Direct valorization of biomass waste to gamma-valerolactone

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SUMMARY

We describe the first direct conversion of raw lignocellulose, starch, and chitin biomass to GVL. 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 GVL in excellent yields (10-26 wt%) from twelve different biogenic or industrially processed biowaste sources, either as individual substrates or a combined pool. This corresponds to 26-48mol% yields, or an average of approximately 80-90 mol% yield in each reaction step.

Biomass, valorization, gamma-valerolactone, catalysis, Brønsted acid, pincer catalyst, lignocellulose, starch, chitin, platform chemical, phosphoric acid, Ru-MACHO-BH, homogeneous catalyst

INTRODUCTION

The annual production of biowaste exceeds 100 Mt in the European Union (EU) and approaches 200 Mt in the United States (USA)[1,2]. Up to >40% ends up in landfills and accounts for the second largest anthropogenic source of CH_4 emission, i.e. 20% in EU and 8% on the global scale[3]. Therefore, a benign transformation of biowaste to industrially useful commodity chemicals would be an efficient method for reducing carbon emissions and fossil fuel dependence[4], and thus not only lowering the output of CH_4 but also of CO_2. Indeed, biomass is the only perennial resource that might provide a negative carbon footprint, i.e. decreasing the net atmospheric CO_2 levels[5–7]. However, huge challenges for viable biowaste to commodity chemicals processes include the highly heterogeneous, complex, and relatively inert composition of biomass. Compelling reasons therefore exist for developing new and effective strategies that allow for benign and selective biomass valorization directly to end-user utilization or platform chemicals. One of the most promising sustainable platform chemicals is gamma-valerolactone (GVL)[8]. It derives from biogenic carbohydrates via multistep processes and has numerous applications, such as fuel additive/biofuel, bulk chemicals, green solvent, and in the syntheses of polymers or pharmaceuticals. Three highly abundant biogenic carbohydrate are lignocellulose, starch, and chitin. Lignocellulosic residues, mainly originating from wood- and agricultural waste, exceed 180 Gtpa worldwide[9]. Starch polysaccharides account for approximately 3 Gtpa through the process of photosynthesis, among which one-third of all food produced for human consumption is lost or wasted globally[10]. Finally, chitin, originating from animal fibers, accounts for 1 Gtpa [11].

To efficiently obtain GVL from carbohydrate-rich biomass feedstock, a wide range of substrates must converge into the same product, and numerous undesired side reactions may hamper the process. The initial step is an acid mediated conversion of the biomass into its constituent polysaccharides (Figure 1). Several types of polysaccharides are present in various biomass sources, including cellulose and hemicellulose from lignocellulose biomass, *N*-acetylglucosamine polymer from chitin, and amylose and amylopectin from starch, which must all be hydrolyzed to their monosaccharides, such as xylose, glucose, fructose, *N*-acetylglucosamine, and *N*-glucosamine. The catalytic system must also be able to withstand the selective dehydration of this pool of monosaccharides to furanics. To obtain levulinic acid (LA), furfural must be both hydrogenated and hydrolyzed, whereas HMF must be selectively only hydrolyzed. Finally, LA is hydrogenated to GVL (see scheme S1 for generally accepted detailed reaction pathways for all three types of carbohydrate-rich biomass).
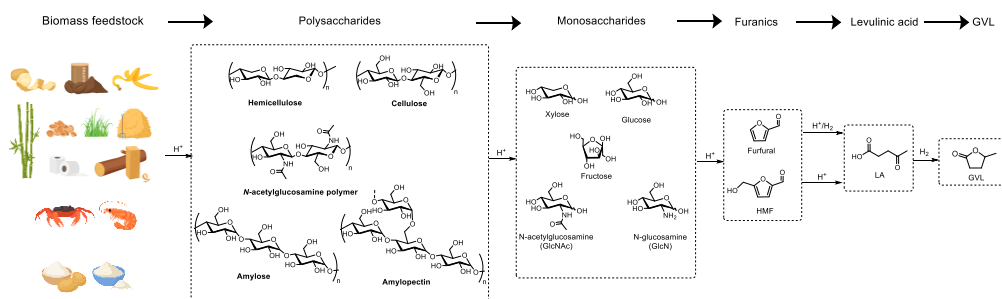

Figure 1. Selection of possible intermediates during the acid- and hydrogenation-mediated process of various biomass waste feedstock to GVL.

To the best of our knowledge, there exists only one example of converting raw biomass to GVL. Huang demonstrated a one-pot conversion of poplar to GVL using mixed Al2(SO4)3 and Ru/ZrO2 catalyst and a sacrificial H-donor (^{i}PrOH) leading to a yield of 12 wt% GVL using 800 W microwave heating to 180 °C[12]. Even transforming the simpler biomass-derived uniform polysaccharides and C6- as well as C5 monosaccharides to GVL are scarcely reported[13–17]. Thus, studies on developing efficient and versatile catalytic systems for the direct conversion of raw biomass to GVL is highly pertinent. Herein, we report the unprecedented direct production of GVL from several raw biomass waste materials in excellent yields up to 48%, covering three major types of carbohydrate-rich biomass sources. By using a novel combination of Ru-MACHO-BH, H_2, and weak acid H_3PO_4(aq), the myriad of cascade steps from biomass to GVL performs highly efficiently and selectively under mild reaction conditions (Figure 2). Notably, there exist relatively few examples of homogeneous catalytic hydrogenations under acidic conditions[18–24]. Furthermore, the Noyori-type PNP pincer complexes[25], such as the Ru-MACHO complex[26] and analogs, have demonstrated excellent activity in both basic[27–29] and neutral media[30–33], but to the best of our knowledge, never under Brønsted acid conditions.

Figure 2. Direct production of GVL from various biomass waste feedstock.

RESULTS and DISCUSSION

We commenced our studies with beechwood sawdust, a lignocellulosic biomass. 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 reaction temperature constant at 0.5 mol%, 30 bar, and 140 °C, respectively. Gratifyingly, employing 7.5 M H_3PO_4(aq) led to an encouraging 15 wt% yield of GVL after 96 hours (Table 1, Entry 1), which was improved to 23 wt% by increasing the concentration of H_3PO_4(aq) to 9.3 M (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 optimal yield of 26 wt% was obtained after 24 hours (Entry 9). Considering that the theoretical weight of GVL from beechwood is limited to 54wt% (assuming completely dry biomass and that only hemicellulose and cellulose are converted to GVL[34]), the yield is 48%. 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 (SI, Figure S24). 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 (SI, Figure S25, S26), 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 optimized conditions (Entry 11).

Beechwood sawdust → Ru-MACHO-BH (1.8 wt%), H_3PO_4, H_2O, 30 bar H_2, 140 °C → GVL | Ru-MACHO-BH

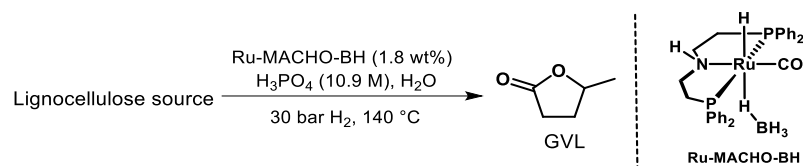| Beechwood sawdust content		Entry	$c(H_3PO_4)$ [M]	Time [h]	GVL yield[a] [wt% (mol%)]
Lignocellulosic content	wt%	1	7.5	96	15 (28)
Hemicellulose	37	2	9.3	24	22 (41)
Cellulose	42	3	9.3	96	23 (43)
Lignin	19	4	9.3	168	20 (37)
		5	10.1	24	25 (46)
		6	10.1	38	21 (39)
		7	10.1	96	19 (35)
		8	10.9	18	21 (39)
		9	10.9	24	26 (48)
		10	10.9	96	18 (33)
		11[b]	10.9	24	14 (26)

Standard reaction conditions: Beech wood (91 mg, corresponding to 0.26 mmol hemicellulose and 0.28 mmol cellulose[34]), Ru-MACHO-BH (1.65 mg, 0.0028 mmol), H_2O at 140 °C and 30 bar H_2, [a] Determined by GC-FID. Yields are calculated with respect to dry biomass. [b] 1:1 V/V EtOH/H_2O (1 mL)

Table 1. Optimization of the direct conversion of beechwood sawdust to GVL.

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 2). 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%[35]. 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 valorizing 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, and LA was still detected in the reaction medium. Extending the reaction hours to 96 hours completely consumed the LA and afforded 20 wt% GVL, corresponding to 46% of the theoretical limit of 43 wt%[34]. Paper accounts for around 26% of total waste at landfills, contributing to air pollution and waste problems[37]. Paper rich in cellulosic content[38] can be utilized in this transformation and after 24 hours, 18 wt% GVL was obtained under the optimized 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[39]. 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[40]. Therefore, pistachio shells have been employed for this transformation as well, and a 12 wt% yield of GVL is obtained after 48 hours (26%[41]). Biowaste such as used coffee grounds, banana peel, and potato peel were also tested. Despite having various valuable 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[42]. 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[43]. 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 mol% of the theoretical maximum yields[44–46]. Therefore, this approach demonstrates the feasibility and potential of utilizing such day-to-day generated waste as feedstock towards fuels and chemicals.

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

Table 2. Conversion of lignocellulosic biomass to GVL using 1.8 wt% Ru-MACHO-BH 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.

We then moved our attention towards valorizing the second-most abundant polysaccharide appearing in nature, the starch biomass. Rice grains and potato flour were tested which contains 100% amylose and amylopectin[47]. While these feedstock 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 3). 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 hydrolyzing 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.
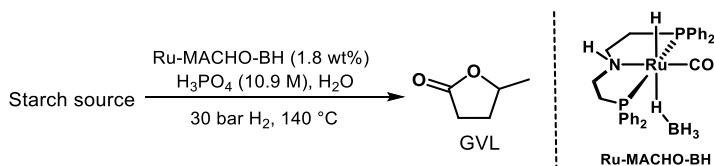
Starch source	Rice grains	Potato flour
Starchy content [wt%]		
Amylose	18	35
Amylopectin	82	65
GVL yield [wt% (mol%)]		
24 h	9 (15)	8 (13)
72 h	16 (26)	20 (32)

Table 3. Conversion of starchy biomass to GVL using 1.8 wt% Ru-MACHO-BH 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.

Next, chitin, which is usually obtained from e.g., shrimp or crab shells, fungi cell walls, or exoskeletons of arthropods[48], 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 4). Extending the reaction conditions to 96 hours improved the yield to 13 wt%, corresponding to 29% yield or approximately 80% in every step 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-hydrolyze amide unit contained in each carbohydrate unit[48] or by the insoluble nature of chitin[49].
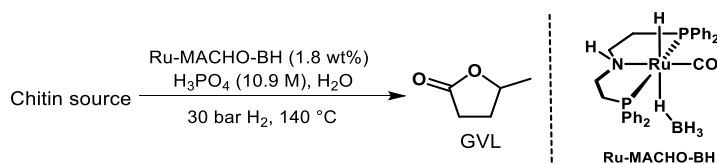
Chitin source	Chitin
Chitin content [wt%]	
N-acetyl-glucosamine	100
GVL yield [wt% (mol%)]	
72 h	8 (18)
96 h	13 (29)

Table 4. Conversion of chitin biomass to GVL using 1.8 wt% Ru-MACHO-BH 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.

Furthermore, all the biomass materials were mixed in the same pot to evaluate the true versatility of the catalytic system (Figure 3). 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.
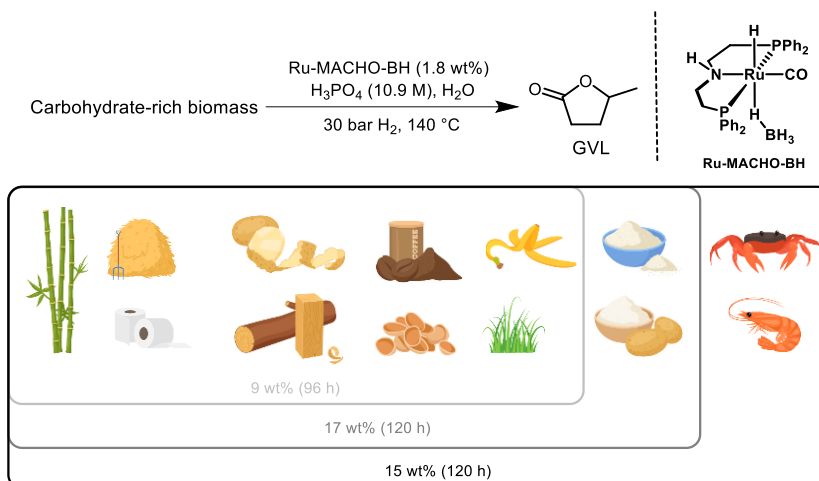
Figure 2. Conversion of carbohydrate-rich biomass to GVL by the Ru-MACHO-BH/ $H_3PO_4(aq)/H_2$ system. Yields are calculated corresponding to the moles of cellulose and hemicellulose.

To elaborate on our results and to assess the origin of the GVL, pure cellulose and hemicellulose were investigated as model substrates using the combination of Ru-MACHO-BH/$H_3PO_4(aq)/H_2$. A total of 49% yield of GVL is obtained from 0.6 M of cellulose using 0.5 mol% Ru-MACHO-BH and 9.3 M $H_3PO_4(aq)$ under 30 bar H_2 pressure at 140 °C after 96 hours. In general, hemicellulose requires significantly milder conditions than cellulose. Two different types of xylans from different biomass sources were employed as feedstock, i.e. from beechwood and corn core. With 0.6 M beechwood xylan, 13% of GVL was obtained when using 0.5 mol% loading of Ru-MACHO-BH and 5.7 M $H_3PO_4(aq)$ at 140 °C and 30 bar H_2 in H_2O for 48 hours. Interestingly, changing the solvent to a 1:1 V/V EtOH/H_2O mixture afforded 43% GVL from beechwood xylan and 33% from corn core xylan. These results indicate that the catalytic system has excellent performance towards integrating the cascade of distinct acid- and hydrogenation-mediated steps of both cellulose and hemicellulose.

Finally, to investigate the fate of the catalyst, a test reaction was performed using Ru-MACHO-BH and 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 (SI, Figure S30). 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 (SI, Figure S31). Alternatively, the hydrido(s) might be interacting with the weak acid, thereby obscuring the NMR signal[50].

In conclusion, we here demonstrate the first direct conversion of raw lignocellulose, starch, and chitin biomass to GVL. 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 GVL in excellent yields (10-26 wt%) from twelve different biogenic or industrially processed biowaste sources, either as individual substrates or a combined pool. This corresponds to 26-48 mol% yields, or an average of approximately 80-90 mol% yield in each reaction step. Furthermore, a number of control experiments reveal that GVL is produced from both cellulose and hemicellulose, allowing to include lignocellulosic material while maintaining excellent yields. Finally, some studies on the catalyst suggest that it remains still intact throughout the reaction.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact
Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Martin Nielsen (marnie@kemi.dtu.dk).

Materials availability
This study did not generate new reagents.

Data and code availability
This study did not generate any datasets.

Material and Methods

Most chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Ru-MACHO-BH, 85 w/w% H_3PO_4 are commercially available and used without further purification. Beechwood sawdust was obtained from a local wood processing company. Peels of potato and banana were sourced from local supermarkets in Copenhagen. Grass and wheat straw were among the feedstock that was collected directly from the surrounding land. Toilet paper, coffee grounds, pistachio shells, potato flour, bamboo, and rice grains were purchased from local supermarkets in the Copenhagen municipality. Used coffee grounds were used as for the reaction. Chitin was commercially obtained from Merck. All the lignocellulosic biomass materials were grinded into powders using ball milling process and dried in vacuum oven before use.

H_2 gas ($H_2O \leq 3$ ppm; O2 $\leq$ 2 ppm) was purchased from Air Liquide. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as the internal standard. The 1H and 13C NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer. The batches for gas analysis, the gas phase was carefully collected in a gas bag and analyzed by MicroGC. TGA was fulfilled under N2 atmosphere (30 mL min^{-1}) using a METTLER TOLEDO thermal analyzer in the temperature interval 25-300 °C with a constant heating rate of 10 °C min^{-1}.

General procedure for catalysis

For a typical hydrogenation experiment, in a glove box, biomass (91 mg) and Ru-MACHO-BH (1.8 wt%, 1.6 mg) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, 1 mL of solvent (H_2O) followed by addition of 85 w/w% aqueous phosphoric acid. Subsequently, the vial was placed in a seven-well reactor with a needle placed through the rubber stopper of the vials for the gas flow. The high-pressure reactor was sealed tightly and flushed with argon/hydrogen (three times) and finally required hydrogen pressure (30 bar) was loaded into the high-pressure reactor and desired temperature of 140 °C was also applied. The reactor was cooled to room temperature before the hydrogen was released and the sample was prepared for GC analysis with 1,4-dioxane as the internal standard.

SUPPLEMENTAL INFORMATION

Supplementary Text
Scheme S1
Tables S1 to S3
Figures S1 to S3

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.

DECLARATION OF INTERESTS

SK and MN is 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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