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Short communication

Rapid determination of furfural in biomass hydrolysate by full evaporation headspace gas chromatography

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ABSTRACT

This paper reports a full evaporation (FE) headspace gas chromatographic (HS-GC) method for rapid determination of furfural in the biomass hydrolysate. The data show that a near-complete mass transfer of furfural in the sample from biomass hydrolysate to the vapor phase (headspace) was achieved within 3 min at 105 °C when a very small (<40 μL) sample was added to a 20 mL headspace sample vial. The acid-catalyzed furfural decomposition under these conditions was negligible. The furfural in the vapor phase was then determined by HS-GC using a flame ionization detector. The results showed that the method has an excellent measurement precision (RSD < 0.5%) and accuracy (recovery = 100.2 ± 1.7%) for furfural quantification in carbohydrate hydrolysate samples. The method requires no sample pretreatment, so it is simple, rapid and accurate, and suitable for applications in lignocellulosic biomass conversion to fuel ethanol or other high value-added products.

1. Introduction

With rising concerns about climate change and the growing need for alternative energy sources, the possibility of deriving energy from renewable lignocellulosic biomass instead of fossil fuels (oil and coal) has received more attention from pulp and paper researchers [1,2] because of the significant amount of carbohydrates (mainly hemicelluloses) that occur as a waste in the chemical pulping processes. Since the hydrolyzed carbohydrates can be converted to fuel ethanol through fermentation, several strategies have been proposed for utilizing the lignocellulosic biomass; e.g., partly and fully utilizing the carbohydrates in biomass materials [3–5]. The extraction (or dissolving) of carbohydrates is the first step in the process. Hot water or weak acid hydrolysis at an elevated temperature is typically used to hydrolyze carbohydrates from lignocellulosic biomass materials [5–9]. However, a byproduct, furfural, may also be produced, to a degree that is highly dependent on the process conditions [10]. Because of its inhibitory effect on fermentation microorganisms during ethanol production [11–13], the amount of furfural in the biomass hydrolysate is one of the key parameters in the process evaluation [14]. Therefore, the quantification of furfural in these effluents is important not only from an ethanol production point of view, but also for a greater understanding of furfural formation during the various carbohydrate hydrolysis methods that are a part of any new process development [15].

Traditional methods such as colorimetry [16,17] and spectrophotometry [18–20], as well as the advanced techniques, such as high performance liquid chromatography [21–24] and gas chromatography [25–27], have been widely used for furfural quantification. However, the products of lignocellulosic biomass hydrolysate contain not only a significant amount of non-volatile species, typically sugars and color substances (mainly dissolved lignin), but also suspended solids. Therefore, it is usually necessary to pre-treat the sample, using procedures such as distillation, filtration, chemical reaction, and solvent or solid-phase extraction, in order to minimize the impact of these interfering species in subsequent furfural analysis. This pretreatment makes the traditional procedures more complicated, time-consuming and subject to errors.

Headspace gas chromatography (HS-GC) is an effective technique for the determination of volatile species in the samples with a complex matrix, in which the impact of non-volatile components in the matrix encountered in a direct GC analysis can be avoided [28]. However, there is a great risk for the acid-catalyzed furfural decomposition and can take place under conditions of conventional HS-GC [29], even in a weak acidic medium, e.g., the resulting solutions from biomass hot water extraction [15,30]. This is because of required a long vapor–liquid equilibration (VLE) period at an elevated temperature. As a result, the amounts of furfural in these

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samples are often underestimated. To address this problem, the full evaporation (FE) HS-GC technique, which uses very small sample size, is used to significantly reduce the time for phase transfer [31–34]. Thus, furfural decomposition during the analysis could be minimized.

The objective of the present work was to develop a simple FE HS-GC method for rapid determination of furfural in the effluents from lignocellulosic biomass hydrolysis. The effects of FE HS-GC conditions (e.g., equilibration temperature, equilibration time and sample size) on experimental results were also explored.

2. Experimental

2.1. Chemicals

All chemicals, of analytical grade, used in the experiment were from commercial sources. A standard furfural solution (1160 mg/L) was prepared by adding 20 μL furfural solvent (98%, Alfa Aesar) in 20 mL water.

2.2. Samples

The samples were obtained from the hydrolysis process of bamboo in a lab-scale digester. The total volume of the MK digester is 10 L. 1000 g of bamboo (on an oven dry basis) was charged to the digester and the liquor-to-wood ratio used in the cooking was 5–1. The cooking temperature was increased from 25 to 170 °C at a rate of 2.09 °C/min, and then held at 170 °C for 60 min.

2.3. Apparatus and operations

All measurements were carried out using an HSS 80.65 Automatic Headspace Sampler (DANI, Italy) and Model GC-2010 capillary gas chromatograph (Shimadzu, Japan). GC conditions were as follows: DB-5 capillary column at 90 °C, high purity nitrogen carrier gas flow rate of 3.8 mL/min. A flame ionization detector was employed with hydrogen and air with flow rates of 40 and 400 mL/min, respectively. Headspace operating conditions were as follows: 3 min strong shaking to obtain sample equilibrium at a temperature of 105 °C, vial pressurization time of 0.2 min, sample loop fill time of 1.0 min, and loop equilibration time of 0.05 min.

The sample preparation and measurement steps were as follows: inject μL level (or weigh the equivalent amount) of sample solution into a closed 21.6 mL vial by micro syringe and place it in the headspace sample tray for HS-GC measurements. Directly applying the sample to a piece of filter paper placed in the vial is helpful for improving furfural transfer from the liquid phase to the vapor phase, especially in highly viscous samples.

3. Results and discussion

3.1. Headspace analysis of furfural from a hydrolysate

Fig. 1 shows a GC chromatogram from FE headspace analysis of a liquor from bamboo hydrolysate, in which furfural was found to be a dominant species in the vapor phase. Thus, the HS-GC method can effectively eliminate the interference from the co-existing non-volatile and volatile species found in this biomass hydrolysate sample.

3.2. Possible decomposition of furfural during the vapor–liquid phase equilibration

The static HS-GC is based on the measurement of an equilibrated vapor phase above the liquid sample, which requires a certain length of time to achieve the phase equilibrium. In a conventional HS-GC mode, it required 45 min for furfural to reach VLE equilibrium between liquid and vapor states at 75 °C when a sample of 2 mL was used. Under these conditions, the results from the comparative experiment, i.e., in a neutral solution, showed about 9% of furfural was missing in an acidic medium due to the decomposition [29]. With FE HS-GC, the equilibrium can be achieved within 3 min for a sample size of 20 μL [35]. Thus, the decomposition of furfural in the same medium under these conditions was negligible even at 105 °C, as shown in the furfural recovery data obtained.

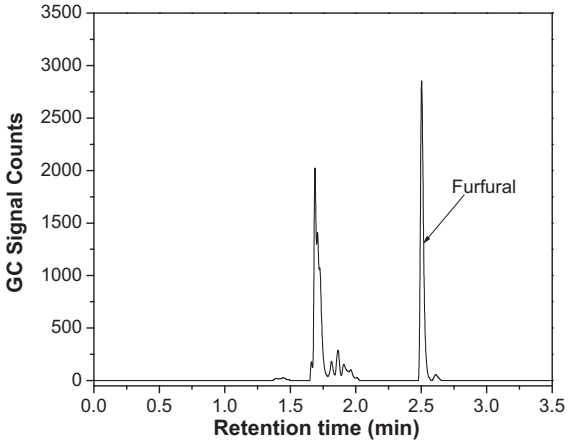

Fig. 1. GC chromatogram from FE headspace sampling for a bamboo biomass hydrolysate sample.

3.3. Conditions for FE headspace analysis

In FE headspace analysis, the key to success is to achieve a near-complete mass transfer of analyte from the liquid phase to vapor phase as quickly as possible. In this section, we report on the effects of major experimental parameters on furfural mass transfer from liquid sample to the vapor phase in the headspace.

3.3.1. Equilibration temperature and completeness of furfural interphase transfer

The VLE partition coefficient is a function of temperature. The effect of the equilibration temperature is shown in Fig. 2. It can be seen that the two-phase equilibrium is achieved at a temperature above 95 °C after 3 min for a sample size of 20 μL. To verify a near-complete interphase transfer under these conditions, we placed 20 μL of hydrolysate sample into a small metal dish that was, in

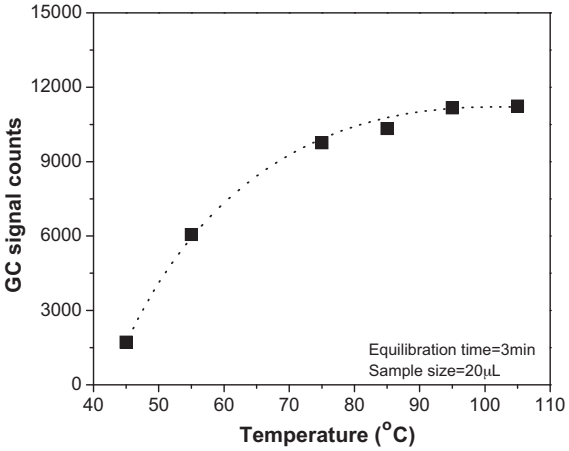

Fig. 2. Effect of the equilibration temperatures.

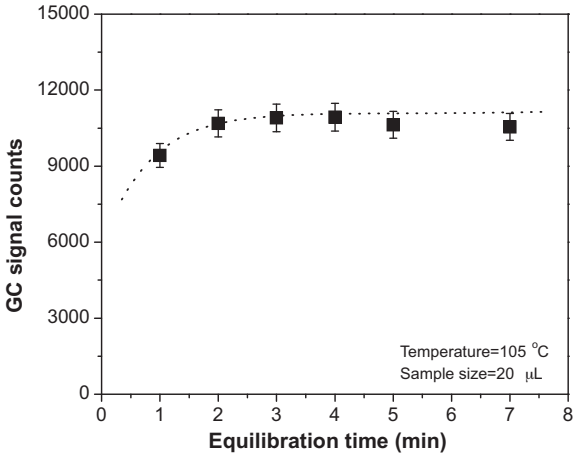

Fig. 3. Effect of the equilibration time on the amount of furfural detected in the vapor phase.

turn, placed in a headspace vial. After the first measurement by HS-GC at 105 °C (headspace sampler oven temperature) with an equilibration time of 3 min, the dish was transferred to another headspace vial for a second measurement at same conditions. The result showed that the ratio of the GC signal peaks (P) of these two measurements (i.e., P_2/P_1) was less than 4%, which experimentally proves that a near-complete full evaporation was achieved within 3 min at this temperature. Therefore, we chose a temperature of 105 °C and 3 min for the rest of the study.

3.3.2. Equilibration time

As shown in Fig. 3, vapor–liquid equilibrium of furfural from an acidic biomass hydrolysate sample can be achieved within 3 min at the given temperature (105 °C). The data also show that a longer equilibration time at this temperature will cause a decrease of furfural in the vapor phase, which is probably due to furfural decomposition. Therefore, a time of 3–4 min was chosen as the equilibration time in order to maximize the furfural in the vapor phase at 105 °C and minimize its potential condensation.

3.3.3. Sample size

A larger sample size is helpful in increasing the sensitivity of the headspace measurement. However, a larger sample size requires a longer sample transfer time or high temperature to achieve near-complete evaporation. Fig. 4 shows the effect of the sample size on the furfural full evaporation of the biomass hydrolysate. It can be

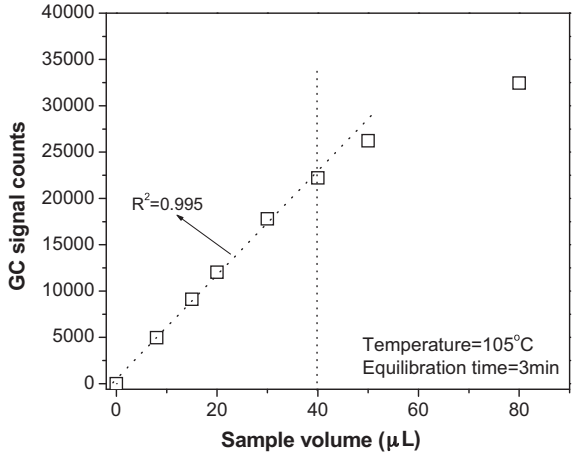

Fig. 4. Effect of sample size on the amount of furfural detected in the vapor phase.

Table 1
Method validation.[a]

Sample No.	Furfural content (mg/L)		Recovery (%)
	Added	Measured	
1	27.8	28.3	101.8
2	54.3	53.5	98.5
3	79.5	78.9	99.2
4	103.6	105.9	102.2
5	126.7	125.8	99.3

[a] 20 μL of sample was used.

seen that there is a linear relationship between the GC peak area corresponding to the amount of detected furfural in the vapor phase and samples sizes less than 40 μL. Therefore, 40 μL is the maximum sample size that could be used for accurate determination of furfural in the present FE HS-GC method. Note that 40 μL is also in the preferred sample size range for the determination of various species by FE HS-GC that were reported previously [31,32,35]. Due to a significant amount of furfural present in the hydrolysate samples, such a small sample size in FE HS-GC analysis did not affect the sensitivity of the method.

3.4. Method calibration, precision and validation

Because of a near-complete mass transfer of furfural to the headspace, the effect of the matrix is eliminated in FE HS-GC analysis. Therefore, a simple external standard calibration can be employed. The calibration was achieved by adding different volumes (0–35 μL) of a standard furfural solution to a set of headspace sample vials and performing the FE HS-GC measurement of the contents in each vial. Using the data from the GC measurement on these samples, a standard calibration curve was obtained that follows this equation:

$$A = 172\ \ (\pm 118) + 8160\ \ (\pm 93) \times C \quad (n = 6,\quad R^2 = 0.9994) \qquad (1)$$

where A and C represent the GC signal peak are of furfural in the vapor phase and its absolute amount (in μg) added in the headspace sample vial, respectively.

The limit of quantitation (LOQ) of the present method is 0.087 μg.

The precision of the present method was studied. The results show that the relative standard deviation for furfural measurement from five replicates based on a biomass hydrolysate is less than 0.46%, in which the random errors are associated with the uncertainties in both sampling and HS-GC detection.

To validate the present method, we prepared a set of sample solutions by accurately spiking different volumes (0–250 μL) of furfural standard solution into 2.0 mL of a biomass hydrolysate sample. The original sample (i.e., without added furfural) was measured as a reference. Thus, the net contribution from the added furfural in the FE HS-GC measurement for these spiked samples can be determined. The absolute amount of furfural in the sample in the headspace vial can be determined by Eq. (1).

Table 1 shows a comparison of the experimental data with the actual amount added. The good furfural recoveries indicate that the present method is suitable for the determination of furfural biomass hydrolysis processes.

4. Conclusions

A FE HS-GC technique for the determination of furfural in biomass hydrolysate was developed. By choosing a very small sample size (<40 μL) and a high temperature (105 °C), a near-complete furfural mass transfer from the liquid sample to vapor phase was achieved within 3 min. The present method is simple, rapid, and accurate.

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