Green Chemistry

CRITICAL REVIEW

Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass

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Lignocellulosic biomass typically contains more than 50 wt% sugars that can be upgraded to valuable platform molecules, such as levulinic acid (LA) and gamma-valerolactone (GVL). This article focuses on upgrading GVL produced from lignocellulosic biomass to various chemicals and fuels, such as polymers, fuel additives, and jet fuel. We also review the use of GVL as a solvent for biomass processing, which led to significant improvements in product yields and a more simplified process for producing biomass-derived chemicals such as LA, furfural, and hydroxymethylfurfural.

1. Introduction

Our society relies heavily on petroleum as the carbon source to produce chemicals and liquid fuels.[1,2] Increasing demand of these products, diminishing amounts of petroleum, and growing instabilities in markets where production is localized are leading efforts to find renewable replacements for petroleum-derived products. For this reason, research has focused on using biomass as an alternative carbon source, as it offers multiple advantages over petroleum. Lignocellulosic biomass is a renewable source of carbon, has the potential to be converted into many chemicals and a variety of fuels, and is available worldwide. For example, in just the United States along, it has been determined that 1.3 billion of dry biomass can be produced per year.[3,4]

Lignocellulosic biomass consists of three main components: cellulose, hemicellulose and lignin. Cellulose accounts for 30–50 wt% of lignocellulosic biomass and is a homopolymer consisting of β-D-glucopyranose units linked *via* β-glycosidic bonds.[5,6] Cellulose can be converted into glucose by chemical or enzymatic hydrolysis[7,8] and can be used to

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produce ethanol, platform chemicals, such as levulinic acid (LA) and 5-hydroxymethylfurfural (HMF), and liquid fuels.[1,2,9] Hemicellulose accounts for 15–30 wt% of lignocellulosic biomass[10] and is an amorphous polymer consisting of C_5 and C_6 sugars; the ratio of which depends on the type of biomass.[11] Hemicellulose is more reactive than cellulose, is easier to remove from lignocellulosic biomass, and is typically associated with the production of xylitol, furfural, and furfural derivatives.[12–14] The final component of lignocellulosic biomass is lignin, an amorphous polymer rich in aromatic monomers that accounts for 15–30 wt% of the lignocellulosic biomass. The structure of lignin depends on many factors and in particular the source of biomass, mainly if it is hardwood or softwood. In general, lignin is composed of three main precursors:[5] p-coumaryl, coniferyl, and sinapyl alcohol. Lignin also has the potential to be converted into fuels and high value chemicals,[15] but the complexity of its structure and the non-uniformity of its composition makes it more difficult to process than the other fractions.

One of the main challenges in converting lignocellulosic biomass is producing chemicals or fuels at high selectivities and yields at economical costs. Single-step methods, like pyrolysis, rely on high temperatures to deconstruct the lignocellulosic biomass and lead to lower costs due to the lack of pretreatment steps, excluding drying and size reduction. Additional costs are required, however, for the downstream separations. The liquid produced (bio-oil) is a mixture of hundreds of compounds, which makes separations difficult prior to upgrading to targeted chemicals and fuels.

To control the reactivity and improve selectivity, two-step processing methods are typically employed. These methods first fractionate the lignocellulosic biomass into its main components, hemicellulose, cellulose, and lignin, which allows for processing each fraction at different conditions to achieve high yields of target products.[16] The highly functionalized and reactive molecules (mainly C_6 and C_5 sugars) are processed at mild conditions to obtain intermediate molecules (Fig. 1), which are less reactive than the original sugars and therefore, more stable, yet they have enough functionality to be used as building blocks to produce a variety of chemicals and fuels depending on the necessities of the market. Information on the many different products that can be produced from biomass can be found in a thorough review by Gallezot.[9]

According to the Department of Energy, in 2004, one of the most promising building blocks is LA,[17] which Bozell and Petersen confirmed in 2010.[14] LA can be produced (in combination with formic acid) from cellulose, starch, or C_6 sugars[18] by acid hydrolysis through HMF as an intermediate,[19–22] and from hemicellulose in a 3 step process through furfural and furfuryl alcohol as intermediates (Fig. 1).[13,23] Additionally, furfuryl alcohol and LA can be esterified with ethanol to produce ethyl levulinate.[24–26] The ethyl levulinate and LA can then be hydrogenated to gamma-valerolactone (GVL).[27–30] GVL has

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Professor James A. Dumesic earned his B.S. degree from UW-Madison and his M.S. and Ph.D. degrees from Stanford University, under the supervision of Professor Michel Boudart. Dumesic joined the Department of Chemical Engineering in 1976, and he is currently the Steenbock Chair in the College of Engineering and the Michel Boudart Professor of Chemical and Biological Engineering. Throughout his career, Dumesic has used spectroscopic, microcalorimetric, and reaction kinetics techniques to study the surface and dynamic properties of heterogeneous catalysts. Dumesic pioneered the field of microkinetic analysis, in which diverse information from experimental and theoretical studies is combined to elucidate the essential surface chemistry that controls catalyst performance. He has recently studied how aqueous-phase reforming of biomass-derived carbohydrates can be tailored to selectively produce H_2 or directed to produce liquid alkanes. Most recently, he has been studying the use of levulinic acid and γ-valerolactone as biomass-derived platform chemicals for the production of fuels and chemicals.
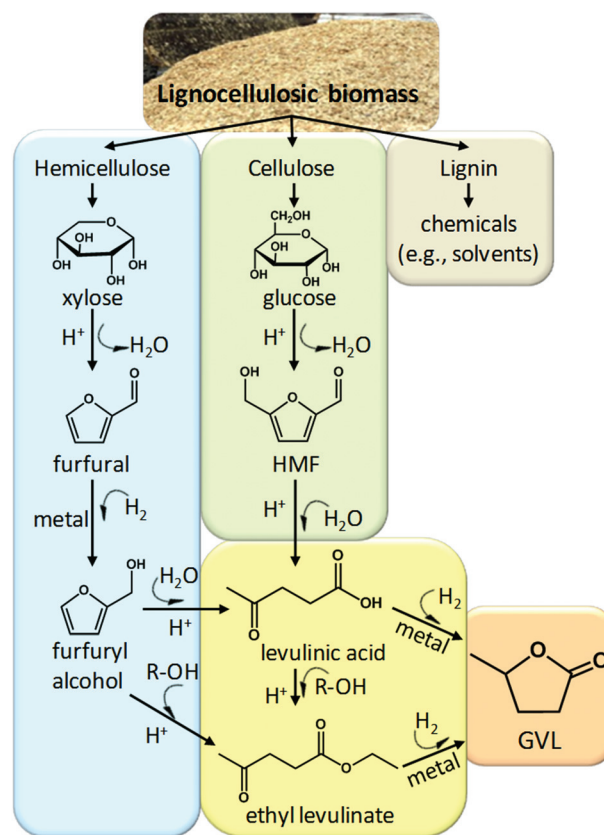
Fig. 1 Fractionation of lignocellulosic biomass and reaction pathways to produce GVL from hemicellulose and cellulose.

excellent properties as solvent[31] and is a precursor for high-value chemicals and fuels.[2,32–34] Being able to upgrade both the cellulose and hemicellulose to LA and then to GVL improves the economics of converting biomass, leading researchers to find more uses for these chemicals and more efficient processing methods. Recently, Wright and Palkovits[32] published an excellent review studying the methods and reaction conditions to produce GVL from LA. Although we briefly describe the production of GVL in this review, we refer the reader to that review and the original references for details concerning this reaction. After discussing recent literature on conversion methods and reaction pathway to produce GVL, we then focus on the use of GVL as a solvent to process biomass and as intermediate to produce chemicals and fuels.

2. GVL properties and synthesis routes

GVL is a 5 carbon (valero-) cyclic ester with 5 atoms (4 carbons and 1 oxygen) in the ring (γ-lactone). GVL is a colorless liquid stable at normal conditions and has a sweet, herbaceous odor, which makes it suitable for the production of perfumes and food additives.[35] The properties of GVL (Table 1) make it both stable and reactive enough to produce a variety of compounds including butene, valeric acid, and 5-nonanone,[33,34,36,37] and allows GVL to be used as a solvent derived from biomass.[31,35] GVL is liquid at normal conditions and has a high boiling point. It does not decompose or degrade with time, even in the presence of water or oxygen, is stable at moderate temperatures, and does not form peroxides in air.[35] GVL has low toxicity (LD50 Oral-rat = 8800 mg kg^{-1}), and the main risk is flammability; however, the low volatility of GVL makes the flammability risk at normal conditions low. Other useful thermodynamic data for several reactions involving GVL have been predicted by Dixon et al.[38]

There are multiple pathways to produce GVL (Fig. 2). Starting from LA, hydrogenation produces γ-hydroxyvaleric acid, an unstable intermediate, which ring-closes by intramolecular esterification and loses a water molecule spontaneously to produce GVL.[41] A second possible LA pathway starts with LA dehydration to form angelica lactone followed by hydrogenation to produce GVL. This secondary pathway requires the
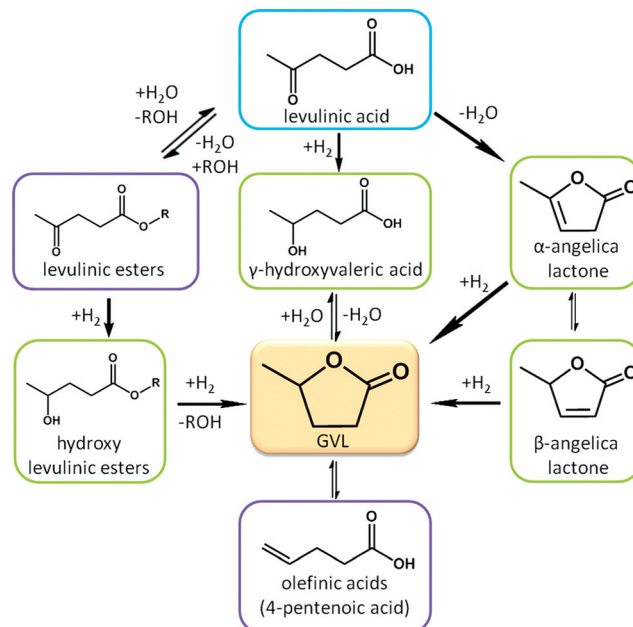

Fig. 2 Reaction pathways to produce GVL.

presence of an acid functionality, and typically leads to lower yields due to coke formation from the angelica lactone catalyzed by the acid.[42] In the case of levulinic acid esters, the reaction proceeds in a similar way as LA: first, the ester is hydrogenated to make the hydroxy levulinic ester, which ring-closes by intramolecular transesterification to produce GVL and the corresponding alcohol.[43,44] If water is present, the ester is typically first hydrolyzed producing an alcohol and LA, which would then proceed through the previously described route. Another option to produce lactones is to ring-close the corresponding olefinic acid,[45,46] which in the case of the GVL, would be 4-pentenoic acid.

3. GVL production

3.1. LA hydrogenation to produce GVL

Many metal catalysts, both homogenous and heterogeneous, have been used for LA hydrogenation with the highest yields being achieved using Ru-based catalysts.[47] Other noble metals, such as Pt and Pd, had high GVL production rates, but also catalyzed GVL hydrogenation to produce 2-methyltetrahydrofuran (MTHF) and 1,4 pentanediol (Fig. 3).[48] Due to the high

Table 1 Main properties of GVL[35,39,40]

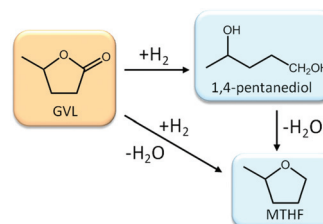| Property	Value
CAS-No	108-29-2
Formula	$C_5H_8O_2$
MW (g mol^{-1})	100.112
Refractive index (n20/D)	1.432
Density (g mL^{-1})	1.05
Flash point (°C)	96
Melting point (°C)	−31
Boiling point (°C)	207–208
Solubility in water (%)	100
ΔH_{vap} (kJ mol^{-1})	54.8
$\Delta_c H°_{liquid}$ (kJ mol^{-1})	−2649.6

Fig. 3 GVL hydrogenation pathway to produce 1,4 pentanediol and MTHF.

cost of the catalyst, several options have been proposed to improve LA hydrogenation to GVL. For example, Martinelli et al.[49] reported that the addition of an acid catalyst to a Ru catalyst achieved high LA conversion and GVL yields at milder reaction conditions than previously used. Other researchers were able to improve the turnover frequency of Ru-based catalysts by adding phosphine ligands; therefore, allowing for a reduction in the amount of catalyst necessary to perform the reaction.[50]

Eliminating noble metals may also reduce the cost of the catalyst. Hengne et al.[51] studied the hydrogenation of LA and its ester over Cu–ZrO$_2$ and Cu–Al$_2$O$_3$ nanocomposites. While Cu–Al$_2$O$_3$ resulted in metal leaching, the presence of methanol suppressed copper leaching when Cu–ZrO$_2$ was used. At complete LA conversion, GVL selectivity was over 90% with Cu–ZrO$_2$. With methanol present, the first product formed was the ester, followed by its hydrogenation to produce GVL and methanol. The catalyst lost selectivity upon reutilization, likely due to metal sintering; however, it is a promising system to replace expensive, noble metal catalysts. Another non-noble metal option studied by Chia et al.[52] involved the use of metal oxides, such as ZrO$_2$ and γ-Al$_2$O$_3$, to produce GVL by transfer hydrogenation through the Meerwein–Ponndorf–Verly reaction using secondary alcohols as the solvent and hydrogen donor. Their highest GVL yield (92%) was achieved with 2-butanol and ZrO$_2$. An advantage of these catalysts is that they can be calcined to regain the initial activity in case of deactivation by coke deposition. Studies of catalyst stability in the presence of formic and mineral acid would be necessary to couple GVL production with LA production, which would reduce the number of processing steps.

A thorough review of recent reaction conditions, including the catalysts used, for GVL production from LA can be found in the review by Wright and Palkovits.[32] From this review, it can be appreciated that GVL production relies heavily on the use of noble metals, which may be an issue for scale-up of the process due to their costs and the uncertainty in future availability due to metal scarcity. Graedel et al.[53] reported that while the availability of base metals such as Al, Cu, Ni, Sn, etc. is not a problem in the future, the increasing use of rare metals such as Ru, Rh, Pd, and Re may jeopardize their future availability. Replacement of noble metals by non-precious and more widely available metals, as well as metal recovery and recycling, will become important issues in the future.[54–57]

3.2. Challenges with biomass derived LA

Most research pertaining to LA hydrogenation to produce GVL has employed pure, commercial LA or mixtures of commercial compounds that simulate the products that would be obtained from the hydrolysis of cellulose or lignocellulosic biomass (e.g., mixtures of LA and formic acid). Few researchers have considered the presence of mineral acids, such as sulfuric acid (SA) or HCl, which are commonly used in the hydrolysis of lignocellulosic biomass to produce LA. According to the reaction pathway presented in Fig. 1, GVL production relies heavily on LA production, and several reviews have been written studying

that reaction.[42,58,59] Here, we address some challenges in using biomass derived LA.

Biofine had success producing LA from the C$_6$ sugars in lignocellulosic feedstocks, such as wood, corn stover, and paper waste, at the pilot scale with reported yields of 75% using SA (0.1 to 1 M) as the catalyst.[60–62] They used a two-reactor system, but the formation of insoluble degradation products, known as humins,[63,64] was an issue in their reactors. Researchers that used LA produced from biomass have observed that GVL yields typically decrease significantly due to impurities and mineral acids present in the feed that deactivate the catalyst.[65] Du et al.[66] converted commercial LA (no SA present) with no neutralization, but required partial neutralization of the SA used to deconstruct glucose in order to achieve high GVL yields. Without SA neutralization, Braden et al.[65] observed an order of magnitude decrease in the reaction rate of a Ru/C catalyst when 0.5 M SA was introduced in the feed solution (2 M LA; 2 M formic acid). The addition of Re to the Ru/C catalyst stabilized the catalyst in the presence of SA, but GVL production turnover frequency was still low.[65] Heeres et al.[67] reported the use of trifluoroacetic acid and Ru/C as catalysts and observed GVL yields up to 62% with fructose as the feedstock; however, the GVL yield dropped significantly when glucose (38%) and cellulose (29%) were used. Although the system is promising, catalyst stability in the presence of trifluoroacetic acid, the separation/purification of the GVL, and the low yields when cellulose was used need to be addressed.

To minimize the problems associated with mineral acids, Dumesic et al. have explored alternatives to separate the SA from the LA. Alonso et al. proposed extracting LA from the aqueous solution containing SA using alkylphenol solvents.[68] In this strategy, the LA was produced from corn stover using a 0.5 M SA aqueous solution followed by liquid–liquid extraction with sec-butylphenol as the organic solvent. The alkylphenol solvent extracted up to 80% of the LA, while the aqueous phase retained all of the SA, and was recycled to produced additional LA. The extracted LA was hydrogenated to GVL over a stable RuSn catalyst[69] while still in the presence of the alkylphenol solvent to eliminate separation steps; however, an outside solvent is required for this process.

An alternative to liquid–liquid extraction is using reactive extraction to produce levulinate esters.[26,44,70] Ethanol has been the most studied alcohol for this reaction due to its low toxicity and ability to be produced from biomass. Therefore, ethyl levulinate[25,26,71] is the most common ester produced; however, the use of larger alcohols, such as butanol or pentanol, is more favorable since they are more hydrophobic, separate more easily from the aqueous phase,[72] and do not partition the mineral acid. An issue with this method is the recovery of the alcohol, which has to be used in excess to achieve high yields of the ester. In place of the alcohol, Fagan et al.[73] reported that is possible to carry out the LA esterification using an olefin. Gurbuz et al.[44] used butene, which can be produced by GVL decarboxylation, to produce the esters.[34,74] The butene used in excess can be easily recovered in the gas phase after reducing the pressure of the system. The butyl levulinate spontaneously

separated from the aqueous solution and was converted into GVL over a dual-bed catalytic reactor containing Pd/C and Ru/C.[44]

Other authors have proposed the use of heterogeneous catalysts (e.g., Amberlyst 70) for the initial reaction of cellulose or glucose to LA, which would eliminate the mineral acid all together. Heterogeneous catalysts have been successful when using glucose and other soluble sugars as the feed,[75–77] but when cellulose was used, the LA yields are low.[78,79] Weingarten et al.[80] reported a two-step process where the cellulose is first converted into glucose followed by glucose conversion to LA using Amberlyst 70 as the catalyst (28% yield to LA). Van der Vyver et al.[81] used polymer catalysts that are sufficiently small to be soluble in aqueous media, but can be recovered by ultrafiltration for cellulose conversion to LA. Recovery of the catalyst was challenging due to the solid humins and only low LA yields (35%) were achieved. Heterogeneous catalyst systems are beneficial since they eliminate the use of mineral acids from the process, which improves downstream processing; however, LA yields must be improved for heterogeneous catalysts to become viable for production of LA. In this respect, the use of GVL as a solvent for LA production can play an important role as will be discussed in the next section.

4. GVL as a solvent

Horvath et al. have proposed using GVL as a solvent as well as a precursor for other green solvents.[31] Concern about what is considered to be "green solvent" has arisen in the scientific community, and more importance has been given to this concept as efforts increase to replace petroleum-derived solvents with biomass-derived solvents. It is clear that a green solvent must reduce health and environmental hazards; however, there is a lack of consensus in the evaluation criteria, and various evaluation methods are considered in the literature.[82] Moity et al.[83] tabulated the toxicity index for 138 green solvents according to the Hodge and Sterner[84] criteria, and GVL was considered to be non-toxic; however, GVL has a vapor pressure greater than 10 Pa, which can make it dangerous due to VOC emissions. Jessop et al.[85] recently reported a series of key considerations, and according to these criteria, GVL has advantages compared to other common solvents. GVL production requires fewer steps than solvents such as trichloromethane, THF, and most ionic liquids. The main intermediates produced when starting from cellulose are glucose, HMF, LA, and formic acid, all of which are miscible with water, which facilitates their biodegradability. There are no dangerous, halogenated or phosphorous compounds involved in GVL synthesis; however, Mascal et al.[86] found that chlorine can be incorporated into products under specific conditions if HCl is used as catalyst to produce LA. In high concentrations, formic acid is corrosive, but can be internally converted into CO_2 and H_2, thereby reducing the requirements of externally supplied H_2 to hydrogenate LA to GVL. The generation of CO_2 needs to be considered, but it is typically

generated in a way that allows for sequestration at high pressures, which facilitates its conversion into valuable chemicals such as methanol[87,88] or polycarbonates.[89,90] While the commercial use of GVL is still limited, mainly due to the high production cost, research focused on GVL is increasing upon anticipation of reduced price stemming from the improvements in LA production. For example, GVL replaced toxic solvents in the production of phosphatidylserine. Additionally, the presence of GVL eliminated the production of undesirable by-products, such as phosphatidic acid, while keeping yields to the desired product over 95%.[92]

Recently, Horvath et al.[93] reported that GVL can be used as solvent to produce the high value platform molecules: HMF, LA, and GVL, from fructose. The system is a significant improvement for GVL production since no separation of the product from the solvent, GVL, is required. There are, however, challenges in terms of catalyst separation as well as LA and HMF purification.

Wettstein et al.[94] mitigated the problem of the catalyst separation by adding an aqueous phase modifier, such as salt or sugars, to create a biphasic system using GVL as the organic layer. The LA partitioned preferentially into the GVL phase and while its purification remained a challenge, it was hydrogenated over RuSn/C catalysts[94] in the presence of GVL to produce GVL. It was found that approximately 50% of the initial SA used in the production of the LA partitioned into the GVL phase, so partial neutralization was still necessary. An important advantage of this system is that lower acid concentrations were used to produce LA compared to when water alone was the solvent (Fig. 4). Additionally, a significant advantage of using GVL as a solvent is that the GVL solubilized both the cellulose and the humins, thereby avoiding solids accumulation in the reactor, which could help implement continuous flow reactors and eliminates a solids filtration step.

The solubilization of the cellulose by GVL was exploited further to promote the use of solid acid catalysts.[91] As previously mentioned, low LA yields typically result when solid catalysts such as Amberlyst 70 are used for cellulose deconstruction reactions. However, the presence of GVL solubilizes
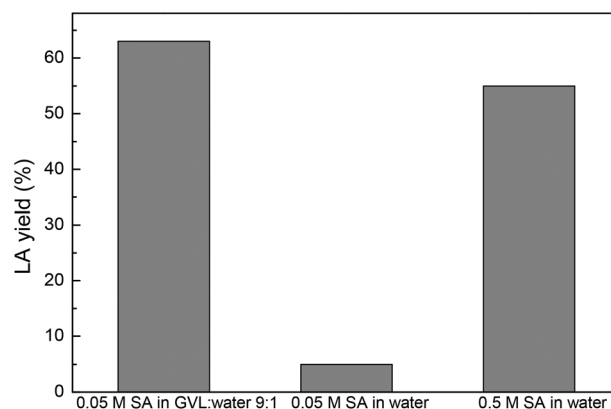

Fig. 4 LA yield from cellulose using GVL/water and water as solvent. 4 h at 160 °C.[91]

the cellulose, allowing it to access the active sites of the solid catalysts. Alonso *et al.* achieved LA yields over 60% from cellulose using Amberlyst 70 and no other acid catalysts. The Amberlyst 70 slowly deactivated due to coke deposition on the catalyst surface, but retained its selectivity to LA. Amberlyst 70 is not stable at temperatures over 190 °C,[95] but the activity was recovered by treating the Amberlyst 70 with dilute solutions of H_2O_2 at room temperature. In this case, the LA produced was hydrogenated to GVL without any neutralization steps although separation of LA as final product remains a challenge as it is produced in dilute solutions (<0.5 M).

Gallo *et al.*[96] used GVL as solvent to produce another high value building block derived from C_6 sugars, HMF. Using a biphasic system consisting of water saturated with NaCl as aqueous phase and GVL as organic phase, HMF was produced at high yields from fructose (80%) and glucose (63%). These yields are similar to other values in the literature that used *sec*-butylphenol,[97] THF,[98] or ionic liquids[99] as solvents. The main advantage of using GVL as the solvent for HMF production is that high yields have also been reported using monophasic system and solid acid catalysts, thus, reducing mixing requirements and eliminating problems caused by separating the phases and catalyst recovery. Gallo *et al.*[96] reported that Amberlyst 70 can be used as a Bronsted acid catalyst to produce HMF from fructose, but the presence of an effective isomerization catalysts such as Sn-beta[98,100] was critical to obtain high yields from glucose.

The HMF can then be upgraded to other valuable compounds without separation from the GVL[96] (Fig. 5). For example, HMF was hydrogenated to produce 2,5 dimethylfuran (DMF) without hydrogenating the GVL using a RuSn/C catalyst.[94] The boiling point of DMF (92 °C) is lower than GVL and can be easily removed by distillation. Oxidation of HMF produces 2,5 furandicarboxylic acid (FDCA) and Davis *et al.*[101–103] extensively studied this reaction in water and achieved high yields (>80%). Unlike the previously described reactions, when the oxidation was carried out in presence of lactones, FDCA yields were lower (56%) and some of the GVL is oxidized to LA.[96] The GVL can be regenerated by LA hydrogenation or

alternatively, the HMF can be extracted into an aqueous phase from the GVL using organic solvents such as cyclopentane before the oxidation step.[96]

Similar advantages to those identified to process C_6 sugars are found when GVL is used as a solvent to convert hemicellulose into furfural. The degradation products (humins) formed during the hydrolysis of the C_5 sugars are solubilized, thereby minimizing the presence of solids. Additionally, the reaction is faster and lower concentrations of mineral acids can be used compared to aqueous based reactions (Fig. 6). Using GVL as solvent reduced furfural degradation reactions that typically lower yields in monophasic systems, and similar yields to those previously reported using biphasic systems[104–108] (70–80%) were achieved with several catalysts using a monophasic GVL system.[109] GVL has a higher boiling point than typical products obtained from hemicellulose (Fig. 5), such as furfural (169 °C), formic acid (101 °C) and acetic acid (118 °C),[106] which facilitates separation by simple distillation. Gurbuz *et al.*[109] reported the use of heterogeneous catalysts (*e.g.*, mordenite) to produce furfural at high yields (80%) using GVL as the solvent. Reducing the amount of water present and eliminating salts, which are not necessary in a monophasic system, allowed the mordenite catalyst to be reutilized 6 times without any observed loss in activity. In addition, when GVL was the solvent and mordenite was the catalyst, it was possible to produce furfural at relative high yields (33%) from glucose compared with the low yields (7%) obtained in water.

The previously described processes upgrade the C_6 (cellulose) and C_5 (hemicellulose) portions of the biomass separately and rely on fractionation to exclusively use one or the other kind of sugars. Typically shorter reaction times and lower acid concentrations are required to convert the C_5 sugars than compared to C_6 sugars. Extending the reaction time after the furfural is produced in order to convert the cellulose resulted in low furfural yields due to rapid degradation reactions at the conditions required to produce LA.[60–62] Dumesic *et al.*[110] eliminated the fractionation step by successfully processing
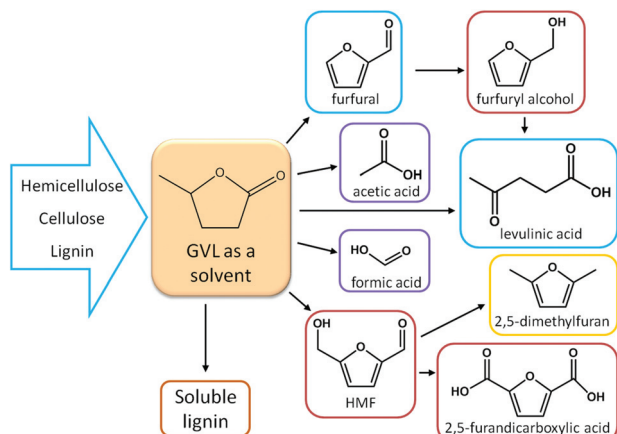

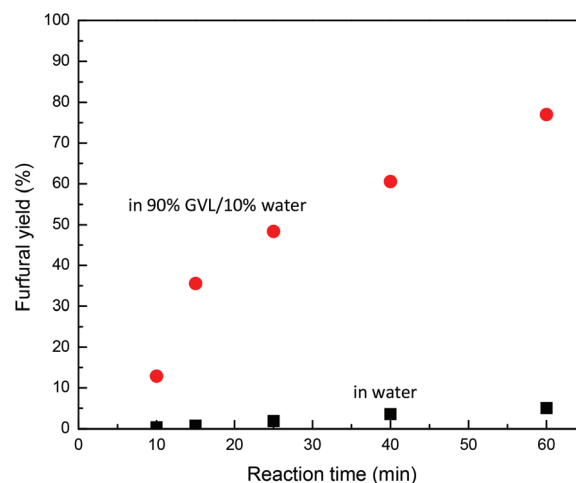**Fig. 5** Lignocellulosicbiomass derived product obtained using GVL as solvent.

Fig. 6 Production of furfural from 2 wt% xylose solutions at 160 °C and 0.01 M SA using as solvent GVL : water 9 : 1 (●) and water (■).

the hemicellulose and cellulose fractions of corn stover simultaneously using GVL as solvent. The presence of GVL during the biomass deconstruction step facilitates LA production from cellulose by reducing the reaction time and the amount of catalyst required, while improving the stability of the furfural. The reaction conditions allowed for simultaneous production of LA and furfural from corn stover. The furfural was hydrogenated to furfuryl alcohol over a PtSn/C catalyst at 100 °C in the presence of the GVL solvent and the LA produced during the corn stover deconstruction, which eliminated purification steps. At the reaction conditions used, the LA was stable or converted into GVL. In a third step, the furfuryl alcohol, still in presence of the GVL and remaining LA, was converted to LA over an acid catalyst, Amberlyst 70. Finally, the LA from the cellulose and hemicellulose fractions was hydrogenated to GVL over a RuSn catalyst. This system allows for better utilization of the lignocellulosic biomass to produce GVL and avoids separation steps; however, the overall GVL yield from the C_5 fraction was still low due to the number of steps in the process.[110]

5. GVL and its products as fuel

GVL can be used directly as a liquid fuel or as an additive to current petroleum fuels similar to ethanol. Mixtures of 90 vol% conventional gasoline with 10 vol% GVL or 10 vol% ethanol were compared by Horvath et al.,[35] and they observed that the mixture with GVL had a lower vapor pressure, which improved the combustion at similar octane numbers. GVL has not been tested as a pure fuel, but it has similar combustion energy to ethanol (29.7 MJ kg^{-1}) and a higher energy density. A major issue with using GVL as a pure fuel is its high water solubility; however, water can be distilled from the GVL as there are no azeotropes, in contrast to the case of ethanol.

GVL can be further hydrogenated to produce fuel additives, such as MTHF, or chemicals, such as 1,4 pentanediol[111] (Fig. 7). Biomass-derived polymers can be produced from 1,4 pentanediol, while MTHF can be used as a solvent and has been identified as a component for the P-series fuel.[112,113] Over an inexpensive, Cu catalyst, Du et al.[114] found that GVL was converted at 93% selectivity to MTHF at 98% GVL
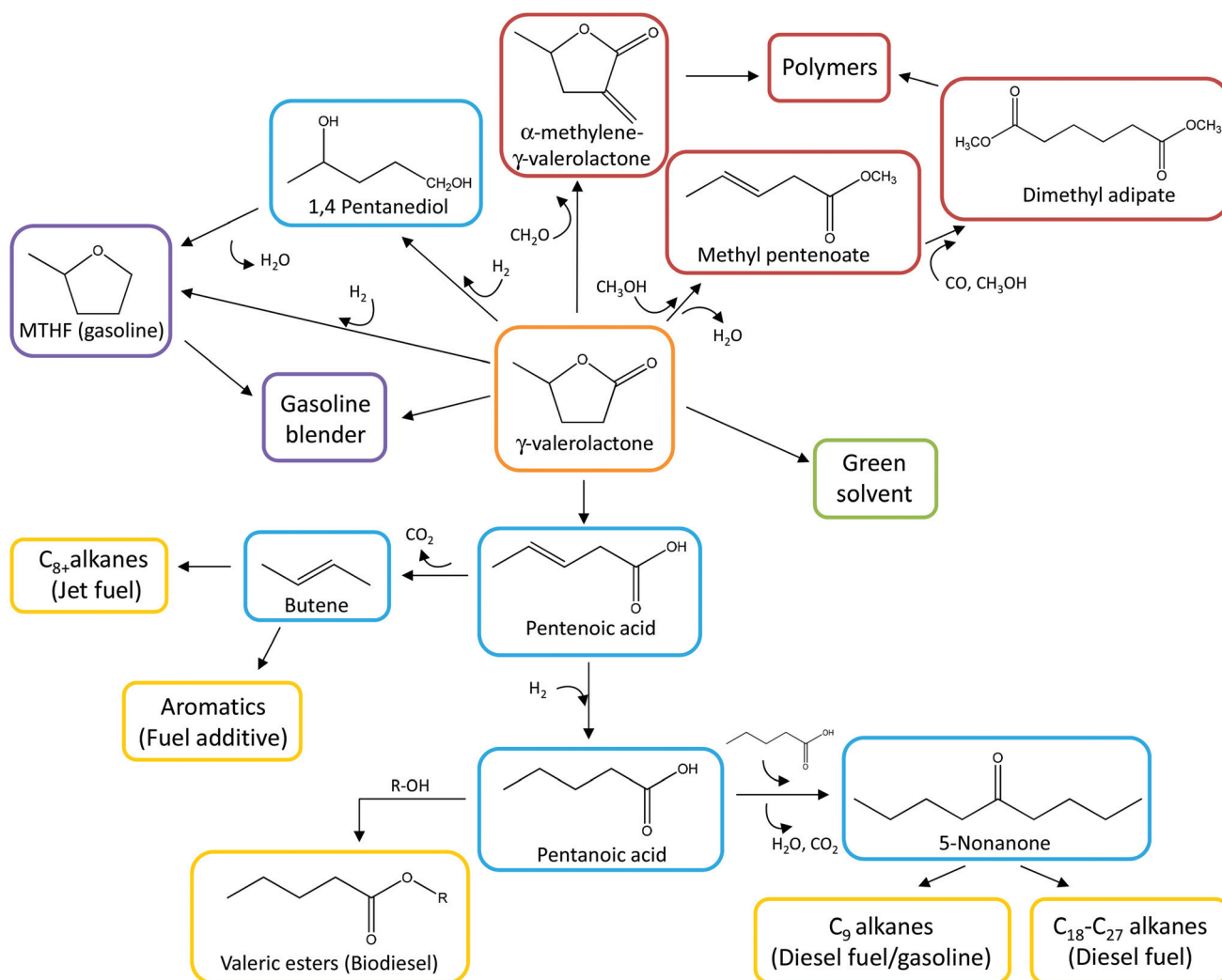

Fig. 7 Reaction pathways for the conversion of GVL into fuels, fuel additives and chemicals (adapted from [74]).

conversion. When the same Cu catalyst was calcined in presence of H_2 instead of air and the reaction temperature was decreased 40 °C, GVL was hydrogenated, not to MTHF, but to 1,4-pentanediol with a selectivity of over 98% at complete conversion in presence of ethanol.[114] These reaction conditions prevented the 1,4 pentanediol from being further hydrogenated to MTHF, and therefore, reaction conditions must be carefully controlled. Using precious-metal catalysts, MTHF can be produced by LA hydrogenation, through GVL and 1,4 pentanediol as intermediates (Fig. 3). In general, higher H_2 pressures and temperatures are required to carry out the hydrogenation of the GVL than for LA.[48] Finally, MTHF can be converted into fuels, C_4–C_9 alkanes, in the presence of an acid and metal catalyst at high pressure and moderate temperatures.[25,48]

Besides using GVL as a fuel or hydrogenating it to MTHF, several strategies have been proposed to convert GVL into energy dense drop-in fuels. Lange et al.[36] produced a new family of fuels using this method, "valeric biofuels", which were successful as fuel additives. These processes normally start with ring-opening the GVL to produce pentanoic acid over a bifunctional metal-acid catalyst (Pt/ZSM-5). In the next step, pentanoic acid undergoes esterification to form valeric esters in the presence of alcohols and solid acid catalysts. Pentanoic acid yields over 90% were achieved over Pt/ZSM-5, which ran for more than 1500 h only requiring intermittent regenerations by calcination in air. Using Pt/TiO$_2$ or Pd/TiO$_2$ at 275–300 °C, they directly converted GVL into pentyl valerate with 20–50% selectivity. Recently, Zaccheria et al.[115] reported the production of pentyl valerate from GVL in a single pot using Cu supported by SiO$_2$–ZrO$_2$ and using pentanol as solvent. They obtained GVL conversions of over 90% and selectivities to pentyl valerate up to 83%. They hypothesized that the production of valeric acid and pentanol from GVL are the rate limiting steps in the process, and that once the acid and alcohol form, the esterification is straight forward. When the reaction is performed in the presence of ethanol, ethyl valerate is formed, but at lower selectivities due to the formation of ethyl 4-ethoxy pentanoate and pentenoic esters.

Dumesic et al. reported a similar strategy using Pd/Nb$_2$O$_5$ to convert GVL into pentanoic acid at yields higher than 92%.[37,116] The reaction took place in the presence of water (50 wt%) and therefore, the metal loading and H_2 pressure was controlled to minimize the formation of by-products, mainly due to decarbonylation and decarboxylation reactions to produce butane and CO$_x$.[37,116]

To upgrade the pentanoic acid into liquid fuels, the molecular weight needs to be increased and the oxygen content decreased. Instead of esterification, Serrano-Ruiz et al.[37] used ketonization of the pentanoic acid over CeZrO$_x$ to achieve nearly quantitative yields of 5-nonanone while removing one equivalent each of water and CO$_2$. The catalysts were combined in a dual-bed reactor to reduce the number of steps required, and they obtained an overall 5-nonanone yield of 84% from aqueous solutions of GVL. The main by-products were other ketones, such as 2-hexanone and 3-heptanone, arising from the scission of the 5-nonanone. The Pd/Nb$_2$O$_5$ deactivated with time on stream due to the poor hydrothermal stability of Nb$_2$O$_5$, which loses surface area as it undergoes transformation from amorphous to a crystalline structure at high temperature. The addition of small amounts of silica stabilized the Pd/Nb$_2$O$_5$; however, sintering of Pd was still a minor problem.[117] Separations during this process were simplified since 5-nonanone is hydrophobic and spontaneously separates from the aqueous solvent.

The 5-nonanone produced from GVL has many possibilities for upgrading. By successive hydrogenation and dehydration reactions over metal and acid catalysts, 5-nonanone was converted into nonane, while the shorter ketones produced as byproducts were converted into C_6–C_7 alkanes that can be removed by evaporation.[116] Nonane can be used as a fuel additive to diesel fuel, or converted into gasoline by isomerization and aromatization reactions over zeolites to produce a mixture of branched C_9 alkanes.[116] The 5-nonanone can also be hydrogenated over Ru/C to produce 5-nonanol, which can be dehydrated in the presence of acid catalysts, such as Amberlyst 70, to produce a mixture of C_9 olefins. To increase the molecular weight, the C_9 olefins can be oligomerized over an acid catalyst to produce a mixture of C_{18}–C_{27} olefins that can be used as diesel fuel.[118] In this strategy, other lower molecular weight ketones produced during the process were converted into C_6–C_7 olefins, which also undergo oligomerization producing a mixture of C_6–C_{27} alkanes. The molecular weight range of the final mixtures can be optimized by modifying the reaction conditions. The higher reactivity of terminal olefins favors the formation of linear alkenes, while the lower reactivity of longer olefins prevents further oligomerization reaction that would lead to the formation of wax and solid olefins.[118]

Bond et al. proposed yet another option to increase the energy density of the GVL. This approach consists of acid-catalyzed decarboxylation to produce butene and CO$_2$.[74,119] The GVL was converted into pentenoic acid and decarboxylated in the presence of acid catalysts, such as silica-alumina. Even when the GVL was directly decarboxylated to produce butene, the reaction pathway with pentenoic acid as an intermediate was more favorable.[119] The presence of water helped catalyst stability, as without water, the catalyst deactivated due to coke formation; however, the coke that formed was able to be removed by calcination in air. Butene yields over 99% were achieved from an aqueous solution of GVL at 35 bar and 375 °C.[34] By removing the butene rapidly from the reaction media, the system produced high-value 1-olefins. Alternatively, to increase the molecular weight for use as a liquid fuel, the butene was oligomerized in the presence of the CO$_2$ co-product over solid acids, such as Amberlyst 70 or ZSM-5. Amberlyst 70 catalyzed the low-temperature oligomerization of butene (150–170 °C), which prevented cracking reactions that take place at higher temperatures. High pressures (35 bar) favored butene oligomerization, and C_{8+} olefins were obtained with yields over 90%. In this strategy, water removal before the oligomerization step is required, since water was found to inhibit the reaction. The water was easily removed since butene has a higher volatility and can be kept in gas phase,

while the water is condensed. Combining all these steps in an integrated continuous flow reactor yields over 75% to liquid C_{8+} olefins from GVL aqueous solutions were reported.[34]

Zhao *et al.*[120] used a similar idea to produce aromatic hydrocarbons from GVL. Using zeolite catalysts, such as MCM-41 and HZSM-5, and higher temperatures (500 °C), they converted GVL in a single reactor to aromatics (*e.g.*, benzene, toluene, and xylene) with yields over 55% and CO and CO_2 as co-products. The GVL was likely converted into pentenoic acid in the gas phase, and the pentenoic acid was then decarboxylated and decarbonylated to produce a mixture of butene, CO, and CO_2. At the high reaction temperatures, butene was converted into aromatic compounds by isomerization and aromatization reactions.[121,122] Although reactions to produce fuels and fuel additives from GVL have been established, simplification of the GVL production process and increasing yields are still necessary for an economical process.

6. Additional uses of GVL

GVL can be used to produce, not only renewable fuels, but also interesting monomers to make polymers similar to those derived from petroleum but with different chemical properties.

Manzer *et al.*[47] produced biomass-derived monomers such as α-methylene-γ-valerolactone from GVL. This compound has similar properties to methyl methacrylate, and the incorporation of the lactone structure increased the thermal stability of the polymer. The reaction of GVL and formaldehyde took place in gas phase at high temperatures (340 °C) and used salts from group I and II of the periodic table as the catalyst, preferably Ba, supported over SiO_2. At these conditions, selectivities of over 95% to the desired product were achieved. The catalyst deactivated, but was regenerated by calcination in air. The reaction was carried out at temperatures similar to the calcination temperature, thereby avoiding the need for cooling–reheating steps in the process.

Other products produced by ring-opening of the GVL are γ-hydroxy(amino)amide compounds (Fig. 8). This reaction was catalyzed by $SnCl_2$ at 50 °C with GVL and an amine present, for example, 1,2 diaminoethane.[123] At these conditions, the GVL ring-opened and incorporated the amine into the lactone carbonyl. According to Chalid *et al.*,[123] the nucleophilicity of the amine played an important role in the addition–elimination reaction. This new family of compounds can be used as monomers to produce polymers such as polyethers or polyurethanes.

Another alternative to produce biomass derived polymers from GVL was proposed by Lange *et al.*[124] for the production of methyl pentenoate *via* ring opening of GVL in methanol over acid catalysts. The authors used catalytic distillation to favor the production of the ester, methyl pentanoate (b.p. 127 °C), which is more volatile than the GVL. They obtained yields up to 98%, and the product recovered at the top was methyl pentanoate, unreacted methanol, and small
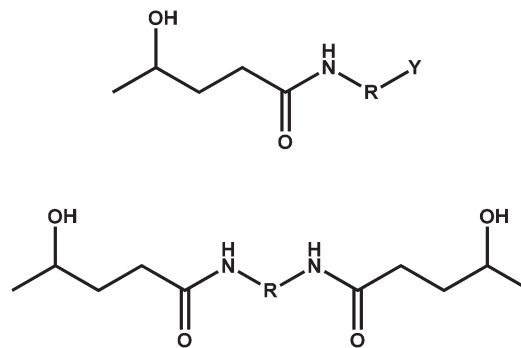
Fig. 8 Examples of hydroxy(amino)amide compounds.[123]

amounts of dimethyl ether. Reactions with longer alcohols led to lower yields of the corresponding ester. The methyl pentenoate was then converted into nylon precursors such as caprolactone, caprolactam, or adipic acid by hydroformylation, hydrocyanation, or hydroxycarbonylation, respectively.[125]

Other compounds derived from GVL can be used as solvents as well, as identified by Horvath *et al.*[31] Alkoxyvalerates are produced by the addition of trialkyl orthofomates in the presence of an acid catalyst. Ionic liquids such as tetraalkylammonium 4-hydroxyvalerate and cholinium 4-hydroxyvalerate were prepared by reacting tetraalkylammonium hydroxides with GVL at room temperature.[31,126] There are many possibilities in using GVL for different chemicals, solvents, and polymers. Process optimization and determination of which processes have the highest commercialization possibility are important steps for the future.

7. Conclusions

GVL is a promising renewable platform molecule that can be produced from lignocellulosic biomass by LA hydrogenation. GVL is non-toxic, can be used as a solvent, and has the functionality/reactivity to be upgraded to a variety of chemicals, fuels additives, and fuels. Additionally, GVL is stable in water and in the presence of air, and can be produced from C_6 and C_5 sugars through LA as an intermediate. Several major opportunities exist for GVL production from biomass. (1) Purification of LA from mineral acids. Many strategies have been developed to overcome the issues related to the use of mineral acids, such as reactive extraction and liquid–liquid extraction; however, the most convenient approach would be the replacement of mineral acids by heterogeneous catalysts for production of LA. (2) Identification of catalysts that are stable in the presence of mineral acids. Although some progress has been made in this area, catalyst stability using real biomass derived feed is necessary. (3) Alternative catalysts to noble metal catalysts. The recent work using non-precious metal catalysts as well as solid acid catalysts with GVL as a solvent may allow for non-precious metals to be used for LA hydrogenation. This would make the overall process more economically feasible, which leads into (4) Technoeconomic analyses of

different pathways will be critical to determine bottlenecks (*e.g.*, product yields, solvent selection, catalyst metal, *etc.*) in these GVL processes. The properties of the GVL make it an excellent solvent as it is able to solubilize lignocellulosic biomass and achieve high yields of LA using solid catalysts. Accordingly, GVL offers new opportunities to replace petroleum-derived chemicals and fuels with biomass-derived options.

Acknowledgements

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