

LETTER TO THE EDITOR

Pyrolysis Products from *Osmanthus Fragrans* Wood

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Osmanthus fragrans is a widely multi-purpose economic plant in China. However, few study was focus on the utilization of *Osmanthus fragrans* wood. In this study, the pyrolysis products of *Osmanthus fragrans var thunbergii* (OFVT) wood were investigated by PY-GC-MS. According the results of PY-GC-MS analysis, there are 185 chemical constituents were identified in 201 peaks of *Osmanthus fragrans* wood. The results shows that the pyrolysis products of *Osmanthus fragrans* wood contained many high-value components, such as acetic acid, methyl glyoxal, azetidine, creosol, vanillin, furfural, trans-isoeugenol, and so on, which can be used as a raw materials for chemicals and fuels. The thermal properties of *Osmanthus fragrans* wood was measurement by thermogravimetric analyzer.

1 Introduction

Osmanthus fragrans is a widely multi-purpose economic plant in China (Hu et al. 2009, Machida et al. 2010, Mu et al. 2014). The flower of *Osmanthus fragrans* can be used as food and medicine. Many research results indicate that the extracts of *Osmanthus fragrans* flowers contained amount of flavonoids and phenolic acids, which can be used as antioxidants to prevent oxidative damage (Cai et al. 2014, Han et al. 2013, Huang et al. 2010, Liu et al. 2015, Wang et al. 2010, Wu et al. 2009, Xiong et al. 2014). And the oxidative damage was related to many disease, such as cancer, inflammation and so on (Moon and Shibamoto 2009). However, few study was focus on the utilization of *Osmanthus fragrans* wood. Fast pyrolysis is an important method for convert biomass into biofuels and fine chemical (Case et al. 2014, Chen et al. 2017, Li et al. 2014, Rouches et al. 2017, Zhang et al. 2017). Through the process of fast pyrolysis, the biomass can form a liquid product, which is called bio-oil. This so-called bio-oil product contains a large variety of high value-added components that can be used as raw materials to extract specific chemicals (Almeida et al. 2017, Jia et al. 2017, Kaewpengkrow et al. 2017, Kim et al. 2016, Lazdovica et al. 2017).

In this study, the fast pyrolysis products of *Osmanthus fragrans var thunbergii* (OFVT) wood were investigated by Py-GC-MS. The thermal properties of OFVT wood was measurement by TG.

2 Material and Methods

2.1. Experimental Methods

To analyze OFVT wood, the sample was ground to a powder (100 mesh) with a plant grinding micro machine.

2.2. TG Analysis.

The samples of OFVT wood was analyzed by thermogravimetric analyzer (TGA Q50 V20.8 Build 34). The nitrogen release rate was 60 ml/min. The temperature program of TG starts at 30°C and rises to 300°C at a rate of 5°C/min (Burhenne et al. 2013, Kok and Özgür 2013, Li et al. 2016, Zhao et al. 2017; Lam et al. 2019).

2.3. Py-GC-MS Analysis.

The powder of OFVT wood was analyzed by thermal cracking-gas chromatography-mass spectrometry (CDS 5000 - Agilent 7890B - 5977 A) (Gao et al. 2017). The carrier gas used for high purity helium, the pyrolysis temperature was 500°C, the heating rate was 20°C/ms, and the pyrolysis time was 15 s. The pyrolysis product transfer line and the injection valve temperature are set to 300°C; Column TR-5MS; Capillary column (30 m × 0.25 mm × 0.25 μm); Shunt mode, split ratio of 1:60, shunt rate of 50 mL/min. The temperature of the GC program starts at 40°C for 2 min, rises to 120°C at a rate of 5°C/min, and then rises to 200°C at a rate of 10°C/min for 15 min. Ion source (EI) temperature of 280°C, scanning range of 28 amu-500 amu (Lu et al. 2018, Wang et al. 2012, Zhang et al. 2017).

3 Results and Discussion

3.1 PY-GC-MS analysis

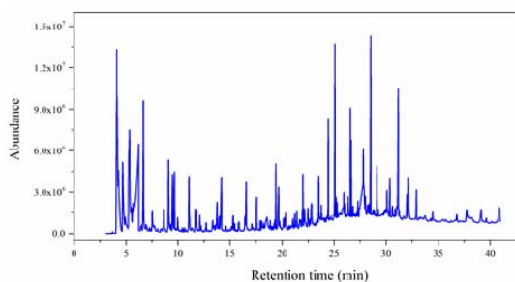


Figure 1. Total ion chromatogram by Py- GC-MS

The pyrolysis process of biomass is very complex, which involved multiple processes, such as decomposition, decarboxylation, dehydration, and so on. Py-GC-MS is a powerful method for the study of biomass fast pyrolysis. In this study, the pyrolysis products of *Osmanthus fragrans* wood were investigated by Py-GC-MS at 950°C. (Gao and Wang 2017) The total ion chromatograms of the *Osmanthus fragrans* wood are shown in Figure 1. The relative content of pyrolysis products was counted base on area normalization.

From Figure 1, it can be seen that there are 185 chemical constituents were identified in 201 peaks of *Osmanthus fragrans* wood. The high content of pyrolysis product of *Osmanthus fragrans* wood were as follow: Acetic acid (8.2193%), cetaldehyde, hydroxy- (5.0036%), 5-Methoxy-4-methyl-2,1,3-benzothiadiazole (3.1320%), Glycidol (3.1154%), 2-Propanone, 1-hydroxy- (2.8306%), Methyl glyoxal (2.7113%), Phenol, 2,6-dimethoxy- (2.6623%), (E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol (3.2389%), 5-tert-Butylpyrogallol (2.3057%), Acetic acid, methyl ester (2.0416%), β-D-Glucopyranose, 1,6-anhydro- (2.3949%), 1,2-Cyclopentanedione (1.6846%), Propanoic acid, 2-oxo-, methyl ester (1.5342%), Succinaldehyde (1.4586%), 2(3H)-Furanone, dihydro-4-hydroxy- (1.3839%), 3,5-Dimethoxy-4-hydroxytoluene (1.3663%), 2-Methoxy-4-vinylphenol (1.3489%), 4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol (1.5376%), 2-Methyliminoperhydro-1,3-oxazine (1.2318%), Furfural (1.1026%), 2,3-Butanedione (1.0903%), 1,2-Benzenediol, 3-methoxy- (0.9987%), trans-Isoeugenol (0.9857%), Azetidine (0.9521%), Phenol, 2-methoxy- (0.9310%), 5-Hydroxymethylfurfural (0.9153%),

2(5H)-Furanone (0.8745%), Acetic acid (0.8582%), 2-Cyclopenten-1-one, 2-hydroxy-3-methyl- (0.7994%), Formic acid (0.9551%), 1,2,6-Hexanetriol (0.9354%), enzeneethanol, 4-hydroxy- (0.7393%), creosol (0.7379%), Benzaldehyde, 4-hydroxy-3,5-dimethoxy- (0.65%), Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- (0.6342%), Imidazole, 4-fluoro- (0.6286%), 2-Pentanone, 1-(2,4,6-trihydroxyphenyl) (0.6280%), 3,5-Dimethoxy-4-hydroxycinnamaldehyde (0.6171%), (E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol (0.5338%), 1,4-Pentadien-3-one (0.5214%), Vanillin (0.5121%), 2-Furancarboxaldehyde, 5-methyl- (0.5025%), 2-Furanmethanol (0.4923%), 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)- (0.7771%), 2-Cyclohexen-1-ol (0.4556%), 5,9-Dodecadien-2-one, 6,10-dimethyl-, (E,E)- (0.4354%), trans-Sinapyl alcohol (0.4203%), 2-Butenoic acid, methyl ester, (E)- (0.3929%), n-Hexadecanoic acid (0.9220%), 2-Piperidinecarboxylic acid (0.3881%), Phenol, 4-ethyl-2-methoxy- (0.3876%), 2-Butenal, (E)- (0.3470%), Maltol (0.3199%), 2,3-Dihydroxybenzaldehyde (0.3091%), 2-Propanone, 1-(acetyloxy)- (0.3091%), Farnesol, acetate (0.3046%), Methyl formate (0.2980%).

According to the functional groups of these substances, the fast pyrolysis products compounds contained acids, alcohols, aldehydes, esters, amines, ketones, aromatics, olefins, saccharides, and others derivatives. Among them, many compounds are effective active substances. (Kang et al., 2018) Alkenes, olefins, alcohols, and aromatics has been considered as valuable products. Acetic acid, methyl glyoxal, azetidene, creosol, vanillin, furfural, trans-isoeugenol, and so on, which can be used as a raw materials for chemicals. Phenolic and their derivatives can be used as raw materials for synthesis resins for replace phenols.

3.2 Thermal properties of OFVT wood

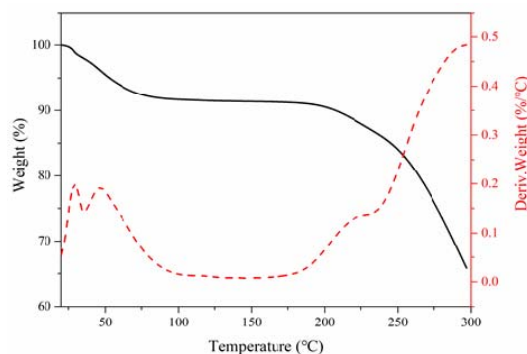


Figure 2. TG and DTG thermal curves of OFVT wood

The TG and DTG curves of the OFVT wood at heating rate of 5 °C/min were exhibited in Figure 2. From the TG and DTG curves of OFVT wood, it can be seen that the weight loss process of sample can be divided into three stages. The first stage from ambient temperature to 100°C is due to the mass loss of the evaporation of water and small molecule volatiles. The weight loss is 9.33%. The second stage occurred in the temperature range of 100-200°C, the weight loss is only 1.13%. The final stage is between 200-300°C, the weight loss is about 24.69%. In this stage, the weight loss main due to the process of decomposition of hemicellulose, extractives and part of lignin and rarely amount of cellulose. Because hemicellulose is the most unstable component in OFVTwood compared with cellulose and lignin. The onset temperature of its decomposition is about 200°C (Zhao et al. 2017).

IV Conclusion

In this study, the pyrolysis products of OFVT wood were investigated by Py-GC-MS. The relative content of pyrolysis products was counted, based on area normalization. The results shows that there are 185 chemical

constituents were identified in 201 peaks of OFVT wood. In addition, according the results of Py-GC-MS analysis, it indicated that the pyrolysis products of OFVT wood contained many high-value components, such as acetic acid, methyl glyoxal, azetidine, creosol, vanillin, furfural, trans-isoeugenol, and so on, which can be used as a raw materials for chemicals and fuels.

References

- Almeida HN, Calixto GQ, Chagas BME, Melo DMA, Resende FM, Melo MAF, Braga RM (2017) Characterization and pyrolysis of *Chlorella vulgaris* and *Arthrospira platensis*: potential of bio-oil and chemical production by Py-GC/MS analysis. *Environmental science and pollution research international* 24: 14142-14150.
- Burhenne L, Messmer J, Aicher T, Laborie MP (2013) The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis. *Journal of Analytical and Applied Pyrolysis* 101: 177-184.
- Cai X, Mai RZ, Zou JJ, Zhang HY, Zeng XL, Zheng RR, Wang CY (2014) Analysis of aroma-active compounds in three sweet *osmanthus* (*Osmanthus fragrans*) cultivars by GC-olfactometry and GC-MS. *Journal of Zhejiang University. Science. B* 15: 638-648.
- Case PA, Bizama C, Segura C, Clayton Wheeler M, Berg A, Desisto WJ (2014) Pyrolysis of pre-treated tannins obtained from radiata pine bark. *Journal of Analytical and Applied Pyrolysis* 107: 250-255.
- Chen X, Yang H, Chen Y, Chen W, Lei T, Zhang W, Chen H (2017) Catalytic fast pyrolysis of biomass to produce furfural using heterogeneous catalysts. *Journal of Analytical and Applied Pyrolysis* 127: 292-298.
- Gao W, Baig AQ, Ali H, Sajjad W, Farahani MR (2017) Margin based ontology sparse vector learning algorithm and applied in biology science. *Saudi Journal of Biological Sciences* 24(1): 132-138.
- Gao W, Wang W (2017) A tight neighborhood union condition on fractional (g, f, n, m) -critical deleted graphs. *Colloquium Mathematicum* 149(2): 291-298.
- Han Y, Wang X, Chen W, Dong M, Yuan W, Liu X, Shang F (2013) Differential expression of carotenoid-related genes determines diversified carotenoid coloration in flower petal of *Osmanthus fragrans*. *Tree Genetics & Genomes* 10: 329-338.
- Hu CD, Liang YZ, Li XR, Guo FQ, Zeng MM, Zhang LX, Li HD (2009) Essential oil composition of *Osmanthus fragrans* varieties by GC-MS and Heuristic Evolving Latent Projections. *Chromatographia* 70: 1163-1169.
- Huang S, Pan Y, Gan D, Ouyang X, Tang S, Ekunwe SIN, Wang H (2010) Antioxidant activities and UV-protective properties of melanin from the berry of *Cinnamomum burmannii* and *Osmanthus fragrans*. *Medicinal Chemistry Research* 20: 475-481.
- Jia L, Buendia-Kandia F, Dumarcay S, Poirot H, Mauviel G, Gérardin P, Dufour A (2017) Fast pyrolysis of heartwood, sapwood, and bark: A complementary application of online photoionization mass spectrometry and conventional pyrolysis gas chromatography/mass spectrometry. *Energy & Fuels* 31: 4078-4089.
- Kaewpengkrow P, Atong D, Sricharoenchaikul V (2017) Selective catalytic fast pyrolysis of *Jatropha curcas* residue with metal oxide impregnated activated carbon for upgrading bio-oil. *International Journal of Hydrogen Energy* 42: 18397-18409.
- Kang, L., Du, H. L., Du, X., Wang, H. T., Ma, W. L., Wang, M. L., & Zhang, F. B. (2018). Study On Dye Wastewater Treatment of Tunable Conductivity Solid-Waste-Based Composite Cementitious Material Catalyst. *Desalination and Water Treatment* 125: 296-301.
- Kim P, Rials TG, Labbé N, Chmely SC (2016) Screening of mixed-metal oxide species for catalytic ex situ vapor-phase deoxygenation of cellulose by Py-GC/MS coupled with multivariate analysis. *Energy & Fuels*

- 30: 3167-3174.
- Kok MV, Özgür E (2013) Thermal analysis and kinetics of biomass samples. *Fuel Processing Technology* 106:739-743.
- Lazdovica K, Kampars V, Liepina L, Vilka M (2017) Comparative study on thermal pyrolysis of buckwheat and wheat straws by using TGA-FTIR and Py-GC/MS methods. *Journal of Analytical and Applied Pyrolysis* 124: 1-15.
- Lam SS, Mahari WAW, Ma NL, Azwar E, Kwon EE, Peng WX, Chong CT, Liu ZL, Park YK (2019) Microwave pyrolysis valorization of used baby diaper. *Chemosphere* 230: 294-302
- Li B, Lv W, Zhang Q, Wang T, Ma L (2014) Pyrolysis and catalytic upgrading of pine wood in a combination of auger reactor and fixed bed. *Fuel* 129: 61-67.
- Li C, Zhang J, Yi Z, Yang H, Zhao B, Zhang W, Li J (2016) Preparation and characterization of a novel environmentally friendly phenol-formaldehyde adhesive modified with tannin and urea. *International Journal of Adhesion and Adhesives* 66: 26-32.
- Liu J, Nakamura S, Xu B, Matsumoto T, Ohta T, Fujimoto K, Ogawa K, Fukaya M, Yoshikawa M, Matsuda H (2015) Chemical structures of constituents from the flowers of *Osmanthus fragrans* var. *aurantiacus*. *Journal of Nature Medicine* 69: 135-141.
- Lu Q, Zhou MX, Li, WT, Wang X, Cui MS, Yang YP (2018) Catalytic fast pyrolysis of biomass with noble metal-like catalysts to produce high-grade bio-oil: Analytical Py-GC/MS study. *Catalysis Today* 302: 169-179.
- Moon JK, Shibamoto T (2009) Antioxidant assays for plant and food components. *Journal of agricultural and food chemistry* 57: 1655-1666.
- Mu HN, Li HG, Wang LG, Yang XL, Sun TZ, Xu C (2014) Transcriptome sequencing and analysis of sweet osmanthus (*Osmanthus fragrans* Lour.). *Genes & Genomics* 36: 777-788.
- Rouches E, Dignac MF, Zhou S, Carrere H (2017) Pyrolysis-GC-MS to assess the fungal pretreatment efficiency for wheat straw anaerobic digestion. *Journal of Analytical and Applied Pyrolysis* 123, 409-418.
- Wang H, Gan D, Zhang X, Pan Y (2010) Antioxidant capacity of the extracts from pulp of *Osmanthus fragrans* and its components. *LWT - Food Science and Technology* 43: 319-325.
- Wang S, Guo X, Liang T, Zhou Y, Luo Z (2012) Mechanism research on cellulose pyrolysis by Py-GC/MS and subsequent density functional theory studies. *Bioresource technology* 104: 722-728.
- Wu LC, Chang LH, Chen SH, Fan NC, Ho JA (2009) Antioxidant activity and melanogenesis inhibitory effect of the acetic extract of *Osmanthus fragrans*: A potential natural and functional food flavor additive. *LWT - Food Science and Technology* 42, 1513-1519.
- Xiong L, Yang J, Jiang Y, Lu B, Hu Y, Zhou F, Mao S, Shen C (2014) Phenolic compounds and antioxidant capacities of 10 common edible flowers from China. *Journal of food science* 79: 517-525.
- Zhang L, Li K, Zhu X (2017) Study on two-step pyrolysis of soybean stalk by TG-FTIR and Py-GC/MS. *Journal of Analytical and Applied Pyrolysis* 127: 91-98.
- Zhao C, Jiang E, Chen A (2017) Volatile production from pyrolysis of cellulose, hemicellulose and lignin. *Journal of the Energy Institute* 90: 902-913.

