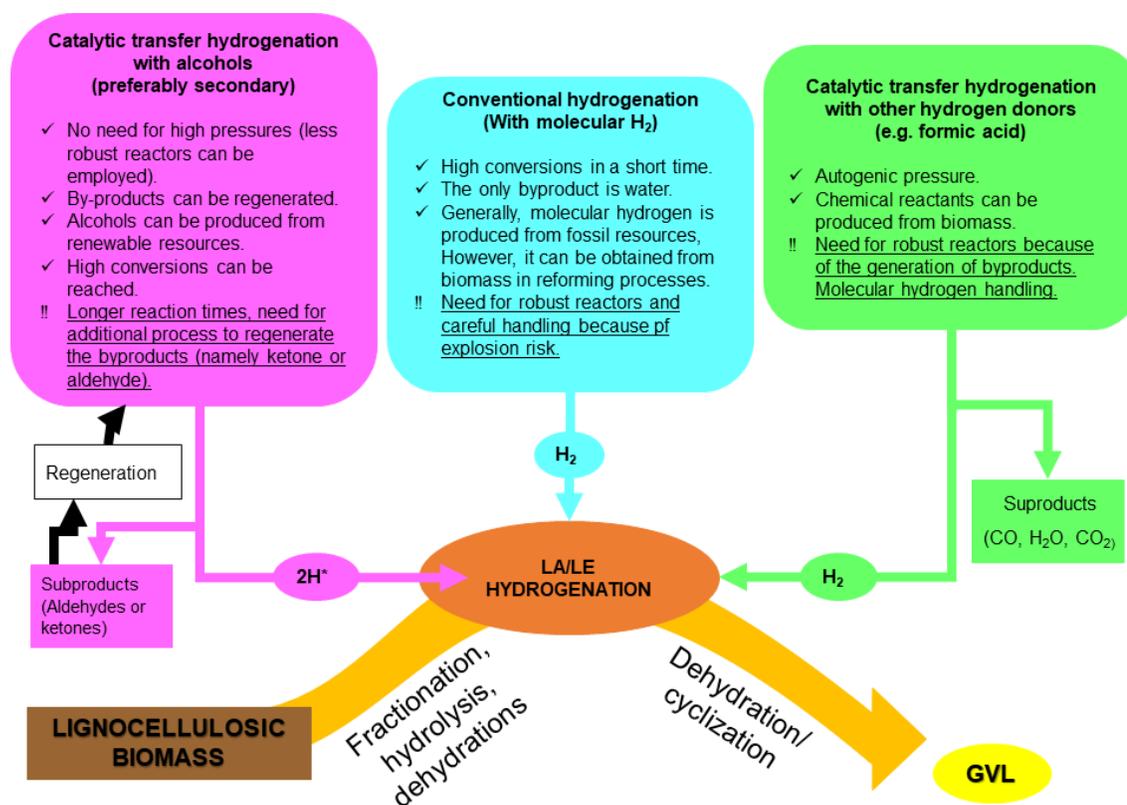


Fig. 4. Possibilities for the hydrogenation of LA or LE

When using a mixture of formic (FA) and levulinic acid as the substrate in the presence of a suitable catalyst with metal sites, FA dehydrogenates into CO<sub>2</sub> and H<sub>2</sub>, and the latter leads to direct/conventional hydrogenation (Al-Naji *et al.* 2020; Deng *et al.* 2009). It is hard to use the CO<sub>2</sub> in other processes or to encapsulate, whereas the CTHC by-products can be regenerated or commercialized (Chia and Dumesic 2011). Furthermore, FA can also become dehydrated, leading to H<sub>2</sub>O and CO as additional by-products, which lowers the selectivity towards GVL. Ruppert *et al.* (2016) found that LA conversion using formic acid as a hydrogen source is sensitive to the catalyst structure and the preparation method (Ruppert *et al.* 2016). Unfortunately, FA is corrosive, and its use in the design of a process requires corrosion-free reactors (Shivhare *et al.* 2020). The hydrogenation with FA could be a great alternative for transition refineries changing from fossil to biomass raw materials. In addition, when handling molecular hydrogen, a reduced atmosphere is crucial because of the hazard of fire or explosion of any form of hydrogen with air, oxygen, or sparks (Chandra and Zebrowski 2016). For that reason, the reactor has to be purged before the hydrogen enters and after the reaction is completed. This situation means that there is an advantage for CTHC because several tests in glass flasks have also given good results (Kumaravel *et al.* 2020; Rojas-Buzo *et al.* 2018). Figure 4 shows the comparison between the three possibilities for hydrogenation.

Depending on the chain length, levulinate esters can be blended with diesel range fuels or used as an oxygenate in diesel fuel (Windom *et al.* 2011). On the other hand, 4-HPA can be used for polyester production (Gorenflo *et al.* 2001). In this respect, if levulinate ester or 4-HPA are generated as by-products, it would still be interesting to obtain both LE and GVL, varying the process conditions (Kasar *et al.* 2018).

## REACTIONS VARIABLES

CTHC comprises two reactions: hydrogenation and cyclization (also called lactonization or intraesterification). When starting from LA, there is also an esterification step with the alcohol (Fig. 2). GVL yield is the product of substrate conversion (of LA or LE) and product selectivity towards GVL.

Many variables are involved in GVL yield via the CTHC, the most important being the substrate (*i.e.*, LA or LE), reaction phase, time, temperature, pressure, agitation, solvent, and catalyst.

### Substrate

Product purity is related to the obtaining method. Currently, the CTCH is carried out using commercial high purity reactants (>95%). Experiences with LA or LEs from biomass use molecular hydrogen in the hydrogenation and (or) noble metals as catalysts (Putro *et al.* 2015; Wang *et al.* 2020b). The obtaining of GVL by CTCH using in-situ biomass-obtained LA or LEs is a challenge.

Levulinic esters have lower boiling points (Geboers *et al.* 2014) and are less corrosive than LA (Wang *et al.* 2020b). The former benefits the separation by distillation of the resulting products. When using LE, there is a risk of transesterification instead of transfer hydrogenation. In this case, the H-donor alcohol exchanges the alkyl chain with the LE (R<sub>1</sub> and R<sub>2</sub> in Fig. 3), which can decrease GVL productivity (Shivhare *et al.* 2020) and generate an alcohol mixture in the product stream (Geboers *et al.* 2014). The use of the same alkyl in the substrate and the H-donor (R<sup>1</sup>=R<sup>2</sup>) can help to overcome this drawback.

However, as previously mentioned, levulinic esters can be valuable in a multi-product biorefinery, and the ratio of the byproduct/GVL can be regulated by tuning the catalyst activity.

Low concentrations are needed to get yields higher than 90% when working with CTHC since there is an increased risk of steric hindrance. The risk is even more if the alcohol donors have a long aliphatic chain. LA concentration in CTH is usually lower than in CDH (Xu *et al.* 2017). Hengne *et al.* (2016) showed that LA concentration in the reactor (5-20% v/v) was indirectly proportional to LA conversion and GVL selectivity, decreasing from 99 and 99% to 79 and 39%, respectively, with an increase in LA concentration from 5-20% using 50%-Ni-MMT (200°C, atmospheric pressure with N<sub>2</sub> purge). Chia and Dumesic (2011) also found that GVL yield improves when the hydrogen donor solvent/substrate ratio increases when starting from LE (butyl levulinate), using ZrO<sub>2</sub> at 150 °C.

To increase the concentration of the reactant in CTHC, Wan *et al.* (2021) employed glucose phosphate carbamide zirconium (GluPC-Zr). Knowing its characteristics could help to find a similar catalyst from cheaper transition metals. GluPC-Zr has Lewis acid-base properties together with high porosity. It was possible to produce GVL with 95-98% yields with IPA, using a solvent/reactant ratio of 7. Since it was possible to manage high concentrations of LA (1.87M), the achieved turnover frequency was up to 8.2 mmol GVL g<sup>-1</sup> catalyst h<sup>-1</sup>, which is higher than for other previously reported Zr catalysts (TOF 0.2-2.4) (Wan *et al.* 2021). In addition, it was possible to reuse it up to seven cycles, still providing 95% GVL yield. However, the reaction time remains high (12 h) since the conversion of LA is already higher than 80% in 2 hours, and it is fully converted at 4 hours. IPL takes more time for cyclization and gets a GVL yield higher than 90% (Wan *et al.* 2021).

## Reaction Phase

LA or LEs are liquids up to 246 °C at atmospheric pressure, and the obtaining of GVL follows the mechanism of the reaction previously described (Fig. 2 and 3). However, it can change when performed at higher temperatures or pressures because of the reaction phase modification to vapor: LA can convert to angelica-lactone by hydrogenation and afterward is dehydrated to GVL (Yu *et al.* 2020a). However, vaporizing LA requires high temperatures (>200 °C). Besides, LA streams derived from carbohydrates may contain traces of the acids used for the hydrolysis of sugars or biomass fractionation. Thus, for scaling up the CTHC process of LA, the use of the vapor phase would not be recommended due to the generation of acid gases (Wright and Palkovits 2012) with their corresponding corrosion problems.

Compared to the vapor phase, the liquid does not need robust reactors and makes the process simpler. However, the leaching of the active phase from catalysts that lead to irreversible deactivation can be a risk not present in the gaseous phase (Sádaba *et al.* 2015). Optimizing the reaction conditions or the catalyst structure can minimize this effect.

## Time

CTH is usually related to longer reaction times compared to CDH. CDH can reach quantitative conversion of the reactant in minutes, whereas for CTH the time is usually in hours. However, the DH needs to employ high pressure to guarantee the contact of the hydrogen with the reactant. Increasing the reaction time improves GVL yields with levulinates of short alkyl chains (Geboers *et al.* 2014). Hengne *et al.* (2016) evaluated

CTHC of LA from 1 to 5 h with 10%Ni/MMT leading to a maximum LA conversion of 98% and GVL selectivity of 81%, which represents an increment of approximately 15 and 35%, respectively. Co-catalysts, electrochemistry, or microwaves can be used to decrease time requirements and enhance GVL yields (Al-Shaal *et al.* 2016; Hsiao *et al.* 2020; Lin and Lin 2019; Yun *et al.* 2020).

### Temperature

The transformation from LA to GVL is relatively slow at 100 °C (Deng *et al.* 2009). Chia and Dumesic found that the CTH is evidenced at temperatures higher than 100 °C (Chia and Dumesic 2011). The preferred starting temperature is 150 °C to avoid intermediates products generation. An increase in temperature leads to a higher GVL yield (Chia and Dumesic 2011; Hengne *et al.* 2016) since it increases the kinetic energy of the molecules and, therefore, the probability of effective contact.

However, low temperatures at longer reaction times give a chance to intermediates to react completely, finally reaching the GVL.

Heat transference from the heat resource to the reaction medium is relevant. In all reactors, the conduction transference from the recipient to the reaction media occurs first. However, how the heat reaches the reactor varies with the equipment. The heat transference can be by radiation (microwaves), convection (bath heated), or conduction (jacket heated by electric resistance). The time seems to be the principal difference since microwaves take less time to heat a reactor at a given temperature than electric resistances (Amarasekara and Hasan 2015; Al-Shaal *et al.* 2016), or a bath heating. The induction time, which is the section of slow reaction rate, is lower in the case of microwave-assisted heating (Amarasekara and Hasan 2015).

### Pressure and Agitation

When carrying out the CTHC in liquid media using alcohols as the hydrogen source, the pressure in the reactor is produced by an inert gas, such as nitrogen, argon, or helium. In these cases, higher pressures do not seem to appreciably improve the GVL yield. On the contrary, an increase in hydrogen pressure leads to a higher hydrogen concentration in the liquid in conventional hydrogenation, resulting in better GVL yields (Gilkey and Xu 2016). Besides, in CTHC, high-agitation systems are relevant to ensure the contact between the catalyst and the reactant.

Formic acid is generated with levulinic acid in an equimolar ratio, making it an inexpensive hydrogen donor. Nevertheless, its decomposition results in CO<sub>2</sub> and H<sub>2</sub> formation, raising the reactor pressure (Yu *et al.* 2020a) and increasing the equipment costs. For this reason, LA should be separated from FA before its use when using CTHC for producing GVL.

### Solvent

Water is the most eco-friendly solvent to consider. However, when the solvent is water, the system achieves an equilibrium 4-HVA (4-hydroxyvaleric acid)/GVL/water at every pH and at or above 100 °C, which can be a problem since 4-HVA can be a ligand for transition metals (Wong *et al.* 2017), which can lower the catalyst activity. This needs to be considered when using LA and long reaction times because LA esterification produces water (Fig. 2). It has been suggested that water harms the CTH reaction at room temperature when using IPA as a hydrogen donor (Yang *et al.* 2013). Kasar *et al.* (2018) converted LA to GVL using methanol/water as a solvent and found that water can lead to

metal leaching from the catalyst. Thus, increasing the MeOH/water ratio to 95:5 suppressed leaching and increased selectivity (Kasar *et al.* 2018). In this line, Hengne *et al.* (2016) obtained 99% conversion with <0.01 ppm metal leaching when IPA was used as a solvent and 72% conversion with 125 ppm leaching when using water (Hengne *et al.* 2016).

Primary alcohols such as 1-butanol or ethanol lead to GVL in mixtures with several by-products, resulting in less selectivity (Chia and Dumesic 2011). Besides, the H-atom required for the hydrogenation is delayed since the rate of decomposition is slower compared to secondary alcohols (Hengne *et al.* 2016). Secondary alcohols have lower reduction potential and are expected to be better H-donors (Amarasekara and Hasan 2015). The longer the alkyl chain of the secondary alcohol used as a hydrogen donor, the lower the hydrophilicity. So, both the diffusion of the catalyst and the proton in the reaction medium could be hampered. Isopropanol (or 2-propanol) is the smallest available secondary alcohol. It is soluble in water, causes low steric impediment (Yu *et al.* 2020b), and leads to acetone by dehydrogenation, a widely used chemical. It has been reported that using secondary alcohol with a longer alkyl as 2-butanol, the GVL yield decreased together with an increase of the ester yield, which could be due to steric hindrance (Al-Shaal *et al.* 2016).

Glycols are also candidates with great potential for transfer hydrogenation. Sung *et al.* (2020) probed triscarbene-modified iridium catalysts for the LA CTHC using glycerol (G), propylene glycol (PG), ethylene glycol (EG), isopropanol (IPA), and ethanol (EtOH) with resulting turnover numbers of 500,000 (G), 339,000 (PG), 242,000 (EG), 334,000 (IPA), and 208,000 (EtOH), respectively (Sung *et al.* 2020). Nevertheless, yields are less than 70%, so this field has to be further explored. G, PG, and IPA are C3 alcohols that differ in their molecules -OH content. Polyols have a great potential in CTHC, but the regeneration of the dehydrogenated molecule should be assessed.

## Catalyst

Catalysts are employed to lower the activation energy, making a reaction more feasible or increasing the reaction rate (Imelik and Vedrine 1994). Solid heterogeneous catalysts are preferred over homogeneous ones due to their recyclability and selectivity, leading to lower costs. Homogeneous catalysts are also usually associated with problems of toxicity, corrosiveness, and difficult separation from the reaction medium. The most famous heterogeneous catalyst for LA hydrogenation is Ru/C, but its susceptibility to corrosion by acids has prompted researchers to consider its replacement or enhancement (Wright and Palkovits 2012; Yang *et al.* 2020). The main catalysts variables to consider are porosity, surface area, structure, nature, and loading of metal, support, acidity, deactivation, and recyclability

Catalytic activity is the rate of substrate conversion per unit of time, and selectivity is the ability to carry out a particular reaction within a group of possibilities, reaching the specifically desired product (Imelik and Vedrine 1994). The catalytic activity varies with the substrate since it can be threatened by the electronic structure modification or the geometric array of the active sites caused by the reactant (Imelik and Vedrine 1994). Chia and Dumesic (2011) obtained different GVL yields when using the same catalyst and reaction conditions, possibly because of the amphoteric nature of the catalyst. It has been suggested that the LA acid functional group is strongly adsorbed onto the basic sites of the ZrO<sub>2</sub> (Chia and Dumesic 2011).

Many experiments have used Zr (Chia and Dumesic 2011; Bui *et al.* 2013; Valekar *et al.* 2013; Hengne *et al.* 2014; Tang *et al.* 2014a; Gao *et al.* 2017; Kuwahara *et al.* 2017;

Li *et al.* 2017, 2018a; Sun *et al.* 2018; Cabanillas *et al.* 2019; Yun *et al.* 2019; Tabanelli *et al.* 2020), or precious metals such as Ru (Kobayashi *et al.* 2011; Yang *et al.* 2013; Gao *et al.* 2017; Shende *et al.* 2019), Pt, or Pd (Hsiao *et al.* 2020) in CTHC, showing excellent catalytic activity. Tuning the structure can lead to comparable results. For example, it has been seen that Hf-MOFs and Zr-MOFs share properties such as high thermal and chemical stability (Rojas-Buzo *et al.* 2018). Finding a comparable catalyst made of non-noble metals is a challenge, but recreating certain structures seems to be a good approach.

Concerning porosity and surface area, catalysts in CTHC reactions are preferred to be micro and mesoporous, but the reaction conditions can hamper the material's porosity. High surface areas increase the diffusion of reactants and dispersion of metal sites (Xu *et al.* 2017). For economic reasons, supported catalysts are preferred because they can reach high metal dispersion with lower charge, improve pore volume, and increase specific surface area, among others (Alonso *et al.* 2012).

Munnik *et al.* (2015) stated that, for practical reasons, catalysts for industrial reactors should have a high density of active sites (*e.g.*, high metal dispersion) for maximizing activity per unit volume due to the size limiting (Munnik *et al.* 2015). Metal macroscopic distribution on the support could overcome some reaction barriers. For fast reactions, or when secondary reactions are a problem, it is preferable to use an eggshell-like distribution. However, when there is a susceptibility to attrition, it is better to choose an egg-white-like one (Munnik *et al.* 2015). Hengne *et al.* (2016) evaluated from 10% to 50% Ni loading supported in MMT. LA conversion increased from 95 to 99% and GVL selectivity from 61 to 99%, which was attributed to the higher availability of active Ni sites (Hengne *et al.* 2016). Cai *et al.* (2017) experimented using acidic Al<sub>2</sub>O<sub>3</sub> without the addition of metal sites, with significantly poorer performance than using NiCu nanoparticles, exposing the importance of metal sites in catalytic performance for CTHC (Cai *et al.* 2017).

Luo *et al.* (2013) found that when using Ru catalysts supported in acidic solids at 40 bar and 200 °C, the higher the acidity of the support, the greater the pentanoic acid (PA) yield (Luo *et al.* 2013). However, the strength of the acidity must be limited for obtaining GVL without producing the ring-opening. Silica and titanium are not acid supports. Since this characteristic is desirable (Hengne *et al.* 2016), they are unsuitable for the CTHC reaction. However, they could be an option if changing their structure since they have good thermal and mechanical stability (Almeida *et al.* 2020). Carbon supports can resist harsh aqueous media but are not resistant to coke burn-off (Lange *et al.* 2010). Besides, activated carbons are not mechanically resistant. Metal-support interactions are critical because they can generate synergistic or antagonistic relationships. Nevertheless, the weakness of one can compensate for the strength of the other. A difference in the support phase can significantly affect the catalytic activity for two possible reasons (Maumela *et al.* 2021), their metal-support electronic interactions and morphology.

GVL yield obtained from LA or LE is highly sensitive to the ratio of Lewis/Brønsted acid sites. The Lewis acid sites (electron acceptors) catalyze the hydrogenation of the gamma hydroxyl of LE to obtain the 4-hydroxy-levulinate, whereas the acidic Brønsted sites (proton H<sup>+</sup> donor) catalyze the subsequent intraesterification to GVL (Hengne *et al.* 2016). It has been proposed that acidic and basic sites in the catalyst play a synergistic role (Xie *et al.* 2016; Sung *et al.* 2020; Vasanthakumar *et al.* 2020; Yu *et al.* 2020b; Wan *et al.* 2021). Wan *et al.* (2021) proposed that the Lewis acidity of the metal cation Zr<sup>+4</sup> contributes to the activation of the LA carbonyl group, whereas the basic O<sup>-2</sup> produces the disaggregation of the hydroxyl groups in IPA, and these effects should

significantly accelerate the CTH reaction (Wan *et al.* 2021). However, catalysts of purely basic nature, such as CaO and hydrotalcite, did not improve 4-HPE lactonization (Geboers *et al.* 2014).

### Catalyst Deactivation and Recyclability

Catalysts' activity and selectivity are related to characteristics such as structure and morphology, among others, which are in turn developed by the preparation method. The active sites are atoms or groups of atoms involved in the reaction, while the others are inactive (Imelik and Vedrine 1994). The quantity and availability of these active sites determine the recyclability of the catalyst, which is the number of times that it can be reused. These active sites can be hampered by different reasons, which leads to catalyst deactivation.

Selective heterogeneous catalysts have an environmental advantage because they do not generate effluents that are difficult to separate. Unfortunately, several works employing these catalysts do not include a recyclability test in their set of experiments. In general, if the deactivation reasons are reversible, *i.e.*, they were not sintered nor poisoned by heavy metals, then the catalyst can be regenerated and therefore recycled. To restore the catalytic activity of the catalyst after deactivation, washing with solvents such as ethyl-ether, acetone, methyl tert-butyl ether (MTBE), or ethanol, and calcination in the air is needed (Chia and Dumesic 2011).

Although deactivation is inevitable, it can be avoided, postponed, or even be reverted, the latter by a regeneration. The deactivation mechanism can be of physical (fouling/coking and mechanical alterations), thermal (sintering), or chemical (poisoning, formation of new inactive phases, and leaching) nature (Sádaba *et al.* 2015). They are often not independent, meaning that deactivation can be caused by more than one.

Leaching of the catalyst components into the reaction medium is one of the most common deactivation problems since most reactions are carried out in the aqueous/liquid phase (Sádaba *et al.* 2015). Changing the structure of the catalyst, adding a promoter, or change the reaction phase can affect this outcome. However, angelica-lactone can be generated in the vapor phase, and this compound can produce coking, which is acids-catalyzed (Alonso *et al.* 2013).

Yu *et al.* (2020) reported minor deactivation in Ni<sub>3</sub>P-CePO<sub>4</sub>(x) catalysts at 180 °C after 4 cycles using 2-propanol as the solvent. They determined that the cause was insoluble organics or polymers deposition, rather than by changes of phase/crystal or acidic/basic properties, or active phase leaching (Yu *et al.* 2020b). Chia and Dumesic tested ZrO<sub>2</sub> in a continuous flow reactor using butyl levulinate as substrate and 2-butanol as solvent. They observed a fast deactivation in 100 h followed by a stable activity, probably due to coking. The activity was restored, and the deactivation followed the same profile after calcination (Chia and Dumesic 2011). However, when using levulinic acid, the strong adsorption of the LA acid functional group onto the basic sites of the ZrO<sub>2</sub> catalyst caused its deactivation. However, adding a MgO base led to a 4-fold increase in GVL yield. Nevertheless, the disadvantage is the generation of a byproduct that has to be separated. So, adding basic sites need a careful evaluation (Amarasekara and Hasan 2015). Another possibility is using an amphoteric catalyst to improve the catalyst performance (Chia and Dumesic 2011).

In comparison, noble metals provide high activity but get poisoned more easily and leached in aqueous media. However, Yang *et al.* (2020) synthesized a stable N-doped carbon shell-like structured catalyst, comprising yolk-like Ru nanoparticles, obtaining

99.4% LA conversion, 99.9% GVL selectivity by DH, with 9 times recycled without significant changes (Yang *et al.* 2020). Feng *et al.* (2020) also immobilized Ru nanoparticles in a Zr-based metalorganic framework (MOF-808) with good dispersion, reaching LA conversion of 100% and GVL selectivity higher than 99% (Feng *et al.* 2021). Both sets of results show that encapsulation and metalorganic frameworks are good alternatives for getting high recyclable non-noble metal catalysts.

Promoters can improve catalytic activity, selectivity, or recyclability. For example, cation exchange with lanthanum can improve the hydrothermal stability of microporous structures of Y-Zeolites (Vu *et al.* 2021)

## REPORTED EXPERIENCES AND DISCUSSION

Table 1 presents the best results reported in the literature, aiming to show the relationship between CTH's previous enounced variables and this work's considerations. Table 2 shows the different techniques used to identify the properties of the catalysts used in the CTHC reaction.

In this reaction, the pore volume and the specific surface area seem to have a low impact on the final result, as shown in Table 3, comparing the results obtained with the catalysts with pore volume in the range of 0.074 to 1 cm<sup>3</sup> g<sup>-1</sup> and in the order of 3000 to 6000 cm<sup>3</sup> g<sup>-1</sup>. A cause could be the low concentration of the reactant employed in CTH reactions. However, this concentration will increase when scaling up the process, which could modify the situation.

Gong *et al.* (2018) explained that LA is captured by electrophilic Cu<sup>+</sup> (the metal cation), and then TH is accomplished by MPV reaction at Cu catalyst. Cu<sup>0</sup> species (metal center) act as active centers for the dehydrogenation of IPA to generate active H\* (Gong *et al.* 2018).

Hengne *et al.* (2016) noted that the strong acidic strength of the catalyst support (montmorillonite, MMT) and the Brønsted nature of the supported catalyst helped the LA esterification with i-PL and also facilitated the cyclization towards GVL. Luo *et al.* (2013) suggest that weak Brønsted acid sites in the support are preferred. The exchange of sites in the catalyst can vary the type of acidic sites and the strength of the acidity (Luo *et al.* 2013). For example, incorporating metal cations in a zeolite framework can increase Lewis acidity, but the acid sites can be weaker, and the framework structure can remain unmodified (Ahmadvand *et al.* 2020).

Wang *et al.* (2019) used a Zr-based MOF, UiO-66-(COOH)<sub>2</sub>, for the esterification of LA with ethanol. They attributed the highest yields of ethyl levulinate to the synergistic relation between Lewis acidic Zr clusters and Brønsted acid sites, conferred by the carboxylic functionalization of the UiO-66 framework (Wang *et al.* 2019). This important issue for LA conversion to GVL was also highlighted by Kuwahara *et al.* (2017), revealing that functionalization can affect the crystallinity and surface area of the catalyst (Kuwahara *et al.* 2017).

An alternative to explore is metal-organic framework production using biomass-derived ligands. The source can be dicarboxylic acid-rich molecules in a biorefineries platform.

**Table 1.** Reaction Conditions and Catalyst Characteristics of CTHC Processes for GVL Production, Starting from LA or LE Without an External Molecular Hydrogen Source Employing Non-noble Metal Catalysts

Experimental							Catalyst					Results				Ref.	
Precursor	H-donor/ Solvent	P (MPa)	T (°C)	Time (h)	Purge	Voc	Name	P M	Vpore (cc/g)	Dprom (nm)	S (m <sup>2</sup> /g)	Le/ Br	R	By-products/ intermediates	Conv (%)	Selec. (%)	
LA 5 mL	IPA 95 mL	Atm	200	1	N <sub>2</sub> atm	100 / 300	50%-Ni-MMT 500 mg	-	0.074	4.3	34	Yes	5	IPA-L, 0.01% 4-H-IPA-L, 1%	99	99	Hengne <i>et al.</i> 2016 (Hengne <i>et al.</i> 2016)
LA 5 mL	IPA 95 mL	Atm	200	1	N <sub>2</sub> atm	100 / 300	50%- Ni/Al <sub>2</sub> O <sub>3</sub> 500 mg	-	0.059	2.9	18	-	-	IPA-L, 0.01% 4-H-IPA-L, 10%	99	90	
LA 5 mL	IPA 95 mL	Atm	200	1	N <sub>2</sub> atm	100 / 300	50%-Ni-ZnO 500 mg	-	0.084	7.8	20	-	-	IPA-L, 64% 4-H-IPA-L, 1%	92	35	
LA 0.02 mmol	IPA 5 mL	2MPa N <sub>2</sub>	220	5	N <sub>2</sub> atm	-/25	17.1 wt%Cu/AC	I	0.31	20.8	800	-	5	IPL < 10%	>99	90	Gong <i>et al.</i> 2018 (Gong <i>et al.</i> 2018)
LA 3 mmol	IPA 50 mmol	0.7- 0.8 MPa N <sub>2</sub>	110	8	N <sub>2</sub>	-/50	SnO <sub>2</sub> /SBA- 15 (Si/Sn=53) 140 mg	G	-	6.5	359	Yes	6	IPL	85	95	Xu <i>et al.</i> 2017 (Xu <i>et al.</i> 2017)
LA 3 mmol	IPA 50 mmol	0.7- 0.8 MPa N <sub>2</sub>	110	4	N <sub>2</sub>	-/50	SnO <sub>2</sub> /SBA- 15 (Si/Sn=53) 140 mg	G	-	6.5	359	Yes	6	IPL	59	91	
LA 3 mmol	IPA 50 mmol	0.7- 0.8 MPa N <sub>2</sub>	110	4	N <sub>2</sub>	-/50	SnO <sub>2</sub> /MCM- 41 140 mg	G	-	-	-	Yes	-	IPL	63	88	
LA 20 mmol	IPA 38 mL	1 MPa N <sub>2</sub>	180	2	N <sub>2</sub> atm, 6x	- /10 0	Ni <sub>3</sub> P-CePO <sub>4</sub> (Ce/Ni=0.1) 200 mg	C P	-	-	47.6	-	4	4-HPA, IPL	100	90	Yu <i>et al.</i> 2020 (Yu <i>et al.</i> 2020b)
EL 4.2 mmol	IPA 10 mL	Atm N <sub>2</sub>	220	6	Atm N <sub>2</sub>	-	NiCu-0.67 (Ni/Cu=2.10) 100 mg	I	-	8.6	163	-	5	10% sel IPL	92	89	Liu <i>et al.</i> 2019 (Liu <i>et al.</i> 2019)

<b>EL</b> 1 mmol	2-BuOH 3 mL	Atm	150	12	-	-	10Cu-5Ni/Al <sub>2</sub> O <sub>3</sub> 100 mg	II	0.36	10.1	143.5	-	10	-	100	97	Cai <i>et al.</i> 2017 (Cai <i>et al.</i> 2017)
<b>ML</b> 1.4 mmol	IPA 7 mL	Atm	120	2	Ar	/20	Raney Ni 300 mg dry	I W I	-	-	-	-	5	4-HPE	100	≈85	Geboers <i>et al.</i> 2014 (Geboers <i>et al.</i> 2014)
<b>LA</b>	IPA (LA/IPA=1/ 4 mol)	Atm	200	3	N <sub>2</sub>	-	Sn/Al-SBA-15 (Si/Sn=25) 100 mg	I	1.41	5.49	710	Yes	5	-	99	100	Kumaravel <i>et al.</i> 2020 (Kumaravel <i>et al.</i> 2020)
<b>EL</b> 1 mmol	IPA 5 mL	1 MPa N <sub>2</sub>	150	10	N <sub>2</sub>	-/25	Hf-USY-8 zeolite Si/Al=73 50 mg	-	0.559	≈14	953	Yes	5	4-HPE	98.5	95.7	Tang <i>et al.</i> 2019 (Tang <i>et al.</i> 2019a)
<b>LA</b> 1 mmol	IPA 4 mL	-	150	4	-	-/22	52% Hf-ATMP 200 mg	-	0.25	16.7	222.6	-	-	-	>99	98	Xie <i>et al.</i> 2016 (Xie <i>et al.</i> 2016)
<b>ML</b> 1 mmol	IPA 4 mL	-	150	7	-	-/22	52% Hf-ATMP 200 mg	-	0.25	16.7	222.6	-	-	-	>99	95	
<b>BL</b> 1 mmol	IPA 4 mL	-	150	7	-	-/22	52% Hf-ATMP 200 mg	-	0.25	16.7	222.6	-	-	-	88	91	
<b>EL</b> 1 mmol	IPA 4 mL	-	150	4	-	-/22	52% Hf-ATMP 200 mg	-	0.25	16.7	222.6	-	5	-	95% EL conversion 86% GVL yield		
<b>EL</b> 1 mmol	IPA 4 mL	-	150	7	-	-/22	52% Hf-ATMP 200 mg	-	0.25	16.7	222.6	-	-	-	>99	97	
<b>EL</b> 0.1 mmol	IPA 0.4 mL	-	120	8	-	-/4	Hf-MOF-808 10 mol%	-	0.30	-	458	-	5	-	94 % GVL yield		Rojas-Buzo <i>et al.</i> 2016 (Rojas-Buzo <i>et al.</i> 2018)

LA 1 mmol	IPA 3 mL NaOH 40mg, 1 mmol		100	10		-/10	MIL-88B(Cr) 3 mg	-		3210	40	Yes	-	-	99 % GVL yield	Vasanthak umar <i>et al.</i> 2020 (Vasantha kumar <i>et al.</i> 2020)		
LA 1 mmol	IPA 3 mL NaOH 40mg, 1 mmol		100	10		-/10	NH2-MIL- 88B(Cr) 3 mg	-		4930	40	Yes	-	-				
LA 1 mmol	IPA 3 mL NaOH 40mg, 1 mmol		100	10		-/10	MIL-88B(Fe) 3 mg	-		1410	40	Yes	5	-				
LA 1 mmol	IPA 3 mL NaOH 40mg, 1 mmol		100	10		-/10	NH2-MIL- 88B(Fe) 3 mg	-		6200	40	Yes	-	-				
EL 1 mmol	IPA	-	80	9	Ar	-	Raney Ni 30 mg	-	-	-	-	-	5	-	>99% GVL yield	Yang <i>et al.</i> 2013 (Yang <i>et al.</i> 2013)		

LA: Levulinic acid; EL: Ethyl levulinate; 2-PL: 2-Propyl levulinate; ML: Methyl Levulinate; BL: Butyl Levulinate; P: pressure, T: temperature, Voc: Occupied volume; PM: Preparation method; Vpore: Pore volume; DProm: Average diameter of pores; S: Specific area; Le/Br: presence or ratio of Lewis/Brønsted acid sites; R: cycles of recycling assessed; Conv.: conversion; Selec.: selectivity, Ref.: reference; I: Impregnation; G: Grafting; CP: Co-precipitation; II: Incipient Impregnation.; IWI: Incipient Wetness Impregnation

**Table 2.** Techniques and Equipment to Assess Different Characteristics of Catalysts

Characterization/Property	Technique/Equipment
Acid strength	Temperature-programmed desorption with ammonia for acid sites (NH <sub>3</sub> -TPD) and CO <sub>2</sub> for basic sites (CO <sub>2</sub> -TPD)
Weak/strong-Lewis/Brønsted sites	Pyridine/collidine adsorption in Fourier-transform infrared spectroscopy
Pore volume, superficial area, porosity, particle size distribution	N <sub>2</sub> Chemisorption isotherms, interpretation with BET, BJH, and t-plot models
Particle size, morphology	Transmission or Scanning Electronic Microscopy (TEM or SEM, respectively)
Dispersion and surface area of the supported metal	Titration (e.g., with N <sub>2</sub> O)
Elemental analysis, metal species, and support phase	Energy Dispersive X-Ray Spectroscopy (EDS or EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray Auger Spectroscopy (XAES)
Metal leaching	Inductively coupled plasma - optical emission spectrometry (ICP-OES)

Xu *et al.* (2017) probed the need for acidity in the support by testing SBA-15, which is non-acidic mesoporous silica ( $S_{\text{BET}}=565 \text{ m}^2$ ,  $D_{\text{pore}}=7.5 \text{ nm}$ ) for the transfer hydrogenation of LA with IPA. The reaction rate was undetectable under the reaction conditions employed (3 mmol of LA, 50 mmol of IPA, 110 mg of catalyst, 140 °C, 20 min) (Xu *et al.* 2017). It is possible to produce a metal catalyst with Lewis and Brønsted acidity from inert silica support by uniformly loading dispersed metal species, since ultra-small metal nanoclusters (such as Sn, Al, Zr) can create Brønsted acid sites from the hydroxyl groups located on the surface (Wang *et al.* 2014; Xu *et al.* 2017). However, high dispersion does not imply high loading. The latter can hamper the acidic sites of the catalyst by aggregation of the metal species, which can obstruct adsorption and decrease both surface area and pore diameter. Xu *et al.* (2017) noticed this in the pyridine adsorption IR spectra when high loads of SnO<sub>2</sub>/SBA-15 (Si/Sn ratio of 13) showed poorer peaks corresponding to interactions of Brønsted acid sites and weaker Lewis acid, compared to the optimum catalyst which had a Si/Sn ratio of 53 (Xu *et al.* 2017).

In CTHC processes, the time-determining step seems to be the esterification of the hydroxy-levulinic ester to generate the GVL, since the conversion of LA (or LE) reaches its maximum in a short time compared with the maximum GVL selectivity. However, in CDH followed by cyclization, the rate-determining step is hydrogenation due to the difficulty of molecular hydrogen diffusion into the liquid. 4-HPA has a lower steric hindrance than 4-HPE, and because of this, lactonization can be easier to achieve.

Compared to direct hydrogenation, lower concentrations of substrate and longer reaction times are required. However, the use of ionic liquids, co-catalysts, microwaves, and electrochemistry, among others, can help to upgrade the processes. The major obstacle to the scalability of the CTHC process is the use of low concentrations and recyclability of the catalyst, which increases the costs of the process. The use of noble metals with good results at high concentrations with almost null loss of catalytic activity (Wan *et al.* 2021) gives hope that a change in structure or preparation method could achieve similar results in shorter times.

The preparation of the catalyst is relevant because the properties can significantly depend on the employed method. For example, zeolites, which are aluminum silicates that

naturally have Lewis and Bronsted acid sites and high acidity, were used in CDH processes (Licursi *et al.* 2018). Clays and mesoporous silicas are high-pore-size versatile catalysts, making them a great alternative to explore. Metal-organic frameworks are promising catalyst types since they can confer excellent catalytic activity using metal centers that can be non-noble (Vasanthakumar *et al.* 2020). Also, a biorefinery can produce plenty of dicarboxylic acids that can be exploited as ligands in these structures. Hence, the combining of these two proposals is strongly encouraged for the CTHC processes to decrease reaction times, which seems to be the last variable to unlock.

The deactivation and recyclability of the catalyst have great importance in the process. Thus, to regenerate catalyst' activity and selectivity, the description of the mechanism is fundamental to find the best alternative. Recyclability improves sustainability in both economic and environmental aspects.

## CONCLUDING STATEMENTS

The development of a suitable system for obtaining GVL from biomass requires the optimization of reaction conditions, catalyst characteristics, and substrates for the LA or LE catalytic transfer hydrogenation without external molecular hydrogen. According to the literature, the desirable conditions to carry out the CTHC at moderate or low pressures ( $\leq 2$  MPa) involve:

- Low reactant concentration.
- The use of secondary alcohols as both solvent and hydrogen donors, using a high solvent: substrate ratio, higher than 4:1.
- Bifunctional metal/acid catalyst, high metal dispersion in the acidic support with good interaction metal/support to minimize leaching, and moderate acidity when using high temperatures. The deactivation mechanism is needed to perform the optimal regeneration step to reuse the catalyst and extend its lifecycle.
- If ionic liquids or other co-catalysts are not employed, temperature ranges from 150 to 200 °C guarantee quantitative raw material conversion without intermediates generation.
- When working with levulinic esters, the solvent should be secondary alcohol of an equal alkyl chain than that of the ester to reduce by-products.

High temperatures guarantee a fast reaction. CTH takes 4 to 10-fold more time compared to conventional hydrogenation. However, temperatures slightly lower than 150 °C could be employed since the intermediates overcome the barrier and form the product. Besides, long reaction times could lead to lower capital investment and energy consumption.

CTHC can be tuned for a single or multiproduct biorefinery to guarantee effectiveness. However, innovation in catalysts of better performance for the reactions involved in GVL production from biomass and the corresponding optimization of their operative conditions is needed.

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