Stability of Gamma-valerolactone Under Pulping Conditions as a Basis for Process Optimization and Chemical Recovery

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Introduction

The global 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 biomass represents an abundant, renewable, and relatively cheap carbon-based material. The main components (cellulose, hemicellulose, and lignin) can be separated and processed into energy or value-added products (Li et al. 2015; Liu et al. 2019). 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. Despite the constant decline in demand for graphic paper, paper-grade pulp is still indispensable for the constantly growing need for tissues, hygiene, and packaging products. The global annual production of chemical pulp is more than 144 Mton (Garside 2017; Haggith et al. 2018).

Dissolving pulp is characterized by a high α-cellulose content (>90%) and targeted for higher-valued applications such as regenerated cellulose, cellulose esters or ethers, nano- or micro-crystalline cellulose. This segment forms a fast-growing niche market with an annual production of 10.2 million tons in 2019 (Engelhardt 2020). The majority of dissolving pulp is currently obtained from wood by chemical pulping using acid sulfite (AS) and pre-hydrolysis kraft (PHK) processes, with the new plants using 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, sulfur-bound lignin, sticky lignin precipitates, 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 at the beginning of the 20th century (Brudecki et al. 2013). Thereby, biomass is treated at elevated temperatures and pressures in organic solvents, which promote delignification after hydrolytic decomposition and fragmentation of the lignin-carbohydrate complex and through good solubility in the respective solvent. Simultaneously to the delignification, the hydrolysis and extraction of the hemicellulose occurs, facilitated either by the addition of mineral acids or autocatalysis by the acetic acid generated from the acetyl groups of hemicellulose (Snelders et al. 2014). The most significant advantage of organosolv pulping is the isolation of a lignin fraction, characterized by a high phenolic content, low inorganic and carbohydrate contaminations, and the absence of chemically-bound sulfur (Brudecki et al. 2013). Furthermore, organosolv pulp exhibits higher bleachability than kraft pulp, implying a potential reduction of chemicals in the manufacturing process and further a decrease of contaminations in the effluent (Cronlund and Powers 1992). However, increased temperatures in combination with acidic conditions promote the condensation reactions between lignin-units, the formation of carbon-carbon bonds, and thus the limitation of the applicability of lignin. Several research attempts have been undertaken to solve the permanent lignin condensation aiming at an optimization of the lignin isolation step while retaining its native structure. Bloom Biorenewables pioneered with an aldehyde-stabilization technology, operating at relatively low temperatures and pressures in the presence of sulfuric acid. In the process, the extraction of uncondensed lignin during fractionation, which can be readily dissolved in an organic solvent while simultaneously producing a relatively pure cellulose fraction, is enhanced (Questell-Santiago et al. 2018; Shuai and Luterbacher 2016; Talebi Amiri et al. 2019).

Up to now, the capability of many organic lignin solvents (like ethanol, methanol, acetone, glycerol, propylene glycol, acetic acid, or formic acid) for the fractionation of biomass have 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 (SO2-ethanol-water) techniques. Both have already reached the pilot and the latter even demonstration scale, but the recently confirmed loss of ethanol, as a consequence of the formation of covalent linkages with lignin and carbohydrates (via ethoxylation reactions), poses a major challenge to the commercialization of these two processes (Heiningen et al. 2018).

Small-scale pilot trials have also shown that ethanol-water Organosolv fractionation of beech wood can produce reactive viscose pulps comparable to those of the acid Mg-based sulfite process under optimized conditions (Peter and Höglinger 1986). Other well-established methods are MILOX (formic acid-peroxymonoc acid) and Clean Fractionation (methyl isobutyl ketone-ethanol-water). An insufficient pulp quality, low recovery rates, and a corrosive character of the solvent prevent these techniques to enter the level of full-scale operation (Lé et al. 2018b). On the other side, Chemopolis has successfully commercialized Formico™, a technology for the production of ethanol, biochemicals, and green power from the cellulose biomass fractionated in formic acid (Anttila 2019). In general, the feasibility of the organosolv method and its market potential relies on many process-related factors like solvent stability, recyclability, price, product yield, safety, and toxicity of the process.

The biomass- originated, green solvent g-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 2015; 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 we contributed to the development of the GVL based biorefineries and demonstrated the uncatalyzed fractionation of hardwood in a 50% 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 (Lē 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. Moreover, more than 90% of the solvent (GVL) can be recovered by liquid CO₂-extraction and optionally in combination with a preceding water-evaporation stage (Fang and Sixta 2015; Lē et al. 2018b, 2018a, 2016a).

GVL (5-methyloxolan-2-one) is a five-membered lactone and is well-known for its non-toxicity, low-volatility, high solubility in water (> 100mg/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 (Lē et al. 2016b). Despite the high stability at neutral and ambient conditions, the lactone ring of GVL tends to hydrolyze in water in an alkaline or acidic environment and forms an equilibrium with its hydrolysis product, the 4-hydroxyvaleric acid (4-HVA) (Wong et al. 2017). For the use of GVL as a solvent in an industrially relevant pulping process, a proper evaluation of its decomposition behavior under pulping conditions has to be performed. Therefore, this study aims to determine the extent of GVL hydrolysis forming 4-HVA in aqueous solutions over a wide pH range and in the spent liquor obtained from the fractionation of Betula pendula sawdust.

**Experimental**

**Material**

GVL (≥ 99 wt% purity, (RS)-Form) and 1,3,5-trimethoxybenzenes (≥ 99 wt%) were purchased from Sigma Aldrich, sulfuric acid (95-97.0 wt%) from Merck, and sodium hydroxide pellets (≥ 98 wt%) from VWR Chemicals. Besides, the solvents for NMR analysis, dimethyl sulfoxide-d₆ (99.8 %), acetone-d₆ (99.8%), acetonitrile-d₃ (99.8%) were obtained from Eurisotop and deuterated water-d₂ (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 MΩ). 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 1H NMR spectra were recorded on a Bruker AV III 400 MHz spectrometer. The spectra were referenced against the 1H 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 (≥ 99 wt%).

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

In total four H₂SO₄ stock solutions (1: c₁ = 18 mol/L, p₁ = 1.84 g/mol; 2: c₂ = 1 mol/L, p₂ = 1.07 g/mol; 3: c₃ = 0.001 mol/L, p₃ = 1.0237 g/mol; 4: c₄ = 0.1*10⁻⁵ mol/L, p₄ = 1.0236 g/mol) and four NaOH stock solutions (5: c₅ = 4.98 mol/L, p₅ = 1.1879 g/mol; 6: c₆ = 1 mol/L, p₆ = 1.04 g/mol; 7: c₇ = 0.002 mol/L, p₇ = 1.0045 g/mol; 8: c₈ = 0.4*10⁻⁵ mol/L, p₈ = 1.0043 g/mol) have been used. 2 g of pure GVL (0.020 mol) are mixed with water, H₂SO₄ or NaOH (stock solutions) in a 10 ml vial (detailed information is given in Online Resource). The solutions were thoroughly mixed for a few seconds and the pH value was recorded. The mixtures were thermostated 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-d₆ directly in the NMR tube. The amounts of HVA in mol% and the pH values before and after treatment are presented in Online Resource.

**Wood fractionation and spent liquor analysis**

Betula pendula wood chips were oven-dried at 40°C overnight and milled to sawdust. Next, the sugars of the starting materials were analyzed. Betula pendula wood showed a composition 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) were mixed with different solutions of H₂SO₄ (1: c₁ = 18 mol/L, p₁ = 1.84 g/mol; 2: c₂ = 1 mol/L, p₂ = 1.07 g/mol; 3: c₃ = 0.001 mol/L, p₃ = 1.0237 g/mol; 4: c₄ = 0.1*10⁻⁵ mol/L, p₄ = 1.0236 g/mol) and NaOH (5: c₅ = 1 mol/L, p₅ = 1.04 g/mol; 6: c₆ = 0.002 mol/L, p₆ = 1.0045 g/mol; 7: c₇ = 0.4*10⁻⁵ mol/L, p₇ = 1.0043 g/mol) (detailed information is given in Online Resource). The solutions were thoroughly mixed for a few seconds and the pH value was recorded. Afterward, they were added to 1.5 g oven-dried sawdust and treated in an Anton Paar microwave reactor at 180°C, for 120 min (liquid-to-wood ratio of 10 kg/kgoven dried wood). 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-d₆ 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 HVA in mol% and the pH values before and after treatment are summarized in Table 1.
Results And Discussion

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

g-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, g-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 g-valerolactone (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, 2013b). In accordance with the conditions proposed by Lê et al. (2016) for the fractionation of Eucalyptus globulus sawdust (Lê et al. 2016a), the stability of GVL was determined in a 50 wt% aqueous solution at 180°C in the absence of wood.

The importance of heating was proven again. Hydrolysis of GVL to 4-HVA was observed only at elevated temperatures. After reaching equilibrium, stability was determined by repeated re-analysis. The extent of hydrolysis depends on the GVL concentration or, conversely, on the amount of water. In the case of 50 wt% GVL, 3.5 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.

At neutral conditions, water acts as a weak nucleophile and an increase of the acidity enhances the basicity of the water. Furthermore, an acid catalyst activates the carbonyl group by protonation of the carbonyl oxygen and thus a nucleophilic attack by water is favored (Fig. 1a) (Graham 2004).

The effect of acidic conditions regarding a 50 wt% GVL aqueous solution was traced by a stepwise elevation of the H2SO4 concentration from 0.2×10^-5 wt% to 6 wt% at elevated temperatures (150 – 180°C) at reaction times between 30-180 min. 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. 2a). Post-synthesis stability was determined by NMR analysis at frequent 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 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 H2SO4 (0.01 - 4.05 mol/L) and HCl (0.02 - 2mol/L), yielding in < 4 mol% of 4-HVA (Wong et al. 2017). In compliance with our results, no decomposition of GVL was recognized at room temperature and at elevated temperatures (~150°C) an equilibrium with its decomposition product 4-HVA was detected. The addition of sulfuric acid resulted in the formation of a stable GVL/4-HVA equilibrium.

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. 1b) (Clayden et al. 2012; Graham 2004). The presence of sodium 4-hydroxyvalerate after the reaction of GVL with aqueous NaOH was also confirmed by Horváth et al. (2008) (Horváth et al. 2008).

The alteration of time and temperature had no significant effect on the GVL hydrolysis (Fig. 3). As a result, the experiments were conducted in an alkaline environment at the constant time (30 min) and temperature (180°C) with the variation of the NaOH dosage. Higher concentrations of NaOH (≥ 0.2 wt%, pH_initial = 8) facilitated the GVL ring-opening (≥ 1 mol%) already before heating illustrated by a gradual drop of the pH (Fig. 2c). After the treatment, stabilization was reached, and no decrease in the pH value was recognized. The addition of less than 0.2 wt % of NaOH resulted in the formation of < 4 mol% of sodium 4-hydroxyvalerate (Fig. 2b), 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 help to shift the equilibrium 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 to values of ≥ 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.

Moreover, a bi-phasic system was observed after the mixing of 50 wt% GVL solution with ≥ 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.

Furthermore, GVL remains stable at the pH range 2-7 at ambient conditions (Fig. 2c).

Effect of 1H NMR solvent on the GVL/4-HVA equilibrium

Choosing a suitable solvent for 1H NMR analysis was one of the prerequisites for the accurate determination of the GVL and 4-HVA equilibria. An equal amount of sample (0.01 g) was dissolved in four different solvents (DMSO-d6, acetone-d6, acetonitrile-d3, and D2O) and immediately analyzed. The change in the solutions was monitored at regular intervals until the equilibria were reached. As expected, the 1H NMR spectra revealed differences in the chemical shift. However, large variations in the 4-HVA concentrations were observed too, which implies that not all solvents used showed inert behavior. The 4-HVA
concentrations measured in DMSO-d$_6$ and D$_2$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$_6$ (0.3 mol%), and acetonitrile-d$_3$ (0.1 mol%) (Fig. 4).

As a result, DMSO-d$_6$ was chosen as the most suitable solvent for $^1$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$_3$ groups of GVL, 4-HVA, and the standard (1,3,5-TMB) (Fig. 5). The DMSO-d$_6$ 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 position 1.01-1.04 ppm. Unlike at basic and acidic conditions a 4-HVA peak was formed (Fig. 5). The complete spectra with detailed shifts can be found in Online Resource.

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

The degradation of GVL during fractionation may negatively influence the recycling of GVL and further increase the operational costs of the whole process. Lê et al. (2018) studied the quantitative recovery of GVL from the spent liquor obtained from the fractionation of *Eucalyptus globulus* in 50 wt% GVL at 180°C during 150 min. Two different approaches were investigated, one by applying the vacuum distillation of water and the other by the extraction of GVL through liquid CO$_2$. The recovery yield of GVL from the feed (spent liquor) for both methods was 90% and 87%, respectively, taking into account the ~5% loss from the total input (handling, operational losses, and analytical errors). The spent liquor consisted of 47.07% of GVL, 47.27% of H$_2$O, 3.73% of lignin, 0.71% of organic acids (e.g. formic, acetic, levulinic), 0.65% of dissolved carbohydrates, and 0.57% of furanic compounds (Lê et al. 2018b). In this regard, it is not excluded that the fraction of organic acids in the spent liquor contains 4-HVA.

Therefore, in this study, the stability of GVL was examined under real pulping conditions. *Betula pendula* sawdust was fractionated in 50% GVL with and without the addition of H$_2$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 (Online Resource). The presence of levulinic acid (LA) and formic acid (FA) was not detected by NMR. In a highly acidic environment (20 kg H$_2$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. 6/ Table 1).

In comparison with the results achieved in the absence of wood, the 4-HVA slightly increased in acidic pulping. The fractionation of carbohydrates is followed by a series of chemical reactions including acidic hydrolysis of 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 4-HVA which lactonizes to GVL (Deng et al. 2010; Yan et al. 2009). Therefore, the slight increase of 4-HVA during the fractionation can be caused not only by GVL hydrolysis but also by the reduction of LA by H$_2$SO$_4$. On the contrary, the carboxylic acids derived from the fractionation of wood, may partly neutralize NaOH and hence, lower the concentration of 4-HVA.

The presence of 4-HVA in the spent liquor complicates the recovery of GVL and shifting the equilibrium toward GVL would be desired. Al-Shaal et al. (2012) suggested conversion of LA to GVL at room temperature using Ru/C as a catalyst, and they discovered that a substantial amount of 4-HVA remained in the solution, indicating that 4-HVA requires higher temperatures or a catalyst to initiate dehydration to GVL at 25°C (Al-Shaal et al. 2012). The suggested conditions could be possibly applied at the beginning of the fractionation enabling one-pot biomass fractionation and complete GVL production. Alternatively, the potential to convert 4-HVA to GVL or to recover it from spent liquor employing liquid CO$_2$ serves as a basis for the upcoming research.

### 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 find out to what extent an amount of 3 to 6 mol% 4 HVA determines the losses of GVL in the context of solvent recovery and identify loss reactions due to covalent reactions with wood components.

### Declarations

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**Code availability:** Not applicable

**Authors’ contributions:** Marianna Granatier: Investigation, Writing-Original Draft, Visualization Inge Schlapp-Hackl: Methodology, Writing-Review & Editing Quang Lê Huy: Writing-Review & Editing, Project administration Kaarlo Nieminen: Formal analysis Herbert Sixta: Conceptualization, Supervision, Writing-Review & Editing, Funding Acquisition

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Tables

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 $\text{H}_2\text{SO}_4$ / t$_{\text{wood}}$ | kg NaOH / t$_{\text{wood}}$ | 4-HVA$_{\text{equ}}$ [mol %] | $\text{pH}_{\text{initial}}$ | $\text{pH}_{\text{spent liquor}}$ |
|--------|---------------------------------|------------------|-------------------------------|------------------|------------------|
| 1      | 0.000                           | 0.000            | 3.96                          | 3.96             | 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                           | $2,009 \times 10^{-5}$ | 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             |