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ABSTRACT: Solid-phase microextraction (SPME) coupled with gas chromatography−mass spectrometry (GC−MS) analysis was used for the at-line sampling of pyrolytic vapors produced during the fast pyrolysis of biomass. The pure and binary blends of switchgrass (SWG) and pine harvest residues (PT6) were used as biomass feedstocks. Sequential SPME sampling allowed for monitoring of changes in the pyrolysis vapors as char accumulated in the fluid bed. The relative concentration and composition of the pyrolysis vapors desorbed from the SPME fibers were investigated using GC−MS, and the resulting chromatograms were analyzed using principal component analysis (PCA) to compare the composition of the pyrolysis vapors over the course of the pyrolysis run. The chemical compositions of both carbohydrate and lignin fragments varied as the char builds up in the reactor bed. Fragments derived from cellulose and hemicelluloses included anhydrosugars, furans, and light-oxygenated compounds. Lignin fragments included methoxyphenols, phenolic ketones, aldehydes, and low-molecular-weight aromatics. The composition of the carbohydrate fragments changed more than those of the lignin fragments as the char built up in the fluid bed. This combination of SPME-GC/MS-PCA was a novel, easy, and effective method for measuring the composition and changes in the composition of pyrolysis vapors during the fast pyrolysis process. This work also highlighted the effect of char build-up on the composition of the overall pyrolysis vapors.

KEYWORDS: *SPME-GC/MS-PCA, pyrolysis vapors, biochar, fluidized-bed reactor, biomass, fast pyrolysis*

1. INTRODUCTION

Biomass pyrolysis oils are a complex mixture of hundreds of oxygenated and aromatic compounds created by fast depolymerization, dehydration, and fragmentation of carbohydrates and lignin.[1,2] The yield and composition of the biocrude are governed by a series of complex decomposition and recombination reactions, which depend on the source of the biomass, the design of the reactor and its operating conditions, and the presence of mineral and other catalytic components. These decomposition and recombination phenomena occur on the millisecond time scale.[3−5] Previous work has shown that a typical biocrude oil may contain 20 wt % of water (generated during thermal decomposition), about 40% of volatile GC-detectable compounds, 15% nonvolatile HPLC-detectable compounds, and around 25% complex higher-molecular-weight lignin component oligomers.[6−9]

This complex array of pyrolytic liquid products originates from the primary biomass components, cellulose, hemicellulose, and lignin, which decompose into a wide array of fragments. In general, pyrolysis of lignin produces alkyl phenols and alkyl-substituted methoxyphenols (guaiacol and syringol moieties) and a large variety of phenolic dimers and higher oligomers. Pyrolysis of cellulose and hemicellulose mainly evolve into organic acids and aldehydes, e.g., acetic acid, acetaldehyde, furans, and dehydrosugars, e.g., levoglucosan and xylopyranose. This mixture of polar and nonpolar compounds makes the chemical characterization of biocrude oils tremendously difficult and laborious, requiring the use of numerous analytical techniques (e.g., gas chromatography−mass spectrometry (GC−MS), HPLC-MS, Py-GC/MS, and GPC). In many cases, the biocrude needs to be subjected to chemical derivatization,[10,11] solvent fractionation,[12] or other pretreatments to better understand the compounds present in the mixtures. In addition, the original biocrudes are unstable and can condense into higher-molecular-weight products.[13]

Given the complexity and molecular weight differences of the biocrude, a series of analytical tools are required for characterization. This can be accomplished by dissolving the biocrude in a suitable organic solvent or collecting aerosol vapors using headspace solid-phase microextraction (SPME), followed by GC−MS analysis. Nonetheless, the wide variability of biocrude oil constituents from polar hydrophilic or hydrophobic compounds, multiple isomers, and compounds with a wide variety of molecular weights is challenging for any single analytical technique. The at-line collection of pyrolysis vapors with SPME provides insights into the composition of the vapors and can potentially be used for process control. This at-line collection can be accomplished by varying locations in

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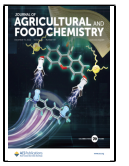

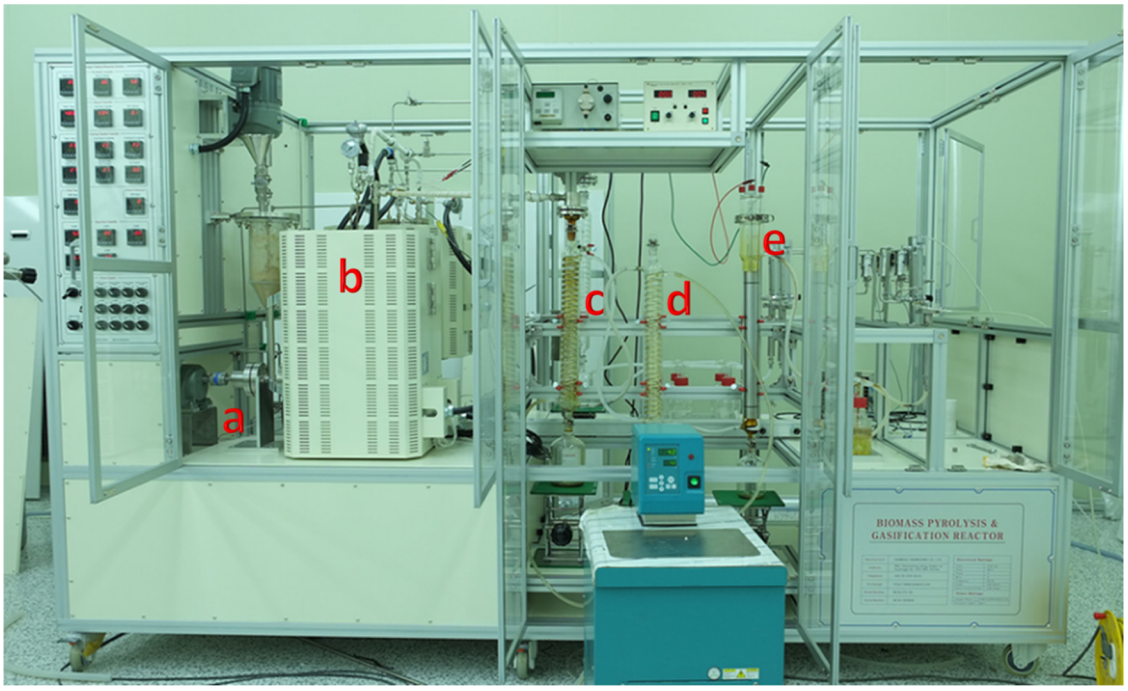

Figure 1. Laboratory-scale fast pyrolysis reactor: (a) screw, (b) fluid bed heater, (c, d) water-cooling condensers, and (e) electrostatic precipitator.

the process and varying the sampling frequency to provide insights into the primary vapors and the secondary condensation processes.[12,14]

The SPME sampling technique was developed in 1990 by Pawliszyn[15,16] and has been widely employed on an extensive range of analytes in many industrial fields and research applications, including forensic, environmental, food, and pharmaceutical chemistry.[17−21] With SPME, the analytes in liquid or gaseous phases are adsorbed/absorbed onto a coated fused silica fiber, which is part of the syringe needle assembly. The SPME fiber adsorbs/absorbs the gases and vapors contained in the sampling stream. For the analysis, the fiber is inserted into a GC injection port where it is thermally desorbed and subjected to chromatographic analysis. Several studies have shown the similarity of SPME coupled with GC or GC−MS, relative to the direct sampling of gaseous streams in thermochemical conversion processes, demonstrating the value of this technique for the at-line monitoring of industrial operations.[22−26] Previous work has demonstrated the viability of using SPME to characterize bench-scale pyrolysis operations.[27] SPME is commonly combined with GC−MS analysis to provide specific information on the actual composition of the individual vapors.[11,20] Thus, SPME-GC−MS sampling is a useful method for fast, solventless, and detailed characterization of biocrude vapors.

To better understand the overall changes in the composition of biomass pyrolysis vapors, SPME coupled with principal component analysis (PCA) was used to monitor trends of the chromatographic data. PCA is commonly used to detect trends in complex chemical data, including vibrational spectroscopy, NMR, and chromatography.[28−33] PCA is particularly useful in detecting related patterns where changes in the major components are highly correlated with changes in minor components, or when changes in one class of compounds, e.g., lignin, are correlated, positively or inversely, with changes in another class of compounds, e.g., carbohydrates.

The aim of this study is to evaluate the potential catalytic effect of biochar accumulation in the fluid bed pyrolysis process on the composition of biocrude vapors. The SPME sampling technique allows the at-line monitoring of changes in biocrude vapor products. To the best of our knowledge, this SPME-GC/MS-PCA approach has not been used to study changes in the composition of a biocrude as a function of reaction time or changes in the composition of a fluid bed over time. Specifically, this work focused on the impact of char build-up in the fluidized bed.

2. MATERIALS AND METHODS

2.1. Materials. Forest and agricultural residues (pine tops and switchgrass, respectively) from the southern United States were provided by Genera Energy Inc. (Vonore, Tennessee).

2.2. Biomass Preparation. *2.2.1. Sample Grinding.* Oven-dried biomass (105 °C for 24 h) was treated by a Wiley Mill (Thomas Scientific, Swedesboro, NJ), equipped with a 0.5 mm screen to help optimize the heat and mass transfer during the fast pyrolysis process. Afterward, the biomass in powder-like form was stored in plastic bags to prevent the adsorption of moisture. The moisture contents of biomass ranged from 5 to 10%.

2.3. Biomass Characterization. *2.3.1. Compositional Analysis.* The biomass sample (40−60 mesh) was extracted with a benzene−ethanol mixture (v/v = 2:1) for 24 h according to TAPPI Standard T204cm-07. The amount of extractives was calculated gravimetrically after vacuum drying. The amounts of structural carbohydrates and lignin were measured by the Klason lignin analysis, followed by HPLC (Model 1200, Agilent, Santa Clara, CA) sugar analysis following the National Renewable Energy Lab (NREL) procedures for structural carbohydrates and lignin in biomass characterization (TP-510-42618).

2.3.2. Elemental Analysis. Carbon, hydrogen, and nitrogen (CHN) analyses of biomass feedstocks were performed according to ASTM-D5291 using an Elemental Analyzer 2400 Series II (Perkin Elmer, Waltham, MA). A sample of 5−7 mg was used for each test, and the analyses were performed in triplicate. The CHN amounts were determined by this quantitative method, and the oxygen contents were calculated by difference. The amounts of individual

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inorganics in the biomass samples were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 8000; Perkin Elmer).

2.4. Fast Pyrolysis Bio-Oil Production. A laboratory-scale reactor (Hanwoul Engineering Co. Ltd., Gyeonggi-do, Korea) was operated for the fast pyrolysis operation process as recently used by our research group.[34] The reactor system consists of a screw feeder, fluidized bed, and a liquid collection system composed of two water-cooling condensers (WCCs) and one electrostatic precipitator (ESP). The fluid bed is heated with an external clamshell heater. Initially, approximately 200 g of sand was deposited at the bottom of the pyrolysis reactor to serve as the fluidizing and heat transfer medium. The fluidized-bed reactor is supported by two streams of nitrogen gas. One stream served as the fluidizing carrier gas, introduced into the bottom of the reactor, and the second was used to prevent plugging in the screw conveyor. Fast pyrolysis was performed at 500 °C with a nitrogen flow rate of 11 L/min and a biomass feeding rate of 150 g/h. The biomass residence time was calculated to be in a range of 1−2 s.

The resulting pyrolysis vapors and aerosols were collected in the two chilled water condensers held at 2 °C and the electrostatic precipitator (ESP) was maintained at 12 kV. The pyrolysis bio-oils were collected at three locations, after the first and second condensers and after the electrostatic precipitator. The overall system is shown in Figure 1. The bio-oils collected after the first and second condensers were combined and labeled as bio-oil condensate (BOC), while the fraction collected at the ESP was labeled as bio-oil precipitated (BOP). The total accumulated biochar was collected from the char cyclone and was estimated to be around 8.7−12.5 wt % according to our previous work.[34]

2.5. Solid-Phase Microextraction (SPME). A Supelco 75 μm carboxen/poly(dimethylsiloxane) (CAR/PDMS)-coated fiber (Supelco, Bellefonte, CA) in extended configuration was used for the adsorption of biocrude vapor stream. SPME sampling was performed using two adjacent sampling ports located after the electrostatic precipitator (ESP). Both ports were constructed from high-pressure, 1/4 inch union tees (Swagelok, Solon, OH) fitted with Merlin Microseals (#21-01) and Bleed Temperature-Optimized (BTO) GC septa to accommodate the SPME device. The SPME fiber needle depth was maintained such that the aerosols remained in continuous contact (∼1/2 inch) to assure good adsorption. Four Supelco fibers were used for each run. Fiber A was in place for the entire 1 h run, while fibers labeled B1, B2, and B3 were exchanged every 20 min. Fiber B1 was used for 0−20 min, fiber B2 for 20−40 min, and fiber B3 for 40−60 min. This sampling sequence was intended to monitor changes in vapor composition during the run, which could be attributed to a build-up of char and active alkaline earth minerals (AAEMs) in the bed. All four fibers were stored in a freezer at 0 °F (−18 °C) and analyzed in less than 24 h after sampling.

All fibers were thermally desorbed before all experiments to ensure that they were free of contaminants with the following sequence: initial oven temperature at 40 °C held for 2 min, followed by heating to 275 °C at 8 °C/min and holding for 30 min. The injector temperature was kept constant at 150 °C for 30 min. Then, the fiber was retracted onto the core housing to prevent contamination or changes in the adsorbed sample.

2.6. Qualitative Analysis of FPBO Compounds. Gas chromatography−mass spectrometry (GC−MS) analysis of biocrude vapors was conducted with an Agilent 7280A GC system (Agilent, Santa Clara, CA) coupled with an Agilent 5977E MS and an Agilent G4567A ALS autosampler. An HP-5MS UI capillary column (30 m × 0.25 mm × 0.25 μm, Agilent, Santa Clara, CA) was used and the National Institute of Standards and Technology (NIST, 2011 version) libraries were used for the identification of the individual compounds. Following sampling, SPME fibers were inserted into the GC−MS in the following order: fiber A, B1, B2, and B3. All GC−MS parameters and fiber conditioning were kept constant for these analyses. Only a fraction of the compounds in the vapor stream could elute from the GC, and only 50 could be identified as shown in the Supporting Information. Not all of the pyrolytic compounds in the original chromatograms could be positively identified using the NIST mass spectral database. Accordingly, only compounds with NIST library hit (probability) factors greater than approximately 60% are included in this work. Given the complexity of the chromatograms (i.e., the number of compounds and the degree of co-elution) and the signal-to ratio of the mass spectral data, this hit factor represents the floor for the reasonable confidence of the prediction.

2.7. Principal Component Analysis (PCA). Principal component analysis (PCA) was performed using Unscramble software version 10.5 (Camo Software, Oslo, Norway). The raw GC chromatograms were normalized to the total peak area (Total Sum Normalization, TSN). The measurement of the peak area is considered from the base to the tip of the peak. The selected peaks of the spectral data set should be symmetrical, narrow, and nonoverlapping. TSN requires dividing the area of each peak in a single chromatogram by the total sum of all peaks within that same chromatogram. Therefore, the ith peak (x_i) of the jth chromatogram is estimated as shown in eq 1. TSN ensures uniformity in how data is displayed, understood, and utilized across all of the data sets. This approach was used to account for small differences in the mass of samples on the SPME fibers, and the normalized chromatograms were used for the PCA.

$$x_{ij}^{\mathrm{TSN}} = \frac{x_{ij}}{\sum_{i=1}^{n} x_{ij}} \tag{1}$$

The PCA provides both "scores," which highlight differences in the composition of the vapors, and the "loadings," which identify the actual structures present in the vapors. Specifically, the "loading" highlights the compounds responsible for the chemical changes in the pyrolysis vapors. PCA was used to evaluate trends in the chromatograms that were correlated with the accumulation of char and ash in the fluid bed. Specifically, the PCA was used to compare changes between fiber "B1" with the vapors collected from 0 to 20 min, fiber "B2" with the vapors collected from 20 to 40 min, and fiber "B3" with the vapors collected between 40 and 60 min. Each of these individual fibers (B1−B3) was also compared to fiber A, where the vapors were collected over the course of the entire run.

3. RESULTS AND DISCUSSION

3.1. Biomass Characterization. The biomass sources selected for this study were chosen based on their vast availability and commercial relevance in the southern United States. Switchgrass has been extensively studied as a dedicated bioenergy crop because it is easily grown on marginal soils. The stem of the pine trees is used for the production of lumber, panels, or pulp chips, but the tops and branches, with minimal bark or needles, are of little value and commonly left in the woods. The forest residues used in this work were pine tops with diameters of 6 inches (PT6). The chemical and elemental compositions of both raw materials are presented in Figure 2.

3.2. SPME-GC/MS and PCA. In this work, SPME coupled with GC−MS was used for the collection and analysis of the biocrude vapors. From a total of 50 GC-detectable compounds, 31 of them have probabilities factors greater than 60% and were further selected for principal component analysis (PCA). It is believed that the presence of pyrolytic compounds in the vapor phase is related to the composition of the biomass feedstock, and the reaction conditions accordingly to previous findings.[35,36] There are a series of primary and secondary pyrolytic decomposition reactions, which are related to the cellulose, hemicellulose, and lignin content of the feedstocks. In this work, the composition of the biomass feedstock was held constant over the course of a run. As expected, char accumulated over the course of a 1 h run and nearly filled the fluid bed. This char fraction also included the inorganic ash.

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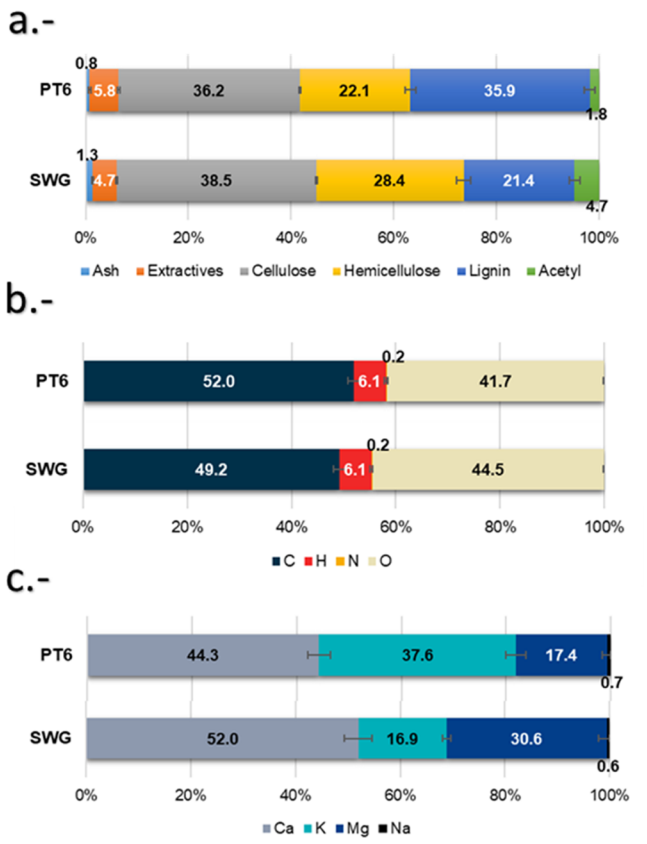

Figure 2. Biomass feedstock characterization (wt % dry basis): (a) chemical, (b) elemental, and (c) alkaline and alkali earth metals analyses.

The specific changes in the vapor composition as a function of biochar and ash accumulation in the bed were the focus of this work. To help clarify the analysis, the fragments were grouped into two classes, aromatic fragments derived from the lignin, and aliphatic oxygenates derived from the carbohydrates. The PCA "score" and "loading" plots are shown in Figures 3−6. PCA shows that the biocrude vapor composition undergoes systematic change as a function of the runtime and char accumulation, potentially due to the increase of the oxygen-containing functional groups and the aromatic rings contained in char.[37−39]

Figures 3 and 4 show the PCA score plot, and the loadings plot for the SWG/PT6 series, based on the carbohydrate fragments. Figures 5 and 6 show the PCA score plot, and the loadings plot for the SWG/PT6 series, based on the lignin fragments. Specifically, Figure 3 shows the effects of changing the ratio of SWG/PT6 and the effects of char and ash accumulation in the fluid bed. The PCA score plots based on the carbohydrate fragments in Figure 3 show a consistent trend along PC1, which explains 66% of the compositional variations based on the sequence runtime or char accumulation. Variations along PC2, which explains 25% of the chemical differences between the samples can be attributed to the biomass feedstock[1]. Given the significant chemical differences between SWG and pine residues, the fact that the runtime and the associated accumulation of char and ash dominated the changes in the carbohydrate vapor composition is noteworthy.

The specific carbohydrate vapor components that show the greatest changes are given in the loading plot in Figure 4. This plot shows that early in the pyrolysis run, primary pyrolysis products such as formic and acetic acid are present in higher concentrations. Later in the run, however, secondary fragments, furfural, furan 2-methyl, benzaldehyde 2-hydroxy, and 2-hydroxy 4,6-dimethylbenzaldehyde increase in concentration. Along PC2, the presence of 2-methyl furan and 2-hydroxy-5-methyl furan is associated with the PT6, and higher amounts of acetic acid are associated with SWG.

Changes in the composition of the carbohydrate fragments with the accumulation of char and ash in the fluid bed are not surprising.[40] However, the PCA score plots based on the lignin fragments in Figure 5 also show a consistent change in composition with char and ash accumulation. In this case, the trends are impacted by both PC1 and PC2, which, respectively,

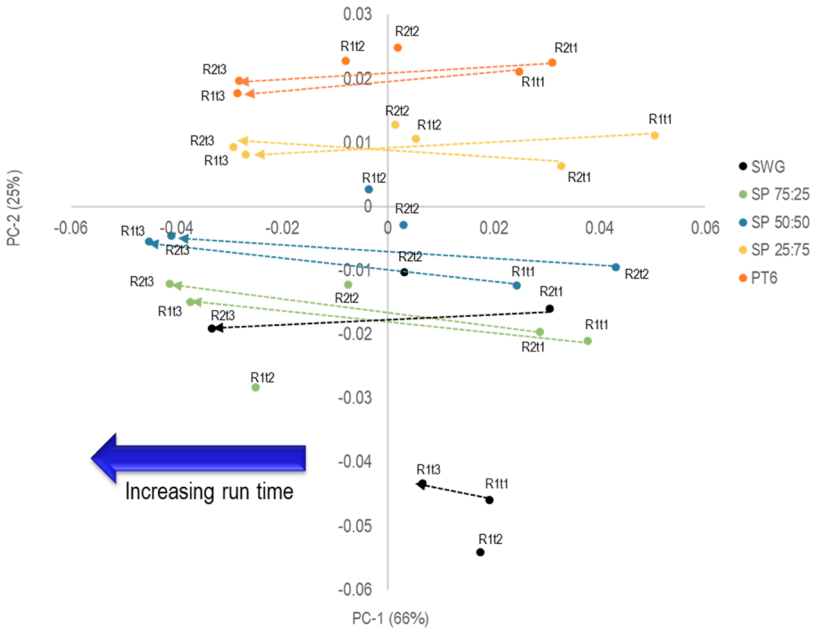

Figure 3. Effect of runtime in carbohydrate fragments (PCA score).

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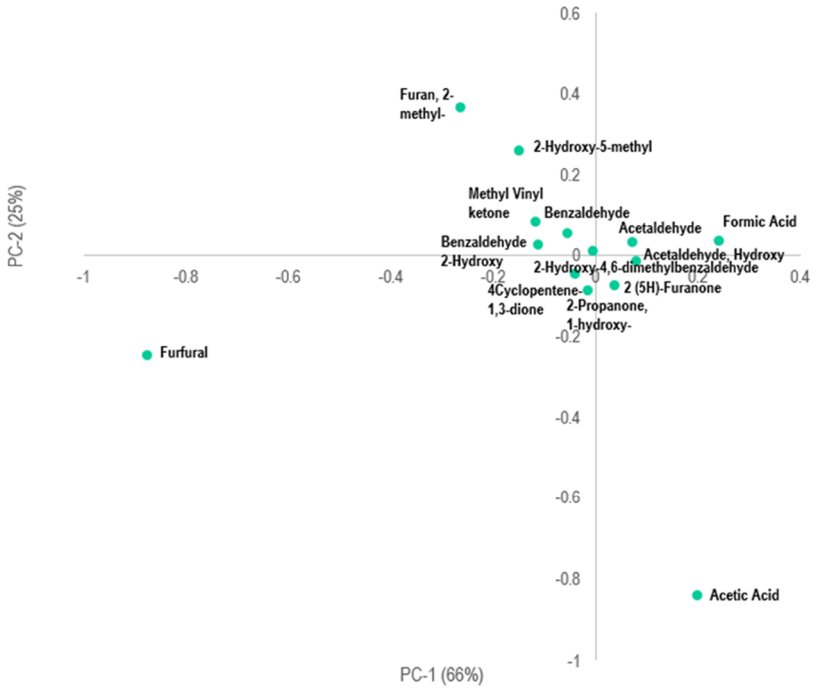

Figure 4. Effect of runtime in carbohydrate fragments (PCA loadings).

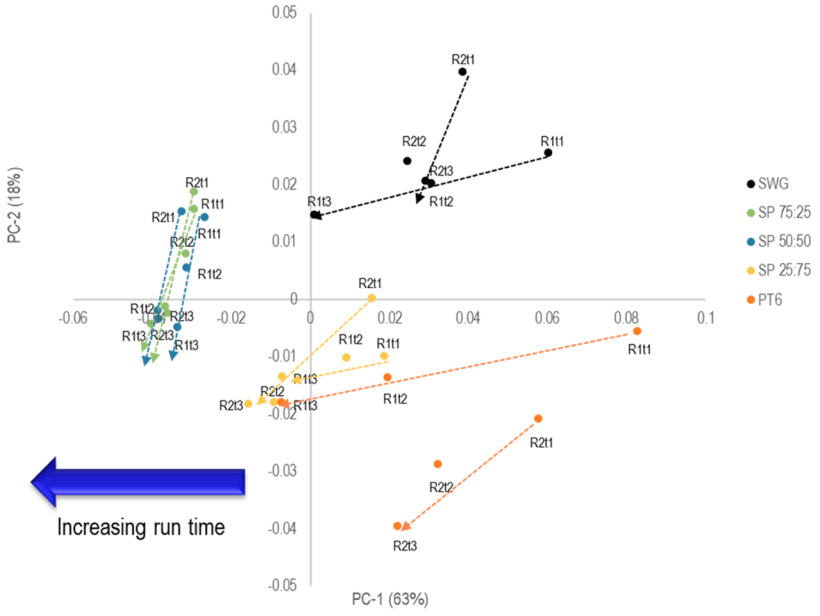

Figure 5. Effect of runtime in lignin fragment (PCA score).

account for 63 and 18% of the information in the GC−MS chromatograms. There is a consistent change in the composition of the biocrude vapors between the first and the last SPME samples, and there is also a secondary, but nonlinear, effect of the biomass source. The nonlinear trend where samples with PT6/SWG ratios of 75:25 and 50:50 suggests that there is some interaction between the two feedstocks that influence the lignin decomposition pathways. Differences in the lignin structures and the ash content of the two feedstocks could play a role in this nonlinear behavior.

Variations in the chemical composition of the lignin fragments are shown in the PCA loadings plot in Figure 6. Early in the pyrolysis run, primary lignin pyrolysis products such as 2-methoxy 4-vinylphenol, trans-isoeugenol, and creosol are present in elevated concentrations. Later in the run, secondary fragments such as 3-methoxy-2,4,6-trimethyl phenol, 2-methoxy phenol, and 4-ethyl-2-methoxy phenol increase in concentration. Along PC2, the presence of 4-ethyl phenol is associated with SWG, and higher amounts of creosol, 2-ethyl 6-methyl phenol, and 4-ethyl 3-methyl phenol are associated with PT6.

4. CONCLUSIONS

The results of this study, conducted on five different types of biomass feedstock substrates, demonstrated that the at-line sampling by SPME is a relatively simple and high-throughput

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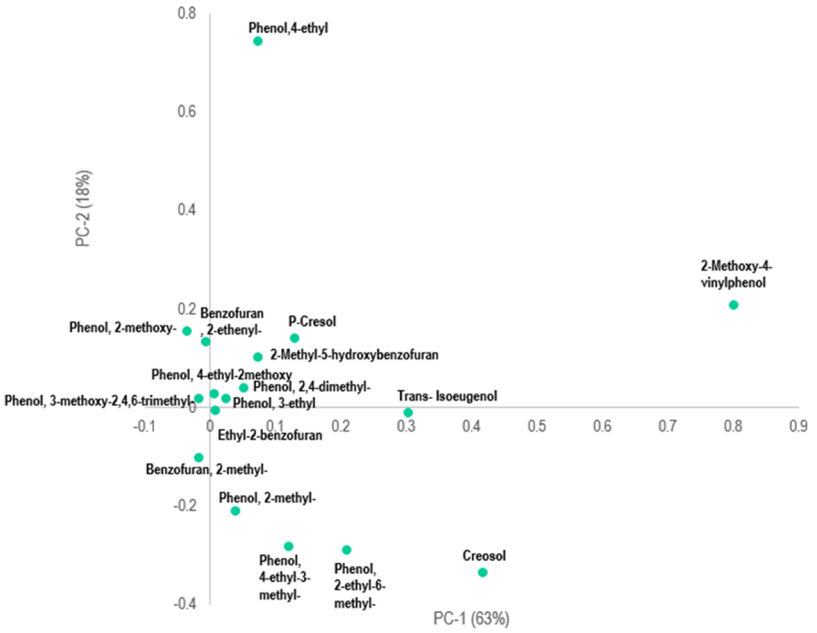

Figure 6. Effect of runtime in lignin fragment (PCA loadings).

method that can be employed at different technologies levels (field, laboratory, biorefinery) to determine the quality and performance of biomass biocrude products. The analytical-qualitative information gathered in a fluid bed reactor system can be considered relatively accurate.

A comprehensive study of the biocrude vapor changes was conducted using sequential SPME fibers combined with GC−MS analysis. The evaluated GC−MS chromatograms with PCA revealed systematic changes in both carbohydrate fragments and lignin fragments, which could be associated with the increasing amount of char and ash (active alkali alkaline earth metals) in the fluid bed reactor. The effects of these significant chemical changes in both carbohydrate and lignin fragments with runtime need to be considered when conducting small-scale tests.

The SPME-GC/MS-PCA approach can be used for monitoring large scale pyrolysis reactors in bio-oil or biochar production or to foresee pyrolytic compounds evolved in biomass thermochemical conversion plants such as torrefaction, gasification, e.g avoiding sample collection and significantly reducing working periods of time. Further investigations in quantitative analysis employing GC-FID would provide more insights into the magnitudes of the changes found in this study.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jafc.2c06043.

SPME data GC/MS identified compounds and GC chromatograms total area normalized (PDF)

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Author Contributions

E.R. designed and performed experiments, analyzed data, and wrote the original manuscript. R.S. helped perform experiments and analyze the data. M.H. collected and analyzed the data. D.T. analyzed the data, polished and revised the manuscript. S.K. designed the experiments, contributed to the related sections, and critically revised the manuscript.

Notes

The authors declare no competing financial interest.

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ADDITIONAL NOTE

[1]Note that one sample, SWG run 1, appears to have an anomalous response, but it is included for completeness.

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