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# Stability of gamma-valerolactone under pulping conditions as a basis for process optimization and chemical recovery

Marianna Granatier · Inge Schlapp-Hackl · Huy Quang Lê · Kaarlo Nieminen · Leena Pitkänen · Herbert Sixta

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**Abstract** This study focuses on the investigation of the extent of the  $\gamma$ -valerolactone (GVL) hydrolysis forming an equilibrium with 4-hydroxyvaleric acid (4-HVA) in aqueous solutions over a wide pH range. The hydrolysis of a 50 wt% GVL solution to 4-HVA (3.5 mol%) was observed only at elevated temperatures. The addition of sulfuric acid ( $0.2 \times 10^{-5}$  wt% to 6 wt%) at elevated temperatures (150–180 °C) and reaction times between 30 and 180 min caused the formation of 4 mol% 4-HVA. However, with decreasing acidity, the 4-HVA remained constant at about 3 mol%. The hydrolysis reactions in alkaline conditions were conducted at a constant time (30 min) and temperature (180 °C) with the variation of the NaOH concentration ( $0.2 \times 10^{-6}$  wt% to 7 wt%). The addition of less than 0.2 wt% of NaOH resulted in the formation of less than 4 mol% of sodium 4-hydroxyvalerate. A maximum amount of 21 mol% of 4-HVA was observed in a 7 wt% NaOH solution. The degree of decomposition after treatment was determined by NMR analysis. To verify the GVL stability

under practical conditions, *Betula pendula* sawdust was fractionated in 50 wt% GVL with and without the addition of H<sub>2</sub>SO<sub>4</sub> or NaOH at 180 °C and a treatment time of 120 min. The spent liquor was analyzed and a 4-HVA content of 5.6 mol% in a high acidic (20 kg H<sub>2</sub>SO<sub>4</sub>/t wood) and 6.0 mol% in an alkaline (192 kg NaOH/t wood) environment have been determined.

**Keywords** Biorefineries · Gamma-valerolactone · Organosolv · Pulping

## Introduction

The worldwide economy is currently highly dependent on the use of fossil raw materials. Various drawbacks associated with the exploitation of fossil resources, such as non-renewability, pollution, insecurity, and the massive climate change crisis, have promoted the transition to a more sustainable bioeconomy, centered on lignocellulosic biomass. Lignocellulosic material is an abundant, renewable, and relatively cheap carbon-based material. In detail, cellulose, with its unique properties, represents the most important component of fractionated lignocellulose (Henriksson and Lennholm 2009) and is mainly processed into paper-grade and dissolving-grade pulps via chemical pulping.

The global annual production of chemical pulp is more than 144 Mton (Statista, 2021). Despite the

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constant decline in demand for graphic paper, the paper-grade pulp is still indispensable for the constantly growing need for tissues, hygiene, and packaging products. On contrary, the segment for dissolving pulp forms a fast-growing niche market with an annual production of 10.2 million tons in 2019 (Engelhardt 2020). Dissolving pulp is characterized by a high  $\alpha$ -cellulose content ( $> 90\%$ ) and targeted for higher-valued applications such as regenerated cellulose, cellulose esters or ethers, nano- or micro-crystalline cellulose.

The majority of dissolving pulp is currently obtained from wood by chemical pulping using acid sulfite (AS) and pre-hydrolysis kraft (PHK) processes. Whereas the new plants are applying the PHK technique almost exclusively (Chen et al. 2016; Schild et al. 2010; Sixta 2006). However, despite a high degree of technical maturity, AS and PHK encounter several drawbacks such as unsatisfactory yields, lignin containing chemically-bonded sulfur, degraded hemicelluloses (PHK), non-reusable cooking ingredients, and alarming environmental concerns (AS) (Gellerstedt 2009; Mendes et al. 2009; Sixta et al. 2013). As a response to these disadvantages, organosolv pulping was introduced (Kleinert and Tayenthal 1931).

Up to now, the capability of many organic lignin solvents (like ethanol, acetone, acetic acid, or formic acid) for the fractionation of biomass has been investigated and various methods have been established. Due to its eco-friendly properties and the capability to separate cellulose, hemicellulose, and lignin, ethanol attracted attention first and has been utilized by the well-investigated ALCELL (ethanol/water) and SEW (SO<sub>2</sub>-ethanol–water) techniques. Both have already reached the pilot and the former even demonstration scale, but the recently confirmed loss of ethanol, as a consequence of the formation of covalent linkages with lignin and carbohydrates, poses a major challenge to the commercialization (van Heiningen et al. 2018).

Recently, one of the biomass-originated, green solvents  $\gamma$ -valerolactone (GVL), which is currently present in a wide range of food and cosmetic products, was introduced by Horváth et al. (2008) as a sustainable liquid for chemical conversion, and proposed by Fang and Sixta (2014) as a solvent for biomass pulping (Fang and Sixta 2014; Horváth et al. 2008). Since then, several research groups tested the capability of GVL for the fractionation of biomass at acid-catalyzed

conditions at mild temperatures or of agricultural waste and its transformation to furfural and fermentable sugars (Alonso et al. 2017; Li et al. 2016; Qing et al. 2018; Shuai et al. 2016).

Previously, Lê et al. contributed to the development of the GVL based biorefineries and demonstrated the uncatalyzed fractionation of hardwood in a 50 wt% GVL aqueous solution at elevated temperatures. Viscose-grade dissolving pulp readily convertible to regenerated fibers for textile applications or nanofibrillated cellulose was successfully separated for the first time (Lê et al. 2018a). Besides, the spent liquor contained extracted wood components, which can be isolated and potentially upgraded to a wide range of biorefinery products such as sulfur-free lignin, xylose, furfural, and carboxylic acids. More than 90% of the solvent (GVL) can be recovered by liquid CO<sub>2</sub>-extraction and optionally in combination with a preceding water-evaporation stage (Fang and Sixta 2014; Lê et al. 2016a, 2018a, b).

Generally, the feasibility of the organosolv method and its market potential relies on many process-related factors like solvent stability, recyclability, price, product yield, safety, or toxicity of the process. GVL demonstrated remarkable properties, but for its use as a solvent in an industrially relevant pulping process, a proper evaluation of its decomposition behavior under pulping conditions has to be performed.

GVL (5-methyloxolan-2-one) is a five-membered lactone and is well-known for its non-toxicity, low-volatility, high solubility in water ( $> 100$  mg/ml), low melting ( $-31$  °C), and high boiling point (205 °C). It is chemically stable under standard temperature and pressure, resistant to degradation and oxidation, and in combination with water, it forms a zeotropic mixture (Lê et al. 2016b). Despite the high stability at neutral and ambient conditions, the lactone ring of GVL tends to hydrolyze in water, especially in an acidic environment and forms an equilibrium with its hydrolysis product, the 4-hydroxyvaleric acid (4-HVA) (Wong et al. 2017). The hydrolysis in an alkaline environment is more detrimental for the lactone ring due to the irreversible salt formation, the 4-hydroxyvalerate. It is noteworthy that in specific cases, which include high reaction temperatures or prolonged reaction times compared to pulping conditions, GVL undergoes a ring-opening reaction followed by an H-shift to form the corresponding Olefinic acid, the 3-pentenoic acid (Alonso et al. 2017; Luterbacher et al. 2014).

This work aims at the examination of the key fundamentals for the practical development of a new organosolv process. In comparison to Wong et al. (2017), the GVL/4-HVA equilibrium is investigated more closely with the stress on conditions that are more relevant to the fractionation process. Additionally, to the best of our knowledge, for the very first time, the patterns of equilibrium between GVL and 4-HVA under actual *Betula pendula* sawdust cooking in the spent liquor are presented.

## Experimental

### Material

GVL ( $\geq 99$  wt% purity, (RS)-Form) and 1,3,5-trimethoxybenzen ( $\geq 99$  wt%) were purchased from Sigma Aldrich, sulfuric acid (95–97.0 wt%) from Merck, and sodium hydroxide pellets ( $\geq 98$  wt%) from VWR Chemicals. Besides, the solvents for NMR analysis, dimethyl sulfoxide- $d_6$  (99.8%), acetone- $d_6$  (99.8%), acetonitrile- $d_3$  (99.8%) were obtained from Eurisotop and deuterated water- $d_2$  (99.8%) from Acros Organics. *Betula pendula* wood chips were supplied by Stora Enso (Finland). The chips were stored at  $-20$  °C and ground by the use of a Wiley mill (Arthur H. Thomas Co., model No. 2, 1 mm screen opening) before usage. The wood composition was screened according to the SCAN-CM 40:01 standard and the amount of sugars was calculated based on the Janson formula (Janson 1970). For the stability experiments, GVL was distilled to a purity of 99.9 wt% (analyzed by gas chromatography). The water used in the experiments was purified by a Millipore Synergy® UV system (water resistivity of 18.2 M $\Omega$ ).

### Analytical methods

Mixtures have been homogenized by the use of a vortex mixer (Vortex-Genie 2, Scientific Industries, Inc., US) and all thermal treatments have been performed in a microwave reactor (Monowave 300, Anton Paar GmbH, Graz, Austria). The pH value was determined by a pH meter (Thermo Scientific). The  $^1\text{H}$  NMR spectra were recorded on a Bruker AV III 400 MHz spectrometer. The spectra were referenced against the  $^1\text{H}$  peaks of the deuterated solvents and the concentration of the GVL and 4-HVA compounds

were determined related to the defined concentration of the standard 1,3,5-trimethoxybenzene ( $\geq 99$  wt%).

### Statistical model

A full factorial design for an experiment having three factors (temperature, time, and pH) each with four levels would require 64 runs ( $4 \times 4 \times 4$ ) for all possible combinations of levels. Selecting a fractional factorial design is a customary method for reducing the number of runs while maintaining an effective cover for most experimental variables of interest. Employing the scheme of connecting the levels of a four-level factor to a pair of two-level factors (the most commonly used) transforms the three-factor all four-level full plan (64 runs) to a six-factor all two-level plan (32 runs). Employing the same scheme in the opposite direction transforms the fractional design back to a design with three four-level factors (Table S1).

### Thermal reaction of GVL in acidic or alkaline conditions

In total four  $\text{H}_2\text{SO}_4$  and four NaOH stock solutions have been used. 2 g of pure GVL (0.020 mol) are mixed with water and  $\text{H}_2\text{SO}_4$  or NaOH (stock solutions) in a 10 ml vial (detailed information is given in SI Table S2). The solutions were thoroughly mixed for a few seconds and the pH value was recorded. The mixtures were thermally treated at temperatures between 150 °C up to 180 °C at a constant stirring speed of 600 rpm. The reaction time was chosen between 30 and 180 min. After the thermal treatment, the samples were cooled to room temperature and the pH was measured. The formation of 4-HVA was analyzed by NMR analysis. The NMR samples were prepared by dissolving 0.01 g of sample and 0.01 g of the standard 1,3,5-trimethoxybenzene (0.000059 mol) in 0.5 ml DMSO- $d_6$  directly in the NMR tube. The amounts of 4-HVA in mol% and the pH values before and after treatment are presented in SI (Table S2).

### Wood fractionation and spent liquor analysis

*Betula pendula* (silver birch) wood chips were oven-dried at 40 °C overnight and milled to sawdust. *Betula pendula* wood comprised of 42.4% cellulose, 28.0%

C5 hemicellulose, 3.6% C6 hemicellulose, 21.8% lignin, and 1.7% extractives. 7.5 g of pure GVL (0.075 mol) was mixed with different solutions of H<sub>2</sub>SO<sub>4</sub> and NaOH (Table S3). The solutions were thoroughly mixed for a few seconds and the pH value was recorded. Afterward, 1.5 g of oven-dried sawdust were added and treated in Anton Paar microwave reactor at 180 °C, for 120 min (liquor-to-wood ratio of 10 kg/kg<sub>oven dried wood</sub>). After the reaction, the raw spent liquor was separated from the pulp suspension by filtration and the pulp was washed with 37.5 wt% aqueous GVL solution (20 g, 5.9 mol/L). The raw spent liquor and GVL washing filtrate were combined and analyzed by NMR. For NMR measurement, 0.01 g of spent liquor and 0.01 g of standard 1,3,5-trimethoxybenzene (0.000059 mol) were dissolved in 0.5 ml DMSO-d<sub>6</sub> directly in the NMR vial. The pulp was subjected to a final washing stage with boiling water with a liquor-to-wood ratio of 130 kg of water/kg wood and dried at 105 °C. The amounts of 4-HVA in mol% and the pH values before and after treatment are summarized in Table 1.

#### Development of an analytical method for quantification of the GVL/4-HVA equilibrium

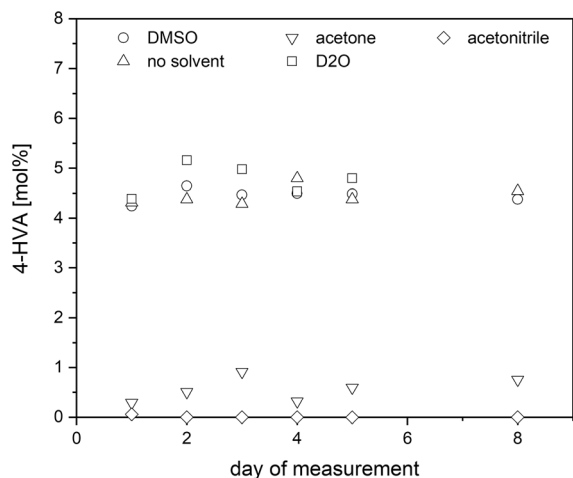
In analogy to the study of Wong et al. (2017) and due to the great solubility of GVL, 4-HVA as well as 3-pentenoic acid in different solvents, NMR was the chosen tool. All of the compounds show peaks of great intensity and due to the nature of the structures, the signals are well separated and distinguished. One of

the prerequisites for the accurate determination of the GVL and 4-HVA equilibria was to choose a suitable solvent for <sup>1</sup>H NMR analysis. Thereby, an equal amount of an acidic sample (0.01 g) of 50 wt% GVL combined with 1.8 wt% H<sub>2</sub>SO<sub>4</sub> at 180 °C treated for 30 min was dissolved in four different solvents (DMSO-d<sub>6</sub>, acetone-d<sub>6</sub>, acetonitrile-d<sub>3</sub>, and D<sub>2</sub>O) and immediately analyzed. The change of the mixtures was monitored at regular intervals until the equilibria were reached. As expected, the <sup>1</sup>H NMR spectra revealed differences in the chemical shifts. Large variations in the 4-HVA concentrations were observed too, which implies that not all solvents showed inert behavior. The 4-HVA concentrations measured in DMSO-d<sub>6</sub> and D<sub>2</sub>O were comparable to a sample analyzed without any NMR solvent (ca. 4.3 mol%). In contrast, lower amounts of 4-HVA were formed in acetone-d<sub>6</sub> (0.3 mol%), and acetonitrile-d<sub>3</sub> (0.1 mol%) (Fig. 1).

As a result, DMSO-d<sub>6</sub> was chosen as the most suitable solvent for <sup>1</sup>H NMR analysis due to the highest accuracy of the results, the good dissolution behavior of all components, and the well-defined, non-overlapping peaks of the -CH<sub>3</sub> groups of GVL, 4-HVA, and the standard (1,3,5-TMB) (Fig. 2). The DMSO-d<sub>6</sub> peak at 2.5 ppm was always defined as an internal reference peak, and the concentration of GVL and 4-HVA was detected via integration of the peak area (shift at 1.29–1.30 ppm and 1.01–1.04 ppm, respectively) with regard to the standard. In pure GVL, no 4-HVA was recognized at between 1.01 and 1.04 ppm. Unlike at basic and acidic conditions a

**Table 1** The concentration of 4-HVA in spent liquor after fractionation of *Betula pendula* in a 50 wt% GVL-water solution at 180 °C and 120 min at acidic or basic conditions

Sample	kg H <sub>2</sub> SO <sub>4</sub> /t <sub>wood</sub>	kg NaOH/t <sub>wood</sub>	4-HVA [mol %]	pH <sub>initial</sub>	pH <sub>Spent liquor</sub>
1	0.000	0.000	3.96	3.97	3.35
2	0.024	0.000	4.06	3.88	3.46
3	0.231	0.000	4.31	3.24	3.49
4	2.232	0.000	5.25	2.36	3.11
5	3.844	0.000	3.65	1.64	2.59
6	6.058	0.000	3.86	1.66	2.30
7	7.541	0.000	4.41	1.38	2.06
8	10.893	0.000	4.08	1.49	1.96
9	17.259	0.000	5.51	1.21	2.06
10	0.000	2.009*10 <sup>-5</sup>	4.18	4.04	3.42
11	0.000	0.019	4.12	4.21	3.40
12	0.000	1.911	3.24	6.00	3.76
13	0.000	192.113	5.88	8.62	5.69



**Fig. 1** 4-HVA equilibria in DMSO- $d_6$ , acetone- $d_6$ , acetonitrile- $d_3$ , and D $_2$ O. Reaction conditions: 50 wt% GVL, pH = 1, 180 °C, 30 min, 1.8 wt% H $_2$ SO $_4$

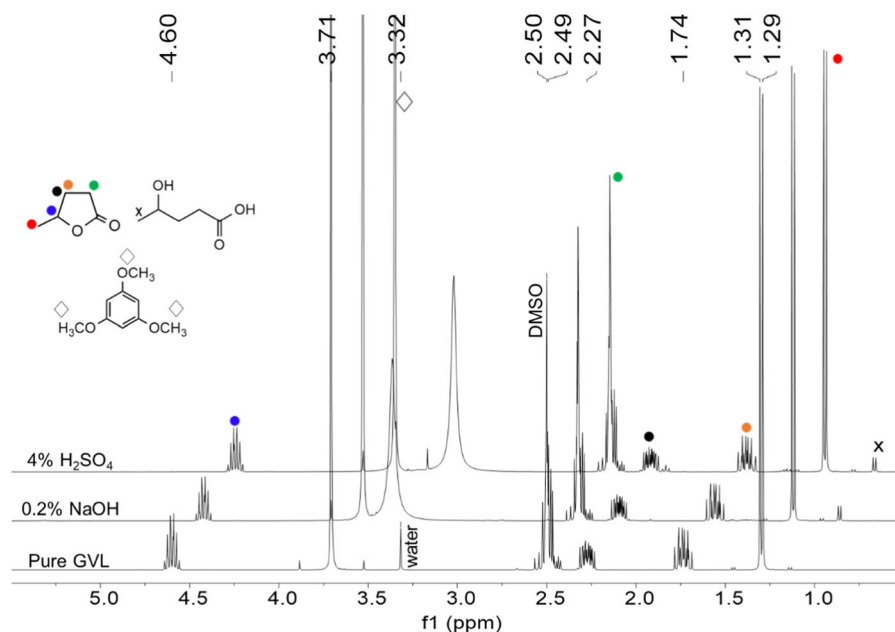
4-HVA peak was formed (Fig. 2). All spectra with detailed shifts can be found in SI (Figure S2-S15). Furthermore, the visibility of 1% pentenoic acid was tested resulting in the detection of these small traces with great intensity (Figure S16).

## Results and discussion

### Hydrolysis of GVL and formation of 4-HVA as a function of pH (time and temperature)

$\gamma$ -Valerolactone (GVL) belongs to the group of carboxylic acid derivatives. The structure exhibits a cyclic ester, which is formed by an intramolecular reaction of a hydroxycarboxylic acid under the elimination of water (Graham 2004). Due to the relatively large size and high energy barrier,  $\gamma$ -lactones are stable heterocycles and do not decompose readily in a neutral aqueous solution at ambient conditions. Hydrolysis only appears via a nucleophilic substitution mechanism in both, acid and basic catalyzed solutions. Thereby, a water molecule attacks the electrophilic carbon of the carbonyl group and causes an acyl-oxygen cleavage. At certain conditions, the heterocyclic ring of GVL is thus opened, resulting in the formation of 4-hydroxyvaleric acid (4-HVA) under the establishment of an equilibrium (Gómez-Bombarelli et al. 2013a, b).

Following the conditions proposed by Lê et al. for the fractionation of *Eucalyptus globulus* sawdust (Lê et al. 2016a), the stability of GVL was firstly determined in a 50 wt% aqueous solution at 180 °C in the absence of wood. The importance of heating was



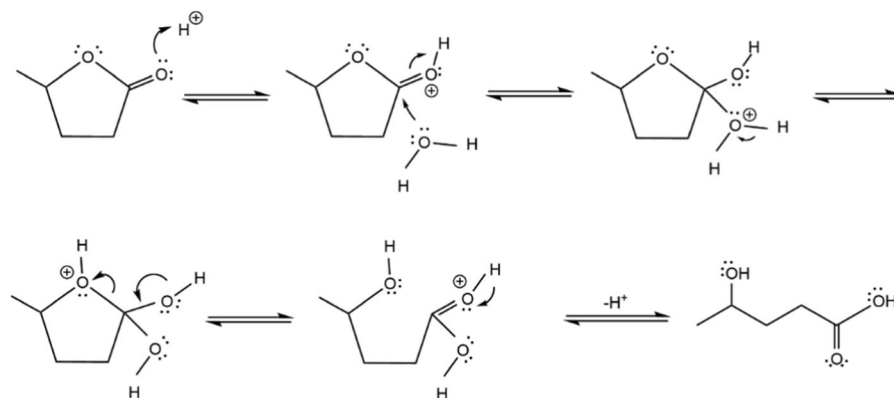
**Fig. 2** Comparison of  $^1\text{H}$  NMR spectra of pure GVL, GVL treated with H $_2$ SO $_4$  and NaOH



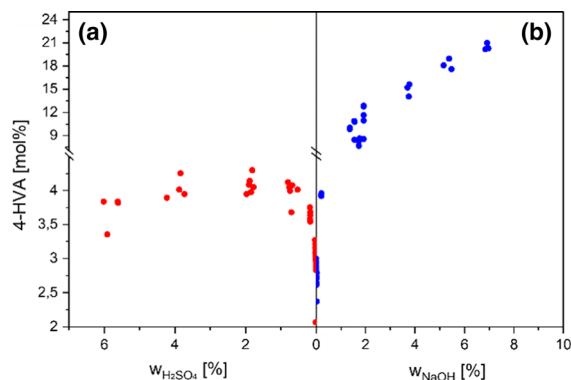
proven again. Hydrolysis of GVL to 4-HVA was observed only after thermal treatment and the reached equilibrium was determined by repeated re-analysis. The extent of hydrolysis depends on the GVL concentration or, conversely, on the amount of water in the solution. In the case of 50 wt% GVL, 3.4 mol% of 4-HVA was obtained. In contrast, in the case of 87 wt% GVL, no more than 0.8 mol% 4-HVA was yielded (Table S4). At neutral conditions, water acts as a weak nucleophile and an increase of the acidity enhances the basicity of the water.

An acid catalyst activates the carbonyl group by protonation of the carbonyl oxygen and thus a nucleophilic attack by water is favored (Fig. 3) (Graham 2004). The effect of acidic conditions regarding a 50 wt% GVL aqueous solution was traced by a stepwise elevation of the  $\text{H}_2\text{SO}_4$  concentration from  $0.2 \times 10^{-5}$  wt% to 6 wt% at elevated temperatures (150–180 °C) at reaction times between 30 and 180 min. The addition of sulfuric acid resulted in the formation of a stable GVL/4-HVA equilibrium. After all, the formation of 4-HVA did not exceed 4 mol% and with decreasing acidity to near neutral, the 4-HVA concentration remained constant at about 3 mol% (Fig. 4a). The equilibrium stability of the mixtures was determined by NMR analysis at regular intervals. As no changes were detected, equilibrium was reached after the treatment.

The results are consistent with the general theory of acidic ester hydrolysis. The acid-catalyzed mechanism is a reversible reaction resulting from the absence of salt formation. In acidic conditions, the protons of the acid are regenerated (Graham 2004) and thus only a



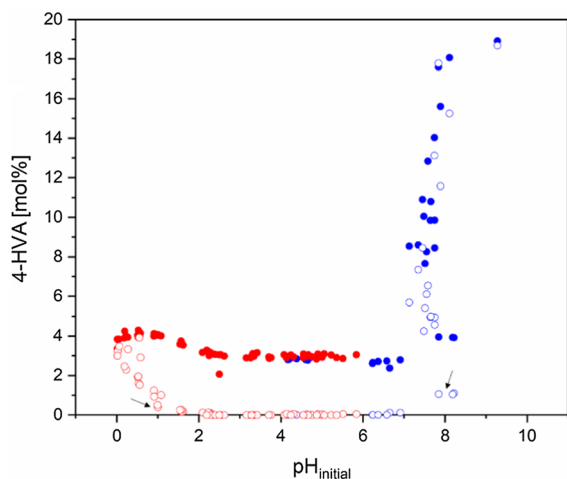
**Fig. 3** Mechanism of hydrolysis of GVL in an acidic environment



**Fig. 4** **a** Concentration of 4-HVA formed in GVL-water solutions after treatment at 150–180 °C for 30–180 min in the presence of  $\text{H}_2\text{SO}_4$  (0.0–6.0 wt%,  $\text{pH}_{\text{initial}} = 0-6$ ) **b** Concentration of 4-hydroxyvalerate formed in GVL-water solution after treatment at 180 °C for 30 min in the presence of NaOH (0–7 wt%,  $\text{pH}_{\text{initial}} = 4-9$ )

small amount of acid (0.7 wt%) is sufficient to reach the maximum concentration of 4-HVA (4.3 mol%).

Previously Wong et al. (2017) investigated the acidic hydrolysis of 87 wt% GVL at room temperature using high concentrations of  $\text{H}_2\text{SO}_4$  (0.01–4.05 mol/L) and HCl (0.02–2 mol/L), yielding in < 4 mol% of 4-HVA (Wong et al. 2017). In our measurements, 4-HVA formation at room temperature was evident only at very low pH ( $\geq 0.5$  wt%  $\text{H}_2\text{SO}_4$ ,  $\text{pH}_{\text{initial}} < 1$ ), which is consistent with the observation of Wong et al. (2017) (Fig. 5). Additionally, this study investigated the GVL ring-opening also at higher pH range (pH 2–6) at room temperature, concluding that with increasing pH near neutral, the 4-HVA formation could not be detected (Fig. 5). However, unlike the reported acid hydrolysis from Wong et al. (2017), the



**Fig. 5** Formation of 4-HVA/ 4-hydroxyvalerate in a GVL-water solution at acidic ( $\text{H}_2\text{SO}_4$ , red) and basic (NaOH, blue) conditions before thermal treatment (red circle, blue circle) and after thermal treatment (150–180 °C). Arrows indicate the threshold of spontaneous ring opening in alkaline ( $\geq 0.2$  wt% NaOH) and acidic ( $\geq 0.5$  wt%  $\text{H}_2\text{SO}_4$ ) environment

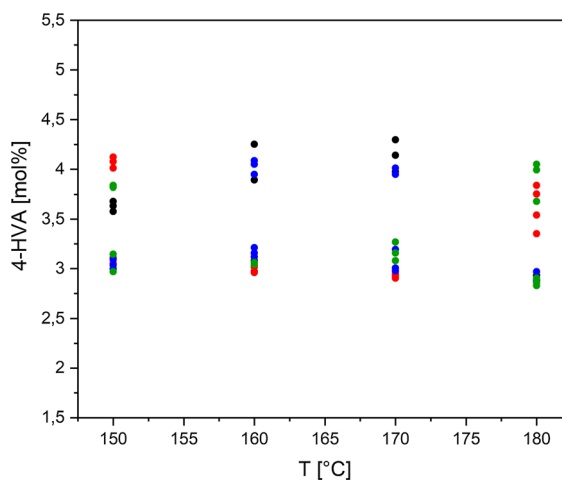
results of this study exhibited an opposite trend, meaning that higher acidity induced the formation of 4-HVA to larger extent. In Fig. 5 the threshold of the spontaneous GVL ring-opening as a function of pH of the solution before heating is presented. In other words, GVL remains stable at the pH range 2–7 at ambient conditions. Moreover, it illustrates the increase of 4-HVA concentration after heating at the initial conditions. The shifts of the pH values (before and after) at specific treatment conditions as well as the corresponding 4-HVA concentrations are listed in Table S2.

To avoid the extensive number of measurements resulting from all possible combinations of reaction conditions (temperature, time, and concentration) for the individual samples, the conditions were chosen based on a fractional factorial design of high resolution. Choosing the model allowed the estimation of the main and first-order interaction effects of the variables on GVL hydrolysis. Further statistical evaluation of experimental data obtained from acidic hydrolysis revealed that the alteration of the time and temperature once the equilibrium is reached has no significant effect on GVL hydrolysis. Consequently, the acid concentration remained the main influence on hydrolysis.

Figure 6 graphically represents the margins in which the time and temperature affect the hydrolysis. Despite the gradual increase of reaction time or temperature, the 4-HVA remained relatively constant. The  $\text{H}_2\text{SO}_4$  concentration ranged from 0.0 to 6.0 wt% ( $\text{pH}_{\text{initial}} = 0\text{--}6$ ) and it can be tracked from Fig. 6 and Table S2.

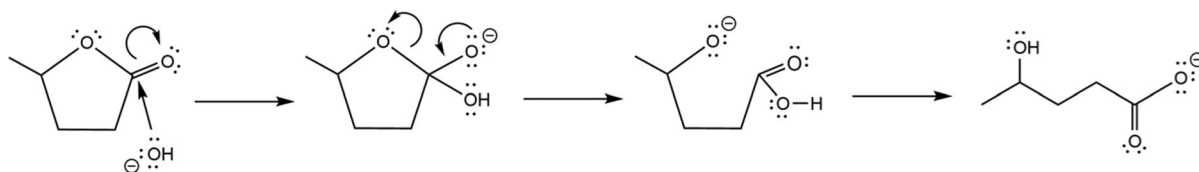
Besides, the hydrolysis of esters is favored in an alkaline environment as well. Thereby, the hydroxide ion gained from a strong base like NaOH acts as a nucleophile, which attacks the electropositive carbon of the ester unit. At these certain conditions, the reaction is irreversible and driven towards the formation of the salt. A carboxylate ion is formed and stabilized by a suitable positive counter ion (Fig. 7) (Clayden et al. 2012; Graham 2004). The presence of sodium 4-hydroxyvalerate after the reaction of GVL with aqueous NaOH was previously confirmed by Horváth et al. (2008).

The experiments in the alkaline environment were conducted at constant time (30 min) and temperature (180 °C) with the variation of the NaOH dosage. Higher concentrations of NaOH ( $\geq 0.2$  wt%,  $\text{pH}_{\text{initial}} > 8$ ) facilitated the GVL ring-opening ( $\geq 1$  mol%) already before heating accompanied by a gradual drop of the pH (Fig. 5). After the treatment, stabilization of pH was reached, and no further decrease in the pH value was recognized. The addition of less than 0.2 wt% of NaOH resulted in the formation of  $< 4$  mol%



**Fig. 6** Formation of 4-HVA as a function of temperature in a GVL-water solution in the presence of  $\text{H}_2\text{SO}_4$  (0.0–6.0 wt%,  $\text{pH} = 0\text{--}6$ ): black filled circle 30 min, red filled circle 60 min, blue filled circle 120 min, green filled circle 180 min





**Fig. 7** Mechanism of hydrolysis of GVL in an alkaline environment

of sodium 4-hydroxyvalerate (Fig. 4b), while an amount of 21 mol% 4-HVA was observed as the largest amount in a 7 wt% NaOH solution. This result confirmed the significant influence of the alkaline environment on the stability of GVL. Higher concentrations of NaOH significantly help to shift the reaction toward the formation of sodium 4-hydroxyvalerate. The linear increase of 4-hydroxyvalerate implied that the GVL hydrolysis could extend beyond 21 mol% by a simultaneous elevation of NaOH (> 7 wt%). However, such high concentrations of alkali are neither favorable nor practical for pulping purposes, and for technical reasons, no further investigations have been performed.

Wong et al. (2017) also investigated the stability of GVL under aqueous alkaline conditions in the presence of a 25 mol%  $\text{NH}_4\text{OH}$  solution at room temperature. Fifteen hours after the reaction, an extent of GVL hydrolysis of 30 mol% was reported (Wong et al. 2017). The amount of hydrolysis in alkaline environment was observed immediately and confirmed by our measurements.

Moreover, a bi-phasic system was observed after the mixing of 50 wt% GVL solution with  $\geq 1.3$  wt% NaOH. Both phases were analyzed. The upper organic phase released an enrichment of GVL and the lower aqueous layer of the 4-hydroxyvalerate. This phenomenon is commonly known as a salting-out effect. A large amount of salt decreases the solubility of GVL and causes a liquid layer formation.

#### Equilibrium model for 4-HVA formation

An addition of  $\text{H}_2\text{SO}_4$  to an aqueous solution of GVL catalyzes the hydrolysis reaction.

In general, the dissociation of sulfuric acid follows a two steps deprotonation, which yields first in the production of hydrogen sulfate ( $\text{HSO}_4^-$ ) and finally in the formation of the dianion sulfate ( $\text{SO}_4^{2-}$ ). As  $\text{H}_2\text{SO}_4$  is a strong acid, the first dissociation reaction will be almost complete. As for the second

dissociation reaction, it can be described by the equilibrium Eq. (1), where  $K$  is an equilibrium constant:

$$[\text{H}_3\text{O}^+][\text{SO}_4^{2-}] = K[\text{HSO}_4^-][\text{H}_2\text{O}] \quad (1)$$

Furthermore, omitting the intermediate steps in the ring-opening mechanism leads to the equilibrium Eq. (2) with the equilibrium constant  $K_{\text{ring}}$ :

$$[4\text{HVA}] = K_{\text{ring}}[\text{GVL}][\text{H}_2\text{O}] \quad (2)$$

As a result, the equilibrium Eqs. (1) and (2) contain six different molar concentrations ( $[\text{H}_3\text{O}^+]$ ,  $[\text{SO}_4^{2-}]$ ,  $[\text{HSO}_4^-]$ ,  $[\text{H}_2\text{O}]$ ,  $[\text{GVL}]$  and  $[4\text{-HVA}]$ ), which are obtained from the considerations of molar balance and electroneutrality.  $\text{H}_2\text{O}$  participates in one reaction forming  $\text{H}_3\text{O}^+$  and another forming 4-HVA, both at mole-to-mole ratio 1:1. Consequently, the denotation  $c_1$  (Eq. 3) concludes that the molar amounts of these constituents must be the same as the initial molar amount of  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  (after the first dissociation of  $\text{H}_2\text{SO}_4$ ). Furthermore, the initial concentration of  $[\text{HSO}_4^-]$  ( $c_2$ ) and GVL ( $c_3$ ) are achieved by Eqs. 4 and 5.

$$[\text{H}_2\text{O}] + [\text{H}_3\text{O}^+] + [4\text{HVA}] = c_1 \quad (3)$$

$$[\text{HSO}_4^-] + [\text{SO}_4^{2-}] = c_2 \quad (4)$$

$$[\text{GVL}] + [4\text{HVA}] = c_3 \quad (5)$$

At the same time, the equation of electroneutrality is defined as:

$$[\text{H}_3\text{O}^+] = [\text{HSO}_4^-] + 2[\text{SO}_4^{2-}] \quad (6)$$

Now, it is possible to solve the system of Eqs. (1)–(6) and obtain an estimate e.g., for the concentration of 4-HVA as a function of initial  $\text{H}_2\text{SO}_4$  concentration and ring-opening Equilibrium constant  $K_{\text{ring}}$ . The fact that the equation system contains products of different concentrations leads to a nonlinear behavior and thus to several solutions one of which being chemically

meaningful. However, there is no way the two equilibrium Eqs. (1) and (2) could account for the observation in the experimental data of the 4-HVA concentration at equilibrium increasing with lower pH. Therefore, we just fit the model to the data points with higher pH values to obtain the estimate  $K_{\text{ring-}} = 5.7 \times 10^{-3}$  for the ring-opening equilibrium constant and extrapolate the model to the lower pH values to compare its predictions to those observed as in Fig. 8.

Wong et al. (2017) proposed the model for the acidic pH range 0–2 (Wong et al. 2017). The suggested model displays a decrease in 4-HVA concentration at low pH values what could be also partly observed in our data. However, the model presented by Wong et al. (2017) does not describe the pH range below 1 (Fig. 8). The peak in the data at a pH value just below 1 would seem to require an additional element in the model where the presence of sulfuric acid promotes the formation of 4-HVA even at equilibrium. The difference between model and experimental data implies that there could be present another reaction. To find a valid proposal for this equilibrium reaction, further measurement is needed.

In the alkaline environment, the NaOH reacts with the GVL forming a salt. Hence, the pH level increases only moderately despite the addition of sodium hydroxide. It is however not obvious what is the mechanism behind the relative stability of GVL under alkaline conditions that according to experimental data prevents the complete conversion independent of

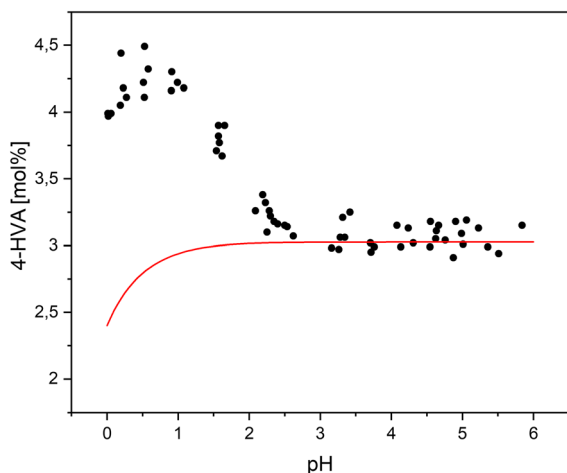
the treatment time. If the alkaline hydrolysis is an equilibrium reaction the equilibrium constant  $K_{\text{AH}}$  is calculated by Eq. (7)

$$[4\text{HVA}^-] = K_{\text{AH}}[\text{GVL}][\text{OH}^-] \quad (7)$$

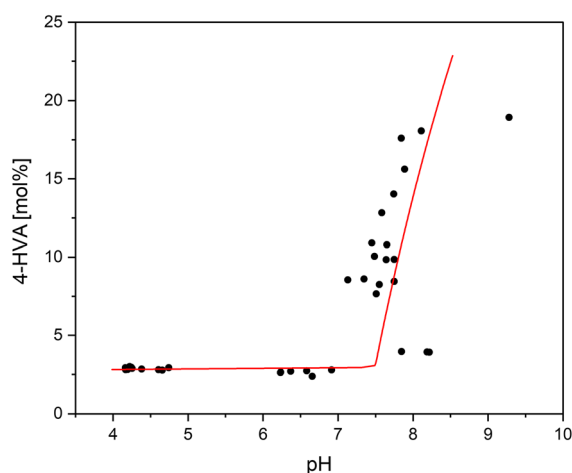
Figure 9 shows a fitted kinetic model assuming an equilibrium reaction between GVL and the 4-HVA salt in addition to the uncatalyzed equilibrium reaction between GVL and 4-HVA, also present during acidic conditions. The alkaline model fit renders the value 0.13 to the equilibrium constant for the reaction of GVL and the 4-HVA salt. The summary of the equilibrium constants can be found in Table S5.

#### GVL hydrolysis and formation of 4-HVA during *Betula pendula* fractionation

The organosolv fractionation excels in its potency to effectively delignify the biomass even without the addition of sulfur-containing chemicals what makes it significantly ecologically approachable. It can run either as auto-catalyzed, when the hydrolysis is enhanced only by acetic acid released from hemicelluloses, with the help of mineral acid, or some of the processes were intended as alkali-organosolv (Azadi et al. 2013). The GVL process was widely studied as an auto-catalyzed or acid-catalyzed process. Consequently, in this study, the stability of GVL was examined under real pulping conditions in acidic and alkaline conditions.



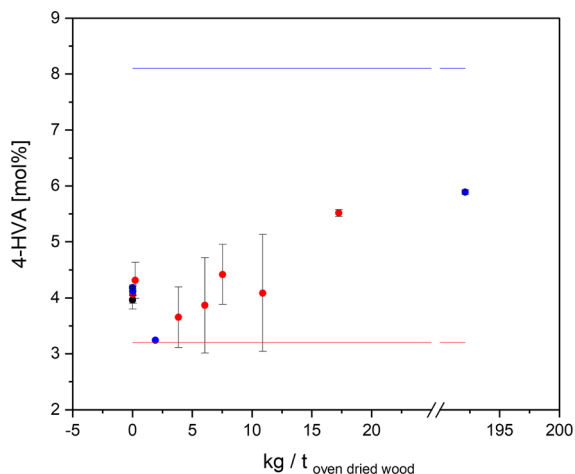
**Fig. 8** Equilibrium model compared to acidic 4-HVA data: black filled circle experimental data, red line model



**Fig. 9** Equilibrium model fitted to alkaline 4-HVA data: black filled circle experimental data, red line model

*Betula pendula* sawdust was fractionated in 50 wt% GVL with and without the addition of  $\text{H}_2\text{SO}_4$  or NaOH at 180 °C using a reaction time of 120 min. The NMR analysis revealed that the spent liquor contained 4-HVA and a small amount of acetic acid (Figure S15). The presence of levulinic (LA) acid and formic acid (FA) was not detected by NMR. In a highly acidic environment (20 kg  $\text{H}_2\text{SO}_4$ /t wood), the formation of 4-HVA was 5.6 mol% and in an extremely alkaline (192 kg NaOH/t wood), the 4-HVA did not exceed 6.0 mol% (Fig. 10, Table 1). In addition, Fig. 10 illustrates the average formation of 4-HVA without wood for comparison.

The carboxylic acids derived from the fractionation of wood, may partly neutralize NaOH and hence, lower the concentration of 4-HVA. On the contrary, in comparison with the results achieved in the absence of wood, the 4-HVA concentration slightly increased in the fractionation with the highest acid charge (17 kg  $\text{H}_2\text{SO}_4$ /t<sub>odw</sub>). The slight increase of 4-HVA during the fractionation can be caused also by the substantial degradation of cellulose under highly acidic conditions (Table S6), which could contribute to the formation of LA and further to 4-HVA. The fractionation of carbohydrates is followed by a series of chemical reactions including acidic hydrolysis of



**Fig. 10** The concentration of 4-HVA in spent liquor after fractionation of *Betula pendula* in an equiponderant GVL-water solution 50% GVL at 180 °C and 120 min: black filled circle without catalyst, red filled circle with  $\text{H}_2\text{SO}_4$ , and blue filled circle with NaOH, red line without wood in acidic environment, blue without wood in alkaline environment. The error bars represent the standard deviation of the individual measurements with the same reaction conditions

glycosidic bonds. As a result, acid-catalyzed reactions lead to the degradation of hexoses forming LA and FA at higher temperatures (Sjöström 1993). Further reduction of LA by hydrogenation yields to 4-HVA which lactonizes to GVL (Deng et al. 2010; Yan et al. 2009). However, to prove this hypothesis, more investigations are needed.

Alonso et al. (2017) also investigated the stability of GVL in the presence of biomass components, but only using acetic acid as a model compound at a concentration of 5 wt.%. After 12 h, at 130 °C and in the presence of 0.1 M  $\text{H}_2\text{SO}_4$ , the formation of 4-HVA together with levulinic acid did not exceed 0.4 mol%. The discrepancy in 4-HVA concentration between Alonso et al. (2017) and this study could be due to the lower water content in the GVL/water mixture (70/30 and 50/50, respectively).

## Conclusion

GVL hydrolysis to 4-HVA under the specific conditions of a biomass fractionation process was investigated. The hydrolysis occurs at higher temperatures (> 150 °C) and in acid and alkaline catalyzed environments. 4-HVA reaches a stable value (> 4 mol%), and only under extreme alkaline conditions, GVL can hydrolyze up to 20 mol%. The same trend of hydrolysis was followed during the biomass fractionation. The pH window (pH = 2–7) demonstrates GVL stability at ambient conditions independent of the concentration of the catalyst. The next step is to investigate the extent to which a 3–6 mol% 4HVA content in the spent liquor affects the recovery of GVL by liquid  $\text{CO}_2$  extraction and, in addition, whether 4-HVA is involved in loss reactions with wood components.

**Authors' contributions** M Granatier: Investigation, Writing-Original Draft, Visualization; I Schlapp-Hackl: Methodology, Writing-Review & Editing; Q. L. Huy: Writing-Review & Editing, Project administration; K. Nieminen: Formal analysis; L. Pitkänen: Formal analysis; H. Sixta: Conceptualization, Supervision, Writing-Review & Editing, Funding Acquisition.

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## Declarations

**Conflict of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Consent to participate** The work in the manuscript is original and conducted by all the authors.

**Consent to publication** All authors agree on submitting the manuscript for publication to Cellulose.

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