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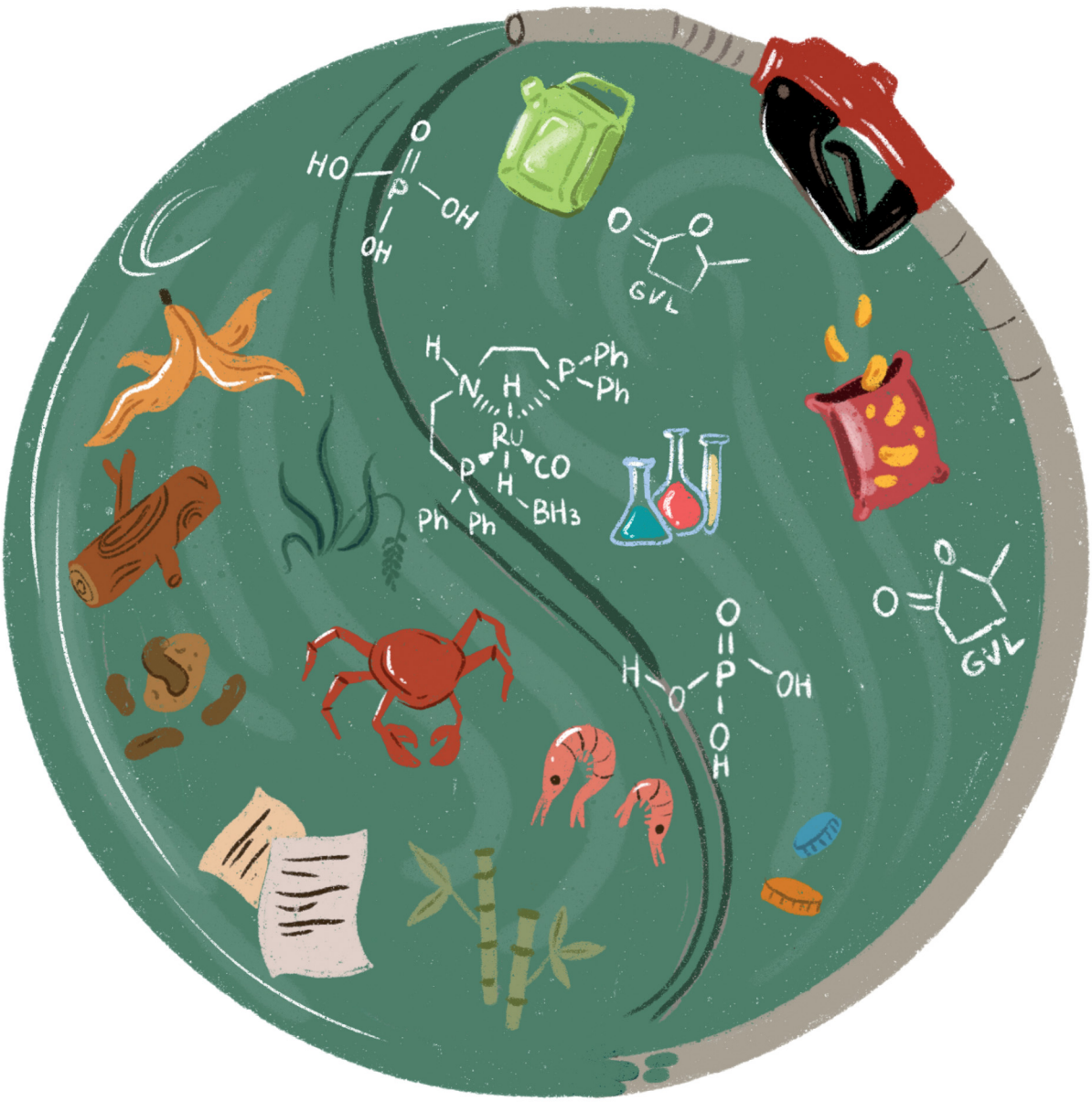

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PAPER
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Direct biomass valorisation to γ-valerolactone by Ru-PNP catalysed hydrogenation in acid†

Sakhitha Koranchalil and Martin Nielsen *

Converting carbohydrate-rich biomass waste directly to γ-valerolactone (GVL) is highly attractive but challenging owing to the inert nature and high complexity of biomass, necessitating a versatile and selective catalytic system. Herein, we describe the first direct conversion of monosaccharides (glucose, fructose, and xylose) and polysaccharides (cellulose and hemicellulose) in high yields under mild conditions. We also present the first direct conversion of raw lignocellulose, starch, and chitin biomass to GVL. Using the homogeneous catalyst Ru-MACHO-BH in H_3PO_4(aq) under 30 bar H_2 at 125–140 °C for 24–120 hours provides GVL in excellent yields (26–48 mol%).

Broader context

Developing direct transformations of raw biomass to desired end-products is crucial for achieving viable and sustainable valorisation of biogenic substances. Performing such transformation under as mild and waste-less conditions as feasible and yet high-yielding is equally important. Gamma-valerolactone (GVL) is a highly attractive and biodegradable product, being valuable as, for example, a biofuel and industrial chemical or solvent. Hence, developing an environmentally benign synthesis route of GVL from raw biomass would potentially give access to a fuel and chemical that is both valuable and sustainable. However, to date there exists only a single example of this synthesis route carried out in a direct fashion, and it leads to a relatively low GVL yield (12 wt%) while employing heterogeneous catalysis, harsh conditions (800 W microwave heating to 180 °C) and using wasteful and expensive isopropanol as a H-donor. Our protocol is first-in-class to show the proof-of-concept of direct transformation of a range of carbohydrate-rich raw biomass substances to GVL in excellent yields under mild conditions. Thus, with 12 different raw biomass substances spanning three biogenic carbohydrate types, GVL yields up to 26 wt% are achieved using homogeneous catalysis and simple, cheap, and waste-free H_2 as a H-donor under mild conditions (140 °C, no microwave).

Introduction

As the only sustainable hydrocarbon resource available on Earth, biomass plays an essential role in the production of green fuels and chemicals.[1] Indeed, biomass is the only perennial resource that might provide a negative carbon footprint, *i.e.*, decrease the net atmospheric CO_2 levels.[2] Moreover, the replacement of petrochemicals by biogenic-derived substances is receiving increasing attention,[3] and developing efficient and direct routes for biomass valorisation is of immense importance. However, biomass transformation is a complex chemical process, and it is highly challenging to develop selective and viable processes. For example, classical thermochemical methods, *e.g.*, gasification, pyrolysis, and liquefaction,[4] have severe drawbacks such as producing biofuels with complex and ill-defined compositions or generating high amounts of undesired side products, for example coke or CO_2. Thus, an alternative conceptual approach of producing well-defined platform chemicals from biomass has emerged,[5] which involves breaking down the biomass into one or a few molecules that can then be converted into biofuels or commodity chemicals.[6]

One of the most promising sustainable and well-defined platform chemicals that can be obtained from biomass is γ-valerolactone (GVL),[6a] which is derived from biogenic carbohydrates in several steps. GVL has many applications, such as biofuel, fuel additive, green solvent, and in the syntheses of numerous end-products such as polymers or pharmaceuticals. Its production can be envisioned to follow two specific multistep cascade processes (Scheme 1).[7] Using lignocellulose as model example of a biomass substrate, in the 'glucose path' acid mediates the hydrolysis of cellulose to glucose followed by the isomerization to fructose, dehydration to 5-hydroxymethyl furfural (HMF), rehydration to levulinic acid (LA), and finally hydrogenation followed by lactonization to GVL. In the 'xylose path', hemicellulose is first hydrolysed to xylose and dehydrated to form furfural, both steps mediated by acid. A subsequent hydrogenation leads to furfuryl alcohol, which is then rehydrated

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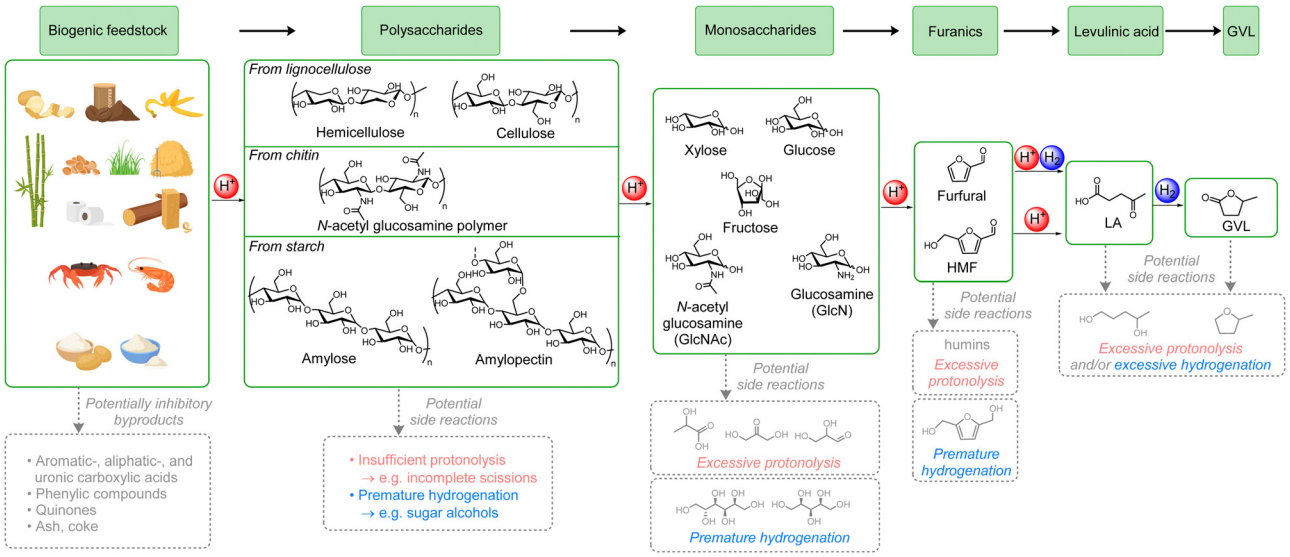

Scheme 1 Generally accepted stepwise mechanism for the conversion of the three major types of carbohydrates-rich biomass, lignocellulose, chitin, and starch, into GVL (grey arrows and products indicate selected examples of the major pitfalls).

by acid to LA, and finally a second hydrogenation leads to GVL. Unfortunately, there are only very few examples of direct transformation of cellulose[8] and hemicellulose[9] to GVL, severely hampering the potential for using biogenic carbohydrates for obtaining GVL.

Lignocellulosic residues, mainly originating from wood- and agricultural waste, exceed 180 Gtpa worldwide[10] and therefore represent a very large non-edible resource. It is mainly composed of cellulose (40–50 wt%) and hemicellulose (16–33 wt%), with lignin constituting the remainder (15–30 wt%).[11] It is, therefore, exceedingly important to develop procedures capable of transforming both cellulose and hemicellulose to GVL. Moreover, other major biogenic carbohydrate sources, such as chitin and starch, follow the 'glucose path' *via* either *N*-acetylglucosamine polymer[12] or amylose/amylopectin,[13] respectively.

The direct conversion of raw carbohydrate-rich biomass to GVL appears straightforward, involving a combination of several hydrogenations and acid mediated transformations. However, the lack of literature precedence underscores the substantial challenge that it in fact represents. Hence, as the only example of directly transforming real biomass to GVL, Huang converted poplar to GVL in merely 12 wt% yield by using a sacrificial H-donor (iPrOH) with mixed $Al_2(SO_4)_3$ and Ru/ZrO_2 catalyst, and 800 W microwave heating to 180 °C.[8b] In addition, most of the protocols developed for later-stage entries, such as poly- and monosaccharides, also employ very harsh conditions between 170–200 °C and either a sacrificial H-donor or high H_2 pressures of up to approximately 100 bar.[8,9] One exception is given by Li who reported the direct production of GVL by 20 wt% Ru/TiO_2 catalyst in combination with 40 wt% of the strong Brønsted acid $H_3PW_{12}O_{40}$ (HPA) in water/γ-butyrolactone mixture at 130–150 °C under 40 bar H_2.[8c] GVL yields from fructose (130 °C), glucose (150 °C), starch (150 °C), and cellulose (150 °C) reached 68%, 55%, 48%, and 41%, respectively.

To the best of our knowledge, there are no examples of direct GVL production from raw biomass in high yields and, furthermore, there are no examples using mild conditions let alone using simple H_2 as hydrogen source. All these factors are pivotal for developing viable biomass valorisation strategies. Interestingly, even though homogeneous catalysis is typically praised for its high selectivity and catalytic activity under mild conditions, the only examples of homogeneous catalysis for direct GVL production employ similarly harsh conditions as the heterogeneous ones[8a] only to reach yields below 40% from pure carbohydrates.

A major reason for the lack of literature examples can be attributed to the potential pitfalls associated with each of the reaction steps (see Scheme 1). Thus, there are numerous possible side products that might inhibit the catalyst(s), and there is an ominously high likelihood of carrying out insufficient, premature, or excessive protonolysis and/or hydrogenation leading to halting or overdoing the transformation process or to following other routes all-together. Thus, a catalytic system for a direct transformation of carbohydrate-rich biomass to GVL must operate with high conversion and selectivity for every distinct acid- and hydrogenation-mediated step and tolerate many different substrates simultaneously. As a note, even though there are numerous examples of direct formations of furanics[9b,c,14] and LA,[15] it is highly unattractive to isolate any of these intermediates in a two-step production of GVL. The furanics are prone to polymerise to humins and their conversion to GVL anyway requires a combination of acid and hydrogenation, and isolation of LA is exceedingly energetically demanding.[16]

Herein, we report a unique homogeneous catalytic protocol, using for the first time a well-defined catalyst for the direct production of GVL from several polysaccharides and monosaccharides with unparalleled high yields of GVL of up to 75% (Scheme 2). In addition, we demonstrate the first example of the direct conversion of raw biogenic waste materials to GVL in excellent yields of up to 48%, which corresponds to more than 90% yield in each reaction step. Furthermore, we achieve this

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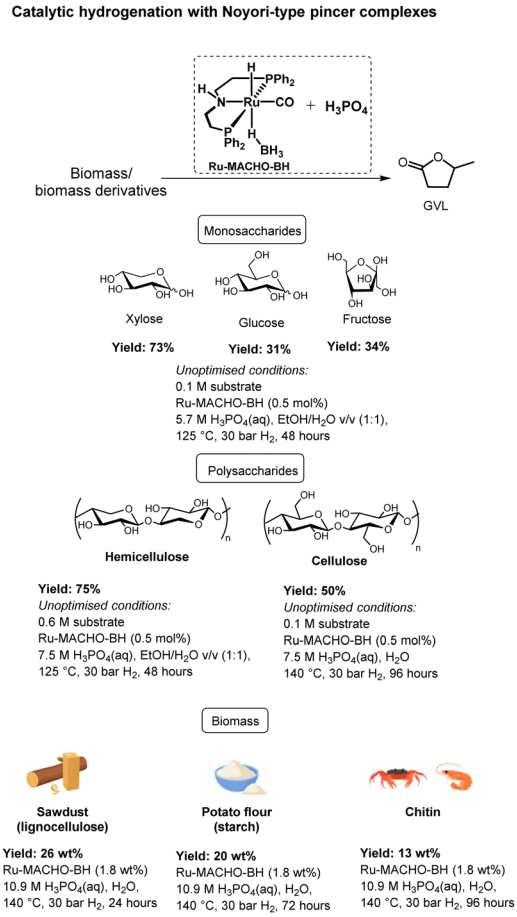


Scheme 2 Catalytic hydrogenation of biomass, its derivatives, and this work.

with an unprecedented combination of weak acid and low H_2 pressure. Finally, also as the first example, with identical reaction conditions we cover the three major types of carbohydrate-rich biogenic sources, *i.e.*, lignocellulose, starch, and chitin.

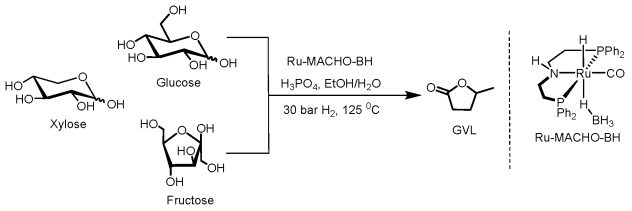
Our catalytic system consists of a novel combination of the PNP pincer complex Ru-MACHO-BH and the Brønsted acid H_3PO_4 under an atmosphere of H_2 in water. Notably, even though Noyori-type PNP pincer complexes,[17] such as the Ru-MACHO complex[18] and analogues, have demonstrated excellent (de)hydrogenation activities in both basic,[19] Lewis acidic,[20] and neutral media,[21] there exist, to the best of our knowledge, no examples of their use under Brønsted acidic conditions. In fact, compared to the plethora of examples in basic and neutral media, there are relatively few examples in general of hydrogenation reactions using homogeneous catalysis under Brønsted acidic conditions.[22]

Results and discussions

Direct conversion of monosaccharides to GVL

Initial efforts were focused on studying the monosaccharides such as xylose, glucose, and fructose. These three carbohydrates were chosen because they all represent important intermediates

Table 1 Direct conversion of xylose, glucose, and fructose to GVL



Entry	Substrate concentration [M]	H_3PO_4 [M]	GVL yield[a] [%] Xylose	Glucose	Fructose
1	0.6	3.8	45	21	25
2	0.6	5.7	60	16	29
3	0.6	7.5	50	13	24
4	0.1	5.7	73	31	34
5	0.3	5.7	55	17	30
6	1.3	5.7	45	10	21

Standard reaction conditions: xylose (0.1–1.3 M), Ru-MACHO-BH (0.5 mol%), 85% w/w H_3PO_4, EtOH/H_2O v/v (1 : 1), 125 °C, 30 bar H_2 in 48 hours. [a] Determined by GC-FID using 1,4-dioxane as the internal standard.

from either cellulose or hemicellulose to GVL, *i.e.*, glucose and fructose are both derived from cellulose, and xylose arises from hemicellulose.

Gratifyingly, with 0.5 mol% of Ru-MACHO-BH and 3.8 M H_3PO_4(aq) under 30 bar of H_2 in 1 : 1 v/v EtOH/H_2O, the conversion towards GVL was 45%, 21%, and 25% from xylose, glucose, and fructose, respectively, after 48 hours at 125 °C (Table 1, entry 1). Employing 5.7 M H_3PO_4(aq) led to an encouraging 60% yield of GVL in case of xylose, whereas 16% and 29% were obtained from glucose and fructose, respectively, after 48 hours (entry 2). However, with higher concentration of H_3PO_4(aq) (7.5 M), the yield diminished to 50% for xylose, 13% for glucose, and 24% for fructose (entry 3). Noticeably, insoluble humins was observed in the reaction medium. Humins are usually produced from the polymerisation of furanics in acidic medium.[23] Hence, we continued with 5.7 M H_3PO_4(aq). Moreover, glucose is first isomerized to fructose towards GVL,[24] likely explaining why fructose consistently leads higher GVL yields than glucose. Next, the effect of concentration of the carbohydrate was investigated. The reaction afforded 73% GVL with 0.1 M xylose, dropped to 55% with 0.3 M xylose, and further lowered to 45% with 1.3 M xylose (entries 4–6). The similar trend was also observed with glucose and fructose, and 0.1 M glucose afforded 31% GVL and 0.1 M fructose led 34%. We speculate that humins are formed to a greater extent in the more concentrated samples.[25]

Hence, we here demonstrate the feasibility of achieving high yields of GVL from monosaccharides even under unoptimized conditions. As our goal is to directly transform real biomass to GVL, we decided not to pursue further optimisations with the monosaccharaides, and instead move a level up in complexity, *i.e.*, to the polysaccharides.

Direct conversion of polysaccharides to GVL

Pure cellulose and hemicellulose were investigated as model substrates for lignocellulosic biogenic material. We commenced

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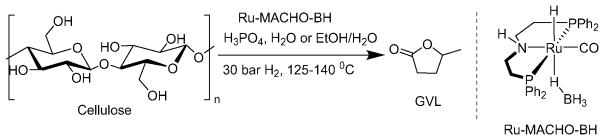
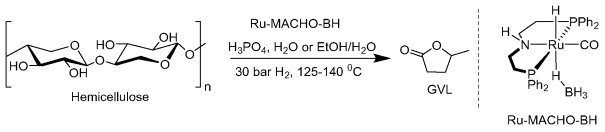
Table 2 Direct conversion of cellulose to GVL



Entry	Cellulose [M]	H_3PO_4 [M]	Solvent	P/T [bar]/ [°C]	Time [h]	GVL yield[a] [%]
1	0.6	5.7	H_2O	30/125	48	19
2	0.6	5.7	H_2O	30/125	96	22
3	0.6	7.5	H_2O	30/125	96	28
4	0.6	5.7	H_2O	30/140	96	31
5	0.6	7.5	H_2O	30/140	48	28
6	0.6	7.5	H_2O	30/140	96	44
7	0.1	5.7	H_2O	30/140	48	37
8	0.1	7.5	H_2O	30/140	96	50
9[c]	0.5	7.5	H_2O	30/140	72	41
10	0.6	5.7	EtOH/H_2O[b]	30/125	48	5
11	0.6	7.5	EtOH/H_2O[b]	30/125	48	10

Reaction conditions: microcrystalline cellulose (0.6 and 0.1 mmol based on glucose monomers), 85% w/w H_3PO_4, Ru-MACHO-BH (0.5 mol%), H_2O (1 mL), 30 bar H_2, at 140 °C. [a] Determined by GC-FID using 1,4-dioxane as the internal standard. Catalyst loading and yield are relative to moles of glucose monomers contained in cellulose. [b] 1 : 1 v/v EtOH/H_2O (1 mL). [c] Microcrystalline cellulose (7.8 mmol), H_2O (15 mL).

Table 3 Direct conversion of hemicellulose to GVL



Entry	Xylan source (M) Corn core	Xylan source (M) Beechwood	H_3PO_4 [M]	Solvent	P/T [bar]/ [°C]	GVL yield[a] [%]
1	0.6		7.5	H_2O	30/125	8
2		0.6	5.7	H_2O	30/140	11
3		0.6	8.4	H_2O	30/140	4
4	0.6		5.7	EtOH/H_2O[b]	30/125	56
5		0.6	5.7	EtOH/H_2O[b]	30/125	24
6	0.6		7.5	EtOH/H_2O[b]	30/125	57
7		0.6	7.5	EtOH/H_2O[b]	30/125	75
8	0.6		5.7	EtOH/H_2O[b]	30/140	29
9	0.6		8.4	EtOH/H_2O[b]	30/140	4
10		0.6	5.7	EtOH/H_2O[b]	30/140	37

Reaction conditions: Ru-MACHO-BH (0.5 mol%), xylan from corn core (76.2% xylose monomers) or xylan from beech wood (95% xylose monomers), 85% w/w H_3PO_4, EtOH (1 mL), 30 bar H_2, at 125 °C in 48 h. Catalyst loading and yield are relative to moles of xylose monomers contained in xylan. [a] Determined by GC-FID using 1,4-dioxane as the internal standard. [b] 1 : 1 v/v EtOH/H_2O (1 mL).

with cellulose with low concentration of acid in water as the sole solvent. Thus, to our delight, using 0.5 mol% Ru-MACHO-BH and 5.7 M H_3PO_4(aq) afforded 20% yield of GVL from 0.6 M cellulose after 48 hours at 125 °C (Table 2, entry 1), which increased to 22% after 96 hours (entry 2). Interestingly, increasing the acid concentration to 7.5 M H_3PO_4(aq) improved the yield to 28% yield (entry 3).

The effect of temperature was also studied as high temperature is known to be detrimental for the acid mediated hydrolysis of cellulose.[26] Thus, at 140 °C with 5.7 M H_3PO_4(aq), 31% of GVL was obtained after 96 hours (entry 4). Using 7.5 M of H_3PO_4(aq) provided 28% of GVL after 48 hours (entry 5), which further yielded 45% after 96 hours (entry 6). Finally, lowering the substrate concentration to 0.1 M cellulose in 7.5 M H_3PO_4(aq) further increased the GVL yield to 50% (entry 8). Moreover, it is worth noting the excellent stability and high activity of Ru-MACHO-BH even in higher acid concentration, which is reflected in the full conversion of so-formed LA to GVL.

The reaction was then scaled up to 1.4 g of cellulose using 0.5 mol% of Ru-MACHO-BH at 140 °C and 30 bar H_2 (entry 9). After 72 hours, a yield of 41% of GVL was obtained, demonstrating the reproducibility of the system at a larger scale. In order to investigate the influence of EtOH as a solvent on the yield of GVL, we performed the reaction with cellulose in a 1 : 1 v/v EtOH/H_2O medium. Thus, employing 0.5 mol% Ru-MACHO-BH and 5.7 M of phosphoric acid under 30 bar H_2 pressure in EtOH/H_2O, afforded only 5% GVL after 48 hours at 125 °C (entry 10). Increasing the acid concentration to 7.5 M led to a significant increase in the yield to 10% (entry 11).

Next, we evaluated the performance of the catalytic system with hemicellulose. Corn core xylan and beechwood xylan were employed as two different xylan types from different biogenic sources. A reaction temperature of 125 °C was found sufficient to reach effective acid-mediated substrate turnover. However, a low yield of 8% of GVL was achieved from xylan from corn core using 0.5 mol% Ru-MACHO-BH and 7.5 MH_3PO_4(aq) in H_2O after 48 hours (Table 3, entry 1). The yield from beechwood at 140 °C with 5.7 M H_3PO_4(aq) was 11% (entry 2). Increasing the acid concentration to 8.4 M H_3PO_4(aq) further diminished the yield to yield to 4% (entry 3). From these observations, we speculate that whether the diminished activity and low yield is as a result of humins formation, which is favoured under higher acid concentration and higher temperature when water is employed as the only solvent.

We then carried out the reaction in 1 : 1 v/v EtOH/H_2O mixture. Thus, using 5.7 M H_3PO_4(aq) in 1 : 1 v/v EtOH/H_2O led to a significant increase in the yield to 56% at 125 °C (entry 4), but merely 29% at 140 °C (entry 8). With 7.5 M H_3PO_4(aq), 57% GVL is obtained at 125 °C (entry 6). To compare the results to that of corn core xylan, we performed the reaction with beechwood xylan under similar conditions. Thus, using 5.7 M H_3PO_4(aq) in 1 : 1 v/v EtOH/H_2O at 125 °C yielded 24% of GVL after 48 hours (entry 5), whereas employing 7.5 M H_3PO_4(aq) yielded 75% of GVL at 125 °C (entry 7).

Having in our hands working conditions for both cellulose and hemicellulose that provide high yields, we decided to test various raw biomass materials.

Direct conversion of real biomass to GVL

We commenced our studies with beechwood sawdust, a lignocellulosic biomass. To our great pleasure, initial investigations revealed that the combination of Ru-MACHO-BH and H_3PO_4(aq) is catalytically active under a H_2 pressure for the transformation to GVL. Hence, we first investigated the effect of H_3PO_4(aq) concentration while maintaining the catalyst loading, H_2 pressure, and

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reaction temperature constant at 0.5 mol%, 30 bar, and 140 °C, respectively. Gratifyingly, employing 7.5 M H_3PO_4(aq) led to 15 wt% yield of GVL after 96 hours (ESI,† Table S1, entry 1), which was improved to 23 wt% by increasing the acid concentration to 9.3 M H_3PO_4(aq) (entry 3). Shortening or extending the reaction time to 24 or 168 hours, respectively, did not significantly change the yield (entries 2 and 4). Further increasing the H_3PO_4(aq) concentration to 10.1 M improved the yield to 25 wt%, which decreased again upon longer reaction times (entry 5 *versus* entries 6 and 7). With 10.9 M H_3PO_4(aq), the optimised yield of 26 wt% was obtained after 24 hours (entry 9). Considering that the theoretical yield of GVL from beechwood is limited to 54 wt% (assuming completely dry biomass and that only hemicellulose and cellulose are converted to GVL[27]), the yield is 48% (Table 4). Again, both shortening and extending the reaction time resulted in lower yields (entries 8 and 10). Moreover, after 18 hours, we still detected the intermediate LA, which was fully converted after 24 hours. It is noteworthy to mention that no hydrodeoxygenation products, such as hydrocarbons, were observed under these reaction conditions, neither in the liquid nor gas phase (ESI,† Fig. S36).[28] Furthermore, a control experiment with GVL as substrate and otherwise identical conditions (Ru-MACHO-BH, 10.9 M H_3PO_4(aq), 30 bar H_2, 140 °C, 72 hours) showed no decomposition products (ESI,† Fig. S37), underpinning the strong selectivity towards GVL production. When the catalyst loading was reduced to 0.9 wt%, the reaction afforded 15 wt% GVL under the optimized reaction conditions after 120 hours. However, LA was still detected in the reaction medium, suggesting the reaction had not finished. Finally, the reaction was also carried out in an EtOH/H_2O mixture to study the solvent effect. With 1 : 1 v/v EtOH/H_2O, a lower GVL yield of 14 wt% was observed under otherwise optimised conditions (entry 11).

To demonstrate the power of our system and its potential to convert raw biowaste mixtures, the same reaction conditions were extended to other lignocellulosic biomass substrates (Table 4). Thus, 12 wt% yield of GVL is obtained from wheat straw after 24 hours, which is increased to 18 wt% after 48 hours. This yield accounts for 46% of the theoretical limit of 39 wt%.[29] Further continuing the reaction to 72 hours results in a slight decrease of the yield. Moreover, these initial results validate the versatility of the catalytic system towards valorising different carbohydrate-rich biomass sources to GVL with approximately 90 mol% yield in each of the six-steps of the reaction pathway.

With bamboo stem, 14 wt% yield of GVL is obtained after 48 hours, with LA still detected in the reaction medium. Thus, extending the reaction hours to 96 hours completely consumed the LA and afforded 20 wt% of GVL, corresponding to a 46% yield of the theoretical limit of 43 wt%.[30]

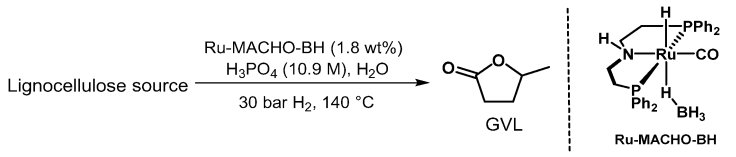
Paper accounts for approximately 26% of total waste at landfills, contributing to air pollution and waste problems.[31] Paper rich in cellulosic content[32] can be utilized in this transformation and after 24 hours, 18 wt% GVL was obtained under the optimised reaction conditions. Extending the time to 48 hours increased the yield to 22 wt%.

Miscanthus, a perennial grass and an agricultural waste, contains high cellulosic content.[33] Indeed, 12 wt% of GVL was obtained after 72 hours, by when the reaction seemed complete (no LA left).

Pistachio production and related dehulling processes generate large quantities of agricultural waste. Taking into consideration the generation volume (approximately 660 000 tons) and lignocellulosic structure, pistachio residues can also be sustainably utilized to yield value-added compounds.[34] Therefore, pistachio shells have been employed for this transformation as well, and a 12 wt% yield of GVL is obtained after 48 hours (26% yield[35]).

Biowaste such as used coffee grounds, banana peel, and potato peel were also tested. Despite having various valuable

Table 4 Conversion of lignocellulosic biomass to GVL



Lignocellulosic source	Beechwood sawdust	Wheat straw	Bamboo	Paper	Grass	Pistachio shells	Used coffee grounds	Banana peel	Potato peel
Lignocellulosic content [wt%]									
Cellulose	37	33	43	85–99	44	43	13	11	8
Hemicellulose	42	25	22	0	24	25	42	26	7
Lignin	19	17	27	0–15	17	16	25	10	33
Starch									23
GVL yield [wt% (mol%)]									
24 h	26(48)	12(31)	14(32)	18(32–34)		12(26)	8(20)	3(11)	8(33)
48 h		18(46)		22(36–42)	12(26)		11(28)		10(41)
72 h		16(41)							
96 h	18(33)		20(46)					10(37)	

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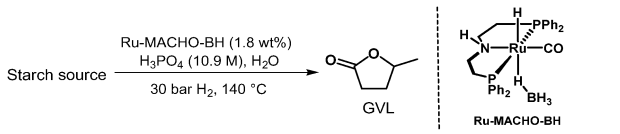
chemical components, used coffee grounds are in general considered as waste that ends up in landfills. Moreover, it is estimated that over 15 Mtpa of spent coffee grounds is produced.[36] Food waste represents 60% of the total municipal biowaste in the EU and is estimated to contribute to global warming corresponding to 186 Mt of CO_2 equivalent.[37] Gratifyingly, employing the same reaction conditions on these biowaste feedstocks led to good GVL yields from all of them. Thus, 10 wt% was obtained from both banana peel and potato peel, whereas 11 wt% was achieved from used coffee grounds. These yields represent 28–41% of the theoretical maximum outcomes.[38] Therefore, this approach demonstrates the feasibility and potential of utilizing day-to-day generated waste as feedstock towards fuels and chemicals.

We then moved our attention towards valorising the second-most abundant polysaccharide appearing in nature, the starch biomass.[39] Rice grains and potato flour were tested, which contains 100% amylose and amylopectin.[40] While these feedstocks are typically considered edible resources, there may be circumstances where it is necessary to classify them as non-food, especially if they are part of food waste. Thus, yields of 9 wt% and 8 wt% were obtained from rice grains and potato flour, respectively, after 24 hours (Table 5). Extending the reaction time to 72 hours improved the GVL yields to 16 wt% and 20 wt%, respectively. These results indicate that the catalytic system is very efficient in hydrolysing not only the α(1–4) glycosidic linkages, but also the α(1–6) linkages between glucose units of amylopectin, which is the major component of starch.

Next, chitin, which is usually obtained from *e.g.*, shrimp or crab shells, fungi cell walls, or exoskeletons of arthropods,[41] was tested. As a note, for safety reasons, we used industrially available chitin instead of the raw biomass sources in this category. To our delight, the reaction afforded 8 wt% of GVL after 72 hours under the optimized reaction conditions (Table 6). Extending the reaction conditions to 96 hours improved the yield to 13 wt%, corresponding to 29% yield or approximately 80% in every step

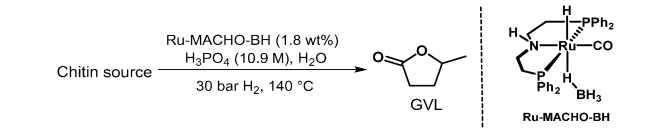
Table 5 Conversion of starchy biomass to GVL



Starch source	Rice grains	Potato flour
Starchy content [wt%]		
Amylose	18	35
Amylopectin	82	65
GVL yield [wt% (mol%)]		
24 h	9(15)	8(13)
72 h	16(26)	20(32)

Reaction conditions: Ru-MACHO-BH (1.8 wt%) and 10.9 M H_3PO_4(aq) in H_2O (1.7 mL) at 140 °C and 30 bar H_2. Yields are calculated with respect to dry biomass and corresponding to the moles of cellulose and hemicellulose.

Table 6 Conversion of chitin biomass to GVL



Chitin source	Chitin
Chitin content [wt%]	
N-Acetyl-glucosamine	100
GVL yield [wt% (mol%)]	
72 h	8(18)
96 h	13(29)

Reaction conditions: Ru-MACHO-BH (1.8 wt%) and 10.9 M H_3PO_4(aq) in H_2O (1.7 mL) at 140 °C and 30 bar H_2. Yields are calculated with respect to dry biomass and corresponding to the moles of *N*-acetyl-glucosamine.

of the seven-step cascade reaction. The comparatively lower yield from the chitin feedstock might be explained by the more challenging structure with a hard-to-hydrolyse amide unit contained in each carbohydrate unit[41] or by the insoluble nature of chitin.[42]

Furthermore, all the biomass materials were mixed in the same pot to evaluate the true versatility of the catalytic system (ESI,† Fig. S31). Thus, all the nine different types of lignocellulosic biomass tested here were mixed. Gratifyingly, 9 wt% of GVL was afforded after 96 hours. The mix of lignocellulosic biomass along with starch biomass (eleven substrates in one pot) gave 11 wt% yield after 96 hours and was improved to 17 wt% after 120 hours. Mixing all twelve substrates, *i.e.*, including chitin, led to 15 wt% GVL after 120 hours. These results suggest the feasibility for the Ru-MACHO-BH/H_3PO_4(aq)/H_2 combination to transform diverse mixtures of carbohydrate-rich biomass waste to GVL.

Finally, to investigate the fate of the catalyst, a test reaction was performed using Ru-MACHO-BH and beechwood sawdust under typical reaction conditions followed by NMR analysis. The persisting ligand phosphine shifts at approximately 63 ppm in ^{31}P NMR suggests that the catalytic complex stays intact (ESI,† Fig. S39). The absence of a hydrido peak, including the disappearance of the hydrido triplet in ^{1}H NMR at −12.3 ppm of Ru-MACHO-BH, might suggest that the resting species is a di-phosphato Ru-complex in presence of excess phosphoric acid and absence of a H_2 pressure (ESI,† Fig. S40). Alternatively, the hydrido(s) might be interacting with the weak acid, thereby obscuring the NMR signal.[43]

Conclusions

In conclusion, we here demonstrate the direct conversion of monosaccharides (xylose, glucose, fructose), polysaccharides (cellulose, hemicellulose), and raw biomass (lignocellulose, starch, chitin) to GVL in good to excellent yields. The direct approach for the catalytic production of GVL from monosaccharides using the

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combination of Ru-MACHO-BH and H_3PO_4(aq) in EtOH/H_2O with 30 bar of H_2 at 125 °C produce GVL yields up to 73%. From the polysaccharides, 50% GVL was obtained from cellulose and 75% from hemicellulose. Finally, with raw biomass, using 1.8 wt% of the homogeneous catalyst Ru-MACHO-BH in 10.9 M H_3PO_4(aq) with 30 bar of H_2 at 140 °C for 24–120 hours provides 10–26 wt% of GVL from twelve different biogenic sources, either as individual substrates or a combined pool. This corresponds to 26–48% yields, or an average of approximately 80–90 mol% yield in each reaction step. Finally, some studies on the catalyst suggest that it remains intact throughout the reaction.

We are currently studying the recycling of the catalytic system for a more comprehensive understanding of the practical feasibility and sustainability of the proposed approach.

Author contributions

SK and MN conceived and designed the project. SK performed the experiments and analysis under the supervision of MN. Writing review and editing was done by SK and MN.

Conflicts of interest

SK and MN are listed as inventors on the European patent application (application no. 22200625.6) by Technical University of Denmark (DTU) which describes this work. The authors declare no competing interests.

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