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Short communication

Determination of γ-valerolactone content in its synthesis and biorefinery processes by headspace analysis technique

Hui-Chao Hu[a,*], Shaokai Zhang[a,b], Tong Zeng[a], Yiying Lin[a], Liulian Huang[a], Lihui Chen[a,*], Yonghao Ni[a,b]

[a] College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou 350002, China
[b] Limerick Pulp & Paper Centre, University of New Brunswick, Fredericton, P.O. Box 4400, Canada

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ABSTRACT

In this paper, a robust method based on solvent-volume controlled full evaporation headspace gas chromatography technique (FE HS-GC) was developed to high throughput quantify γ-valerolactone (GVL) concentration in sample solution. The results showed that the full evaporation of GVL can be achieved by the equilibration process in headspace sampler at 150 °C for 5 min. For eliminating the matrix effect and pressure effect on GVL quantification, the sample volume added in headspace vial should be controlled within 15 μL. The present method was proved that has a very high precision (error < 1.11%), high precision (recoveries from 95.6% to 102.1%), and an excellent limit of quantification (153 mg/L). The present method was applied in valuation of GVL yield in a heterogeneous catalytic system and its recovery in a GVL-based biomass pretreatment process, and has given some valuable information. The present method is simple, rapid, efficient, and can be an excellent tool for screening reaction medium and catalysts in GVL synthesis and its related biorefinery processes.

1. Introduction

Gama-valerolactone (GVL) is a versatile sustainable platform compound derived from lignocellulosic biomass [1]. It is also one of the most promising precursors in the many applications, e.g., to produce liquid fuels and high-value chemicals [1–3]. Attributed to its excellent solvent effect on hydrogen ion and lignin, the GVL-based solvent system is regarded as a perfect medium to directly produce high reactivity lignin, fermentable sugars, and other biomass platform chemicals in the biorefinery processes [4–9]. Therefore, many researches, aiming at finding the cost-effective way, have been conducted for synthesizing GVL based on the compounds such as levulinic acid, carbohydrates, and lignocelluloses [10–12]. Obviously, it is highly desired to have a simple and high throughput method for the GVL quantification in its synthesis and the related biorefinery processes.

Currently, the quantification of GVL in its synthesis related biorefinery process solutions are mainly based on the gas chromatography that coupled with flame ionization detector or mass spectrometry (GC-FID/MS) [13–16]. Because there are numerous non-volatile and dissolved substances (e.g., inorganic salts, low molecular weight saccharides and lignin) in the GVL synthesis or its related biorefinery process, the sample pretreatment procedures, typically solvent extraction and desalination, are required. Thus, the contamination problems from the non-volatile compounds on the GC injection port and column system can be greatly minimized. However, the pretreatment is not only very complicated and time-consuming but also very difficult to obtain a good separation yield for GVL (e.g., only 73% of GVL can be extracted by ethyl acetate in an aqueous solution containing 5% of GVL [17]). Moreover, the pretreatment procedure cannot completely eliminate the GC contamination problem mentioned above, because some species (e.g., sulfuric acid) could be also extracted by the solvent system [17].

The 1H NMR technique was also suggested to be used for the GVL quantification. In several previous works, the studies were conducted aiming at elucidating the synthesis mechanism of GVL from a simple or pure levulinic acid system and its chemical stability in an acidic or alkaline medium [18–20]. However, the GVL analysis based on the 1H NMR technique used in the above studies is not suitable to the samples with complicated matrices from the biomass based system [5,7–8]. This is because the interferences of baseline noise from dissolved organic compounds are too significant in the measurement and thus affect the accuracy of the results.

Because of completely eliminating the problems associated with the deposit and contamination on GC injector port and column system, headspace gas chromatography (HS-GC) has been widely used in the quantification of volatile compounds for the samples with very complicated matrices [21–23]. Compared to the conventional HS-GC

* Corresponding authors.
E-mail addresses: hhc_huichao@163.com (H.-C. Hu), fafuclh@163.com (L. Chen).

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technique (i.e., based on the vapor-liquid equilibrium of analyte(s) [22], the full evaporation HS-GC (FE HS-GC) technique greatly simplified the method calibration procedures as those in the conventional HS-GC measurement (typically by the internal or standard addition) [24]. Moreover, a very small sample volume (in μL) used in the FE HS-GC allows a quick headspace equilibration and thus greatly reduced the time required in the conventional HS-GC measurement [25–31]. As reported [25–27], most of FE headspace analysis was conducted at ~105 °C, just above water boiling point. Due to a high boiling point of GVL (207 °C), a high temperature is required in order to achieve adequate saturated vapor content in its analysis. However, such high temperature leads to a high pressure in the sample vial, it creates a risk of sample leakage during headspace equilibration. Therefore, it is a great challenge for the FE HS-GC technique to be used in the GVL quantification.

In this study, we developed a method for the quantification of GVL content in its synthesis and biorefinery process samples, based on a FE HS-GC technique. The main focuses were on the minimization of the pressure caused the sample solvent in the vial and exploration of the conditions in the sample preparation, headspace equilibration and GC measurement. The performance (precision and accuracy) of the method on the GVL analysis was evaluated. The present method will become an effective tool to be used in the GVL related research and application.

2. Materials and methods

2.1. Chemicals and samples

Levulinic acid (99.0%, AR), formic acid (≥98.0%, GC), the Shvo's catalyst (98.0%), furfural (99.0%, AR), acetic acid (99.8%, GC), glucose monohydrate (98%, CP), sodium chloride (99.5%, AR), and γ-valerolactone (99.0%, AR) were purchased from Aladdin Reagent and Sigma-Aldrich (Shanghai, China). A 10.0 g/L of GVL standard solution was prepared by dissolving a 1.00 g of GVL in deionized water to make 100 mL with volumetric flask.

2.2. Apparatus and operations

The HS-GC measurements were performed in a static headspace sampler (Thermo Fisher Scientific TriPlus™ 300, Italy) and a gas chromatograph (Agilent GC 7890B, US) equipped with a flame ionization detector operated at 300 °C with a 30 mL/min of hydrogen and a 400 mL/min of compressed air. The injection port of GC was operated at 250 °C, a 1:1 of the split ratio, and a 20 psi of pressure. A HP-Innowax capillary column (30 m × 0.32 mm × 0.5 μm, Agilent) was operated at a 150 °C of constant temperature with a 0.5 mL/min of carrier gas flow rate and a 3.5 min of eluting time for each run. The headspace sampler was operated at the followed conditions: oven temperature = 150 °C, loop temperature = 155 °C, transfer line temperature = 160 °C, carrier gas pressure = 20.1 psi, auxiliary gas pressure = 30 psi, pressuring time = 0.2 min, pressure equilibration time = 0.1 min, venting time = 0.2 min, loop filling equilibration time = 0.1 min, sampling time = 0.5 min.

2.3. Sample preparation and HS-GC measurement

A set of sample solution were prepared by a typical heterogeneous catalysis process for production of GVL from levulinic acid and formic acid [18]. Firstly, a 1.0 g of levulinic acid and 0.6 g of formic acid was added in a 3.0-mL glass vial with a 9 mg of the Shvo's catalyst. The reaction mixture was mixed well by magnetic stirrer, and then it was placed in a laboratory oven at a 100 °C of temperature for 0.5–2.5 h. After that, the reaction vial and a 10.0 g of deionized water were put into a glass vial and mixed well, by which the reaction was terminated. Then, the Shvo's catalyst in suspension was removed by filtering through a 0.22 μm filter. The supernatant solution was performed the HS-GC measurement after ten times dilution by weight.

A 10 μL of sample solution was added in a 20 mL of headspace vial, and then which was sealed with a PTFE/ butyl rubber pad and aluminium cap. After the equilibration at 150 °C for 10 min, the vapor in the vial was withdrawn into GC by headspace sampler and analyzed by GC-FID.

2.4. Evaluation of GVL recovery efficiency in dissolving pulp production process based on GVL/H_2O solvent

A 7.0 g of eucalyptus sawdust and a 70 g of GVL/H_2O solvent (60:40, w/w) were added in a 100 mL of reaction vessel. After sealing the vessel, it was putted in a high pressure water bath reactor for the autocatalytic reaction, which was conducted by a ramping rate of 1.7 °C/min and holding 3 h at 180 °C. After that, the reacted eucalyptus sawdust was defibered into pulp, and then the suspension was filtered using vacuum filtration with a Buchner funnel (equipped a 400 mesh of nylon net). The filter cake was weighted, and then put it in a 70 g of GVL/H_2O solvent (60:40, w/w) and stirring 5 min for the dissolved lignin removal. After vacuum filtration, following above procedure, the filter cake was washed three times with deionized water. For each filtration, the filtrate was collected, and its GVL content was measured using the present method after diluting by 1–100 times.

3. Results and discussion

3.1. The temperature-dependent pressure profile in the headspace vial

According to the state equation of ideal gas and the mass balance of solvent involved in a closed vial, the total pressure in the sample vial at the temperatures (T_E), higher than that desired for the full evaporation of the added solvent (m), can be calculated by Eq. (1).

$$P = \frac{mRT_E}{M_{Solvent}V_T} + \frac{P_0T_E}{T_0} \quad (1)$$

All symbol, definition, and units have been listed in Table 1.

Combining the saturated vapor pressure of solvent at different equilibration temperatures, the maximum pressure can be obtained by Eq. (2) if the sample size added in headspace vial is sufficient to form the solvent saturation vapor.

$$P_{max} = P_S + \frac{P_0T_E}{T_0} \quad (2)$$

Fig. 1 shows the temperature-dependent pressure profiles in a 20-mL vial containing different aqueous sample sizes. In the supersaturated region, part of the water will be presented as liquid water in headspace vial, and that make the analyte cannot be fully evaporated to gaseous phase due to the gas-liquid equilibration. In the full evaporation region, it can be seen that a small solvent size will greatly reduce the total pressure in the vial. Thus, the risk of sample leakage due to a high pressure could be avoided. In addition, the linearly response of analyte's GC signal as sample size need to assure the total pressure in each sample vial always lower than the pressurizing pressure of headspace sampler, i.e., 300 kPa used in this paper. According to Fig. 1, the pressure in the vial will be always within 300 kPa at the equilibration temperatures below 190 °C when a 10 μL of sample size is used. Therefore, we chose the 10 μL of sample size for the following studies.

3.2. GC conditions for GVL measurement

Fig. 2 shows the chromatogram from a FE HS-GC measurement on GVL in the washing filtrates of pretreated eucalyptus using GVL/H_2O as reaction medium and a standard solution of GVL, formic acid, furfural, acetic acid, and levulinic acid with 2 g/L. It can be seen that a constant high column temperature (> 150 °C) is necessary for the given column to separate GVL species from the others. The GVL retention time is