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Hydrothermal transformation of Chinese privet seed biomass to gas-phase and semi-volatile products

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ABSTRACT

Hydrothermal (HT) treatment of seeds from Chinese privet (*Ligustrum sinense*), a non-native and invasive species in the southeastern United States, was examined with respect to the generation of gas-phase and semi-volatile organic chemicals of industrial importance from a lipid-rich biomass resource. Aqueous seed slurries were transformed into biphasic liquid systems comprised of a milky aqueous phase overlain by a black organic layer. Present in the headspace were elevated levels of CO_2 and acetic acid. Analysis of the semi-volatiles by GC–MS showed the formation of alkyl substituted benzenes, oxygenated cyclic alkenes, phenol, substituted phenolics, and alkyl substituted pyridines. Compared to immature seeds, mature seeds gave high relative amounts of oxygenated cyclic alkenes (cyclopentenones) and alkyl pyridines. The presence of fatty acids in the HT products likely resulted from both lipid hydrolysis reactions and the inherent stability of fatty acids under HT treatment conditions. Estimates of lignin and protein contents showed no definite trend that could be linked to the HT data. The proportion of aromatic HT products appeared to derive primarily from the proportion of extractives. Thus, variations in extractives yields impact HT product yields and thereby demonstrate the importance of timing in feedstock collection to favor targeted HT products.

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1. Introduction

Biomass of all kinds can be transformed into gas-phase and semi-volatile chemical mixtures in hydrothermal (HT) reaction systems (Kruse, 2008). Many HT reaction systems utilize water heated (300–500 °C) and pressurized (15–40 MPa) under anoxic (reducing) conditions (Kruse and Gawlik, 2003). Reaction times can vary widely from minutes to hours (Catallo and Junk, 2001). Bio-based HT reactions can be conducted with slurries, biphasic liquid systems (i.e., plant oil/water), emulsions, and with true solutions. Past work by the authors has focused primarily on the identities, approximate yields, and prominent pathways of HT transformations of biomolecules (e.g., glucose, starch, lignin) as well as applications of HT treatment to numerous biomass substrates, including noxious aquatic and terrestrial plants (Catallo et al., 2008; Shupe and Catallo, 2006), and decommissioned preservative-treated wood (Catallo and Shupe, 2003, 2008; Catallo et al., 2004).

With respect to lignocellulosic biomass substrates used for HT transformations, there are a number of relevant treatment issues. These include (1) substrate elemental stoichiometry (e.g., polysaccharides are constituted of greater than 60% oxygen by mass, and are limited in reducing hydrogen equivalents, i.e., about 7% by weight in starch and cellulose) and (2) treatment time (reaction pathway and rate studies have confirmed that relevant HT reactions achieve equilibrium on time scales of minutes to hours; reaction times past the equilibrium point decrease yields and increase the generation of char and oxidized products such as CO_2), and (3) the presence of competing reactions *in situ* (metal surface and acid- and base-catalyzed hydration reactions can be significant determinants of product yields). With these issues in mind, invasive or noxious organisms, sewage sludge, and decommissioned preservative-treated wood may be appropriate substrates because HT treatment allows for large volume reductions, recovery and recycling of toxicants, and the generation of industrially-useful chemicals (Catallo and Comeaux, 2008; He et al., 2008).

While HT treatment of lignocellulosic biomass usually results in the generation of similar chemical products, major differences in yields and certain gas-phase and semi-volatile chemicals exist between plant types. Also, previous work with Chinese tallow tree (*Triadica sebifera* syn. *Sapium sebiferum*) seeds, stems, and leaves (Shupe and Catallo, 2006), and subsequent unpublished work with other plant species, have shown that HT product differences are

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found when (1) different plant tissue types (e.g., stems, seeds) and (2) samples from different intervals in the growing season are treated. As a result, one area of interest is to examine HT treatment of different plant materials at various stages in the plant life cycle.

The subject of the current study is Chinese privet (*Ligustrum sinense* Laur.). This plant is a non-native and invasive species that "occupies" 1.21405 hec (3,199,246 ac) of southern forest land (Miller, 2003). Currently, it has little or no commercial use or value. Chinese privet is an abundant semi-evergreen small tree or large shrub, most commonly found invading the understory of moist areas (Duke University, 2009). It has become a nuisance plant throughout the southeastern United States (USDA NRCS, 2009) as a result of its prolific and invasive growth, adverse effect on the natural ecosystem, and no current industrial use. The purpose of this work was to evaluate the generation of semi-volatile chemicals of industrial importance from the HT treatment of a lipid-rich biomass resource, immature Chinese privet seeds, and to assess any differences to the HT products resulting from changing biochemical compositions during seed maturation.

2. Methods

2.1. Sample collection

Bulk whole seeds of Chinese privet were collected monthly, from June through October, at the Bob R. Jones–Idlewild Research Station near Clinton, Louisiana. Bulk samples, approximately 500 seeds, were brought to the laboratory and dried under ambient conditions for 7 days. Dried seeds were ground using a Wiley Mill equipped with a 2 mm mesh screen plate and stored in a refrigerator until analyzed.

2.2. Determination of plant biochemical fractions

Triplicate samples of ground Chinese privet seed were exhaustively extracted using a method adapted from the ASTM standard (ASTM, 1996a). Samples were extracted with hexane (6 h), ethanol:toluene (7:3, 6 h) and then ethanol (6 h) using a Soxhlet apparatus. Organic solvent extracts were concentrated by rotary evaporation, transferred to small glass vials, and dried under a stream of N_2 to afford oils that were further dried under vacuum before weighing. Extractive yields were corrected for moisture in the seed samples as determined by drying a separate set of samples in an oven (103 ± 2 °C). Extractive-free residues were dried and ground further in a Wiley mill (425 μm mesh) before being subjected to the Klason lignin determination by a standard procedure (ASTM, 1996b). FT-IR spectra of the extracts were collected using a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet smart golden gate MKII single reflection ATR accessory. Nitrogen contents for seed samples were determined by Galbraith Laboratories (Knoxville, TN) using a Perkin–Elmer 240 elemental analyzer.

2.3. HT treatment of ground seed samples

Ground (2 mm mesh) seed samples were weighed and suspended in filtered tap water at pH = 9 to afford slurries of 28 g L^{-1}. Each slurry was put into a custom-made/high-pressure/corrosion-resistant Hastelloy X autoclave reactor (internal dimensions: 67 mm length × 10 mm diameter) and sparged with argon for 10 min. The reactor was purged with argon, sealed, and then immersed in a molten tin bath at 400 °C. The treatment time used for HT reactions in this study was 7.3 min including heat up (200 s or 3.3 min) to equilibrate the reactor and contents at temperature in the molten tin bath, 4 min of HT temperature and then immersion of the reactor in a cold water bath for two minutes. [Heating rates of 5 mL Hastelloy-X reactors in the molten tin bath were determined prior to the HT runs using sealed reactors containing magnesium shavings. The reactors were placed into the molten tin at 400 °C for varying lengths of time, removed, opened, and temperature was immediately measured internally using a thermocouple. Heating rates were found to be 2–3 °C/s, so the pre-HT heat up time from room temperature to 400 °C in these reactors after submergence in the molten tin was taken to be 200 s]. Internal pressures during HT treatment approached 30 MPa. Pre- and post-treatment pH measurements were accomplished using a pH meter with a standardized and temperature-compensated electrode.

As a result of HT treatment, the aqueous Chinese privet seed slurries were transformed into biphasic liquid systems comprised of a cloudy or milky aqueous phase overlain by a black organic layer, along with small amounts (1–5% by weight) of suspended particles. Collection of these particles showed them to be carbonaceous ash retaining some fuel value (i.e., after drying they were combustible). This post-HT product mixture was extracted repeatedly by shaking with ultra-pure dichloromethane followed by phase separation, recovery of the organic phase and subsequent drying of the recovered organic extract with anhydrous sodium sulfate. Concentrated extracts were analyzed by gas chromatography–mass spectrometry (GC–MS). As a control, ground (2 mm mesh) seed samples were also weighed into cellulose thimbles and extracted with dichloromethane in a Soxhlet apparatus to determine the presence of any semi-volatile compounds or related materials in the substrates prior to HT treatment. The resulting extracts were analyzed in the same manner as above for the HT products.

2.4. Analyses by GC–MS

Pre- and post-HT headspace gas samples were collected from the headspace of the loaded HT reactors, before and immediately after the HT treatments, using a 100 μL gastight syringe. Gas samples were analyzed with a GC–MS system (Shimadzu QP500) equipped with a DB-5 capillary column (30 m; 0.25 mm id; 0.25 μm film) using the following parameters: injection port was isothermal at 150 °C, 50 μL injection volume; oven temperature program was isothermal at 50 °C, and ionization in the MS was by electron impact (70 eV). Runs were conducted in the full scan mode with a mass acquisition range of 30–200 amu.

For semi-volatiles, the same GC–MS system and column were used but under different parameters: injection port isothermal at 250 °C, 1 μL sample injection volume, splitless; oven temperature program 70 °C (4 min) ramp 4 °C min^{-1} to 250 °C, analyte transfer to the mass spectrometer source was at 280 °C and ionization in the MS was by electron impact (70 eV). Runs were conducted in the full scan mode with a mass acquisition range of 50–300 amu. For semi-volatiles, target ions spanned the inclusive molecular weight range between C_2-benzenes (xylene isomers and ethyl-benzene at 106 amu) and coronene (300 amu).

Tentative product identifications were performed using (a) comparison of experimental data with authentic standards, (b) interpretation of mass spectra (molecular ions, isotopic structures, and logical fragment losses) and, (c) comparison of spectra with computerized libraries of mass spectra. Mass spectra were considered acceptable if there was a signal:noise ratio greater than 3 for the base peak of interest, and minimal background interference with respect to isotopic clusters and fragments. MS tuning (perfluorotributylamine) was performed at least once daily, and all MS analyses for comparison were conducted under the same tune. Digital background subtraction and chromatographic overlay

algorithms were used for further evaluation of GC–MS data from standards, controls, and experimental extracts.

3. Results and discussion

3.1. Characterization of Chinese privet seeds

While the chemistries and the proportions of the biopolymers comprising plant cell walls (e.g., cellulose, lignin) may have an impact on HT product compositions, a recent study showed the provenance of HT product differences to be primarily from the extractives (Catallo et al., 2008). Accordingly, extractions of the ground Chinese privet seeds used in the present study were carried out to quantify extractive content changes occurring upon seed maturation. Seed lipids, serving as an energy reserve necessary for germination (Baud et al., 2002), were first extracted with hexane, a solvent commonly used for lipid analyses (Hinrichsen and Steinhart, 2006; Ramadan and Mörsel, 2003). This added step, before the standard extractions with ethanol:toluene (7:3) and ethanol, afforded about 6% of the dry mass for the seed sample collected in June (Table 1). Yields of hexane-soluble extractives gradually increased over time and reached almost 11% for the October sample.

Analysis of the dry hexane extracts by FT-IR spectroscopy confirmed that they were primarily comprised of seed lipids (e.g., waxes and triglycerides). The spectra for the hexane extracts (Figs. 1a and b) are dominated by aliphatic CH signals (2922 and 2852 cm^{-1}) expected for methylene and methyl functionalities; smaller signals at lower wavenumbers, 1456 and 1366 cm^{-1}, are also consistent with these functionalities. The strong signals at 1732 and 1688 cm^{-1}, indicative of the carbonyls in esters and/or organic acids, would be expected for seed lipids. It is interesting to note that early in the season, the carbonyl signal at 1688 cm^{-1} is greater than that at 1732 cm^{-1}. These vary over the next 3 months, and then for the October sample the signal at 1732 cm^{-1} has a greater intensity than that at 1688 cm^{-1}. This may coincide with a conversion of the lipids from fatty acids to esters (triglycerides) upon seed maturation.

Unlike the hexane extracts, the amounts for the ethanol:toluene (7:3) extracts decreased with seed maturation. Specifically, the amounts for the ethanol:toluene-soluble extractives in the June sample were greater than 50% and declined steadily to less than 30% for the October sample. No absolute trend was observed with the ethanol extracts which varied from 2.5% to 7%. Should the amount for the ethanol extracts in the August sample (2.54%) be an outlier, it would appear that over the maturation process, the seeds steadily accumulate extractives at the extremes in polarity (i.e., very low or very high polarity).

Analysis of the ethanol:toluene (7:3) extracts by FT-IR spectroscopy gave similar spectra for all 5 seed samples. The spectra for the June and October extracts are shown in Fig. 1c and d. Compared to the hexane extracts, the signals indicative of methylene and methyl functionalities (*ca.* 2920 and 2850 cm^{-1}) are much reduced. Signals of particular interest are those indicative of hydroxyl functionality (broad signal centered at 3321 cm^{-1}) and aromatics (*ca.* 1600, 1500, and 1400 cm^{-1}). Thus, it would appear that these extracts are comprised of a wide array of aliphatic and now, aromatic compounds. The spectra for the ethanol extracts (Fig. 1e and f) were quite similar to those for the ethanol:toluene extracts. Thus, it would appear that the ethanol:toluene and ethanol extractives have chemical similarities even though the latter extractives require a solvent of higher polarity for their isolation.

The total extractives contents for the seed samples decreased from 61% to 48% over the maturation process. The Klason lignin contents showed no obvious trend, thus, the differences in seed composition are dominated by the extractives and not cell wall chemistries. At this juncture, it should be noted that in addition to the accumulation of energy reserves in the form of lipids, seeds are also known to accumulate storage proteins (Fischer et al., 1987; Wang et al., 2001). Lignin determinations by the Klason method are best applied to primarily lignocellulosic samples given that proteins can contribute to the values for Klason lignin content (Brunow et al., 1999). Nevertheless, despite this caveat, the Klason method is still routinely applied to non-wood samples (Hatfield and Fukushima, 2005). Determination of nitrogen contents before and after extraction showed that a high proportion of the nitrogen present in the seeds was not extractable with organic solvents as would be expected for nitrogen present in proteins. Estimating the protein content by the nitrogen contents ($N \times 6.25$) (Berner and Brown, 1994) indicated that the seed samples could contain from 7% to 14% protein. Thus, the true lignin contents of the seed samples are likely to be much lower than those suggested by the Klason lignin determinations.

3.2. Hydrothermal treatments

After verifying that we did indeed have a suitable series of samples showing significant differences in the chemical composition, we then directed our attention to the HT treatments. As a control, HT treatments of water alone (no sample) were carried out and gave rise to significant decrease in pH. This has been repeatedly observed in previous studies by the authors, the decrease in pH typically being around two units. When seeds were slurried into the

Table 1
Extractives, Klason lignin, and nitrogen determinations for Chinese privet seed samples at different stages of development.

Sample collection time	Extractive yields				Klason lignin % (SD)	Nitrogen contents	
	Hexane % (SD)	Ethanol/toluene (7:3) % (SD)	Ethanol % (SD)	Total % (SD)		Unextracted sample (%)	Extractive-free sample (%)
June[a]	6.36 (0.20)[b]	50.46 (0.12)	4.07 (0.65)	60.90 (0.96)	10.82 (0.66)	1.98	3.81
July	8.19 (0.36)	46.85 (0.43)	4.35 (0.60)	59.39 (0.67)	12.69 (0.02)	1.65	3.42
August	9.19 (0.26)	41.34 (1.65)	2.54 (0.00)	53.07 (1.38)	10.60 (0.79)	1.18	2.68
September	8.79 (0.96)	35.16 (1.83)	4.59 (0.36)	48.54 (0.51)	14.92 (0.17)	1.86	2.38
October	10.95 (0.19)	29.34 (0.20)	7.26 (0.11)	47.55 (0.11)	12.99 (1.05)	2.28	3.32

[a] Seed samples collected mid-month.
[b] All values based on the oven-dry weight of unextracted starting material except for parallel determinations of nitrogen content for oven-dry extractive-free samples; SD = standard deviation.

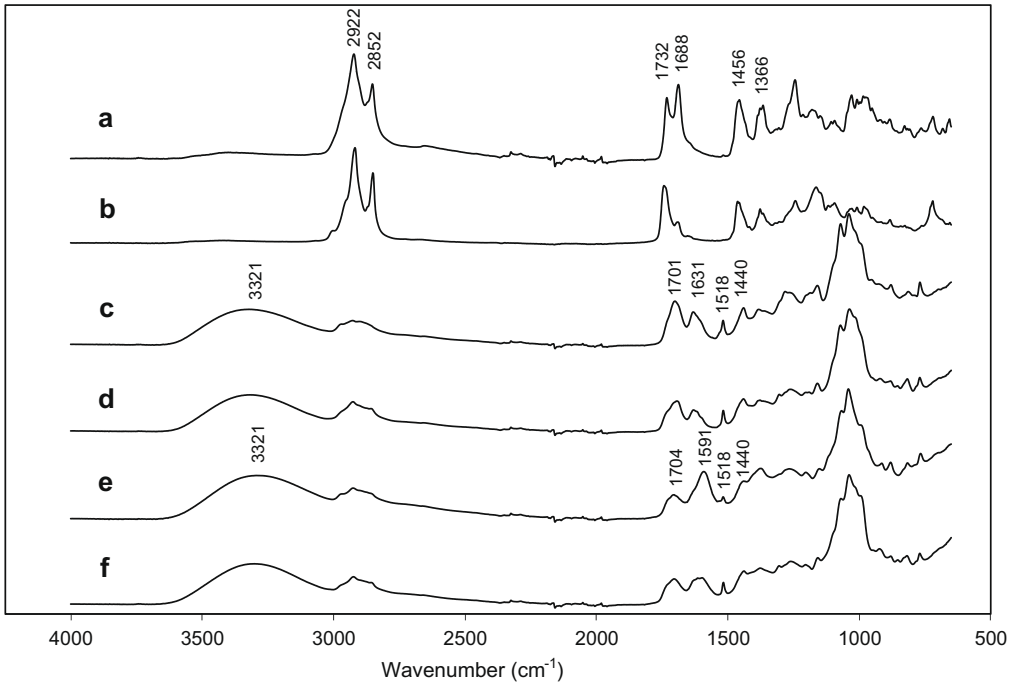

Fig. 1. FT-IR spectra of hexane (a, b), ethanol:toluene (7:3;c, d) and ethanol (e, f) extractives for Chinese privet seed samples collected early (June; a, c, e) and late (October; b, d, f) in the growing season.

water, and then HT treated, the observed decreases in pH were consistently greater than in the control (i.e., HT of water alone). Thus, identical HT treatment of the same water plus seed slurries (28 g L^{-1}) resulted in decreases of pH of 3.5–4 units (i.e., pH 9 initially to pH 5.5). The generation of CO_2 from hydration and related carbohydrate reactions *in situ* could account for the decrease in pH along the formation of acidic organic products (e.g., acetic acid).

Indeed, present in the headspace were CO_2 and acetic acid; upon opening the reactors, the aqueous phases were observed to effervesce in a way reminiscent of a shaken carbonated beverage. Rough estimates based on integration of sample peaks suggested that the CO_2 in the headspace of the HT-treated seed slurries was at least 10-fold higher relative to the headspace analyses for the controls. Based on very approximate comparisons with external standard calibration curves, acetic acid yields could exceed 25% on a substrate basis. Note that this study was not designed to quantify volatile chemicals and the above estimate was also based on models of air/water partitioning of acetic and other carboxylic acids (Abraham, 2003). Significant generation of acetic acid by HT treatments has been shown by others for a variety of biomass substrates (Goto et al., 2004; Hsieh et al., 2009) and biopolymers (Karagöz et al., 2005a; Zhang et al., 2008), especially under alkaline conditions upon the addition of inorganic reagents (Karagöz et al., 2005b, 2006) or oxidants such as hydrogen peroxide (Jin et al., 2007). In the current study, it now appears that a biomass resource rich in extractives may also provide a viable feedstock for acetic acid generation.

3.3. Semi-volatile products

As a result of HT treatment, the Chinese privet seed samples afforded complex semi-volatile hydrocarbon mixtures. Total ion chromatograms for the June and October samples are shown in Figs. 2 and 3. Inspection of these chromatograms suggests that perhaps a hundred privet-derived HT product compounds were present in the product mixtures and at least one fatty acid was carried through the HT treatment. For the June seed sample, oleic acid was sufficiently present to be detected by library search among those compounds constituting the broad peak appearing late in the chromatogram. Oleic acid was not detected in the broad peak in the same position on the chromatogram for the HT product from the October seed sample. While we cannot state that oleic acid was absent from this sample, it was not present in a sufficient amount to obtain an acceptable library match. However, for the October seed sample, an earlier peak with a high abundance could be readily assigned to palmitic acid. As for the controls (i.e., extracts of Chinese privet plant seeds before HT treatment) the very few identifiable peaks were for stearic and oleic acids. The detection of palmitic acid is likely from its release from lipids by hydrolysis reactions during the HT treatments or simply extraction as suggested for the HT treatment of tree bark (Quitain et al., 2003). It is known from past work that unsaturated carbon–carbon bonds (e.g., alkenes and alkynes) are labile in HT systems whereas saturated carbon–carbon bonds (i.e., alkanes) are not. Accordingly, saturated fatty acids may also be derived from unsaturated analogs.

Further inspection of the chromatograms for the HT products showed the formation of alkyl substituted benzenes, oxygenated cycloalkenes (cyclopentenones), phenol, substituted phenolics, and alkyl substituted pyridines. Comparison of the two chromatograms showed that many of the products formed from the October seed sample were also formed for the June sample collected earlier in the growing season. In some cases, while a peak on one chromatogram paralleled that on the other on the basis of retention time, it may have been of insufficient abundance to permit identification by mass spectrometry.

The most abundant HT products for the June sample were aromatic compounds (e.g., alkyl benzenes, phenol, alkyl phenolics). The HT products for the October sample also included significant amounts of aromatic compounds, however, accompanying them were high relative amounts of oxygenated cyclic alkenes (cyclopentenones) and alkyl pyridines. In addition, a major peak in the October sample, assigned to hydroxybenzeneethanol, was not identified in the June seed sample. Thus, while prior research has shown differences in HT product yields from different biomass

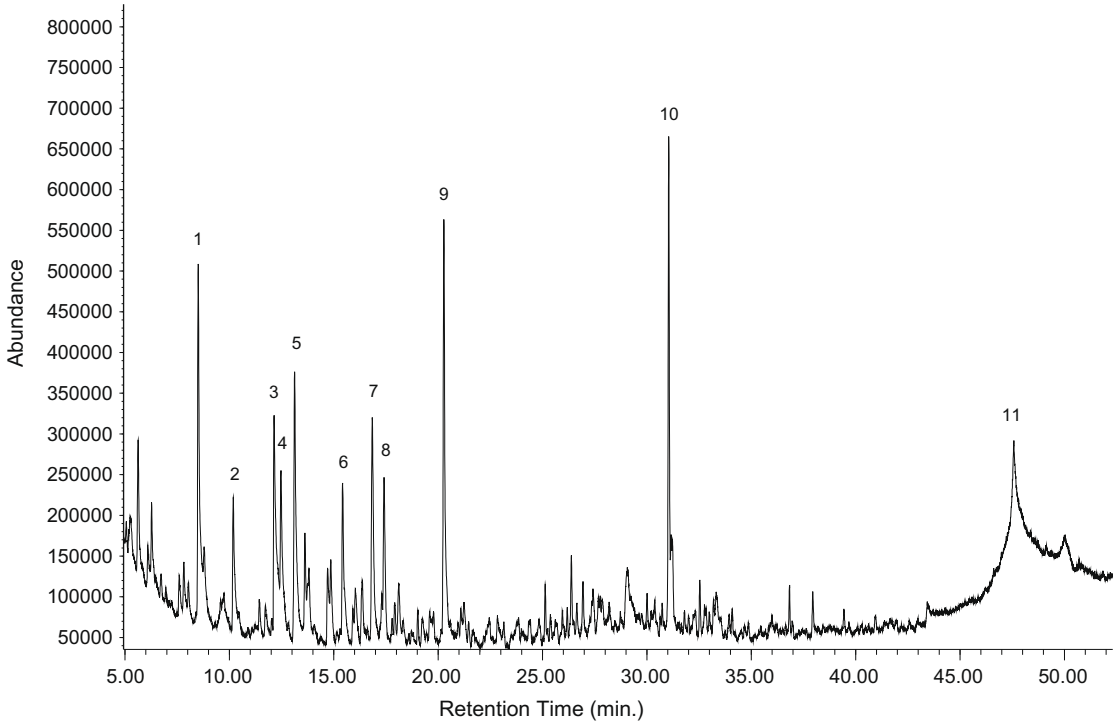

Fig. 2. Semi-volatile products generated from HT treatment of Chinese privet seed samples collected early in the growing season (June): 1. C_2-Benzene; 2. C_1-Cyclopentenone; 3. C_2-Pyridine; 4. C_1-Cyclopentenone; 5. Phenol; 6. C_2-Cyclopentenone; 7. C_1-Phenol; 8. C_3-Pyridine; 9. C_2-Phenol; 10. C_4-Tetralin; 11. Oleic acid.

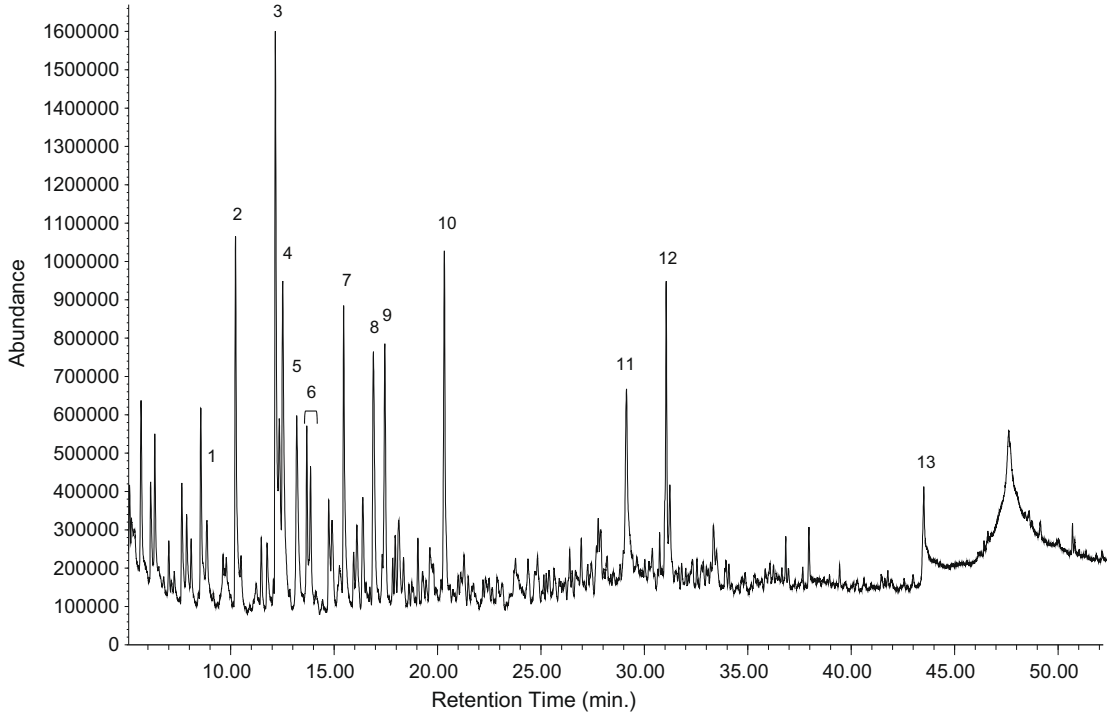

Fig. 3. Semi-volatile products generated from HT treatment of Chinese privet seed samples collected late in the growing season (October): 1. C_2-Benzene (2 isomers); 2. C_1-Cyclopentenone; 3. C_2-Pyridine; 4. C_1-Cyclopentenone; 5. Phenol; 6. C_2-Cyclopentenone (2 isomers); 7. Cyclopentenone; 8. C_1-Phenol; 9. C_3-Pyridine; 10. C_2-Phenol; 11. Hydroxybenzeneethanol; 12. C_4-Tetralin; 13. Palmitic acid.

resources, here we now demonstrate the significant impact on HT product yields by different stages of development for a single biomass resource.

Research has shown that aromatic compounds can be formed from aliphatic and highly oxygenated molecules (e.g., glucose) and biopolymers (e.g., starch, cellulose), even in the

absence of a catalyst (Catallo et al., 2008; Karagöz et al., 2005a). As to be expected, much higher yields of aromatic compounds would more readily be formed from the HT treatment of aromatic biopolymers, specifically, lignin (Catallo et al., 2008; Quitain et al., 2003; Zhang et al., 2008). The greater proportion of aromatic HT products observed for the June seed sample cannot be attributed to lignin given that the Klason lignin content is similar to that determined for the October sample. While the proteins that undoubtedly contribute to the Klason lignin values could differ in their makeup of aromatic amino acids, it is unlikely that this has a significant impact on the abundance of aromatic hydrocarbon HT products. However, structural differences could have contributed to the apparent greater abundance of substituted pyridines given that the similar nitrogen contents between the two samples suggest similar contents of protein.

As in a prior study on aquatic plants (Catallo et al., 2008), here the difference in HT products also appears to be the result of differences in extractives contents, in particular the contribution of ethanol:toluene-soluble extractives to aromatic HT products. Offsetting the higher content of ethanol:toluene-soluble extractives present early in the growing season (June) were lower contents of hexane-soluble extractives and seemingly also the ethanol-soluble extractives. In comparison, broad distributions of alkyl substituted benzenes (C_1—C_6), phenols (C_1—C_4), and light polycyclic aromatic compounds (e.g., C_1—C_3 substituted naphthalenes and phenanthrenes) dominate the HT products from Chinese tallow seed (Shupe and Catallo, 2006); extractions of Chinese tallow tree seed has also afforded high extractives content (45%) upon extraction with ethanol:toluene (7:3) and ethanol (Eberhardt et al., 2007). However direct comparison here is not possible given that the reaction time used here was significantly shorter (minutes vs. hours).

The apparent greater presence of cell wall polysaccharides later in the growing cycle most likely contributed to the greater presence of alkyl cyclopentenones in the HT product for the October seed sample. Given that HT treatments can afford aliphatic products from aromatic starting materials and aromatic products from aliphatic starting materials, direct assignments of HT products to specific biomass constituents are tentative. Nevertheless, results shown here demonstrate that HT products can be significantly impacted by the developmental stage of a given biomass resource and thus control over the HT product mix requires control over both biomass resource selection, and in some cases, special attention to the time of collection.

4. Conclusions

The HT treatment of Chinese privet seeds was investigated and demonstrated the production of semi-volatile hydrocarbons and oxygen-containing chemicals of industrial importance from a non-conventional biomass resource. The presence of fatty acids in the HT product likely resulted from both lipid hydrolysis reactions and an inherent stability of fatty acids in such aqueous environments involving high temperatures and pressures. Even in the absence of a catalyst, and using short treatment periods, extractive-rich biomass feedstocks such as seeds can afford significant yields of acetic acid. Among the semi-volatile HT products, higher extractives contents, excluding neutral lipids, would appear to yield higher proportions of aromatic HT products. Variation in extractives yields and HT products demonstrates the importance of timing in feedstock collection to favor the production of target HT transformation products.

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