Characterization of Selected Pyrolysis Products of Diseased Orange Wood

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Orange trees in Brazil are often burned as a means of eradication when they become infected with Huanglongbing disease. Rather than destroying them, which is a low-value proposition, one potential option is to utilize the biomass through pyrolysis. In this preliminary work, orange trees (*Citrus sinensis*) otherwise selected for purging, were sampled and pyrolyzed at 500 °C, and the charcoal and bio-oil were evaluated for potential value-added use. The results showed that the pyrolysis process resulted in 26.3% charcoal, 57.6% bio-oil, and 16.0% non-condensable gases. Qualitative analysis of the bio-oil by gas chromatography/mass spectrometry found 178 chemical compounds; however, only 25% of those compounds could be reliably identified. Potential applications of the compounds identified in the bio-oil were determined by examining the published literature, and it was found that at least 73% of them showed promise. Finally, initial studies on the immediate analysis of the pyrolysis charcoal showed that it potentially meets the standards set forth for Brazilian domestic use.

Keywords: Pyrolysis; Orange wood; Bio-oil; Charcoal; Chromatography

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INTRODUCTION

Orange fruit accounts for the third highest agricultural income in São Paulo State, Brazil and comprises 80% of crop production (CITRUSBR 2011). In fact, according to Porto *et al.* (2013), the production area for oranges is around 465,000 hectares. Unfortunately, low market demand for this fruit over the last decade (Neves *et al.* 2010) has forced Brazilian producers to abandon their trees, which, in turn, has resulted in many of them succumbing to greening, or Huanglongbing – HLB disease. Greening affects the vascular system of the plants which causes irreversible damage. Neves *et al*. (2010) estimated that millions of citrus trees per year are destroyed because of this phytosanitary problem.

Orange trees affected by greening are most commonly destroyed in the field, without energy recovery, *via* burning. This course of action is problematic for many producers because they have issues obtaining environmental permits (Bortolan 2012; Fundecitrus 2013). Additionally, burning the biomass is not recommended since it 1.) has a negative impact on the environment due to the production of toxic gases and particulate materials (Arbex *et al.* 2004), and 2.) does not add value. Thus, an alternative to combusting the diseased plants is needed.

Previous laboratory work examined the feasibility of using various solvent systems to directly extract value-added chemicals from the orange wood rather than burning it (Kravetz *et al.* 2017). In that study, 221 different compounds were extracted from small samples and 33 of them were identified using gas chromatography followed by mass spectrometry (GC/MS). It was found that 79% of the identified compounds would have commercial value if captured and used.

In this brief communication, the researchers examined the use of pyrolysis for generating value-added products from greened orange wood. Pyrolysis uses high temperatures and constant pressures in an oxygen-free environment to thermally decompose organic material (Lin *et al.* 2015; Hu and Gholizadeh 2019). Broadly, its products consist of solid char or ash, liquid bio-oil, and permanent (non-condensable) gases (Almeida 2010; Santos *et al.* 2010a). Variously, the output products of pyrolysis can be used as input feedstock for power generation, sorbents, the production of other chemicals, *etc.*, depending upon the ultimate goal (Demirbas 2007; Almeida 2010).

The application of pyrolysis to generate biochar-based sorbents from the materials obtained from orange fruit, *e.g.*, peels, has been successful. Thus, it has been demonstrated that this type of thermal conversion technology may be used on this agricultural product to generate value-added products (Chen and Chen 2009; Tran *et al.* 2016; Adeniyi *et al.* 2020).

The preliminary work reported here focuses on the charcoal/biochar (solid) and bio-oil (liquid) pyrolysis products generated from the diseased orange wood, and this was done for two major reasons. First, biomass-derived charcoal has gained an increasing importance in Brazil due to interest in using it as a clean energy source. Brazil, in particular, stands out as the largest producer/consumer of charcoal (8 to 10 million tons per year), mainly for use in the steel industry. Rocha (2011) has stated that the use of biomass-derived charcoal in steel production results in a “green steel” which helps mitigate greenhouse gases.

Secondly, this work examines the bio-oil product because it has been studied extensively for use in the agriculture sector, such as for growth stimulation, pest control, and as a substitute for preservatives in the sanitizing and cosmetic industries (Almeida 2012). It has also been examined for use as a petroleum fuel replacement (Isa and Ganda 2018).

In this initial report, orange wood destined for eradication was pyrolyzed in two different reactors, and then the char and bio-oil components were collected and chemically assessed. For the biomass char, an immediate analysis was performed to determine whether it would be suitable for Brazilian domestic use. The bio-oil, on the other hand, was probed using a gas chromatograph coupled with a mass spectrometer detector in order to qualitatively identify as many components as possible. For bio-oil characterization, GC/MS analysis is accepted as a useful technology, although it is limited in that only the higher volatility components in the bio-oil can be detected (Meng *et al.* 2012). Finally, following the identification of the bio-oil components, they were evaluated for potential use by examining the literature.

EXPERIMENTAL

Materials

Orange trees (*Citrus sinensis*) destined for eradication were collected from plantations belonging to the Citrosuco company located in the region of Bebedouro, São Paulo State, Brazil. Sample discs between 5 and 10 cm in diameter were cut along the orange tree trunk, processed in a hammer mill, and sieved to pass a 40-mesh particle size. The wood possessed a lignin content of 22% according to the analysis performed using the standard TAPPI T-222 om-02 method (TAPPI T222om-02 2006) and an average moisture of 10 %. All samples were stored in closed plastic bags at room temperature (20 °C) at the laboratory.

Immediate Analysis of Charcoal

To obtain the charcoal for the immediate analysis, approximately 5 g samples of biomass were pyrolyzed over nitrogen in a Gray-King apparatus. Figure 1 shows the experimental system. The temperature in the reaction zone was monitored with a thermocouple, and the process was conducted in triplicate from room temperature until the system stabilized at 500 °C for 5 min (25 to 35 min total). All samples were dried to remove moisture prior to pyrolysis.

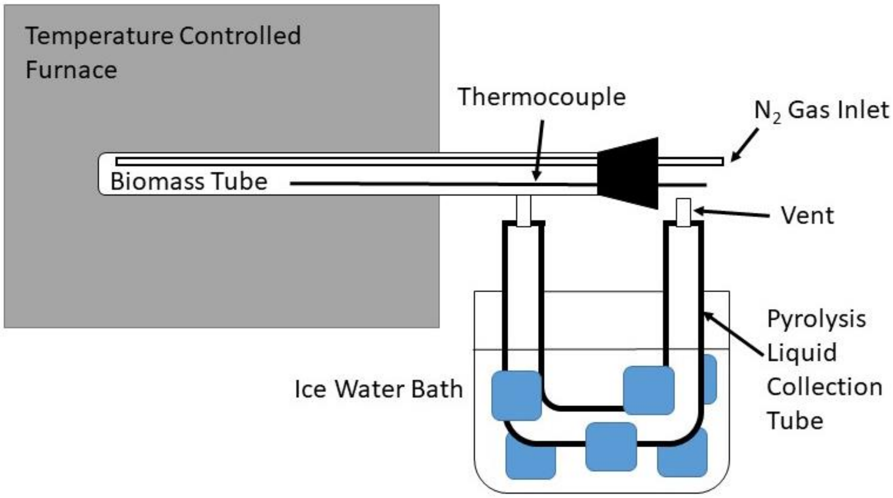

Fig. 1. Modified Gray-King apparatus used to generate charcoal

After the pyrolysis, the charcoal was analyzed according to standard ABNT NBR 8112 (ABNT NBR 8112 1986) to obtain the range of wood charcoal, fixed carbon, volatiles, and ash content.

Pyrolysis and Bio-oil Analysis

Condensable pyrolysis gases (*i.e.*, bio-oil) were collected from a fluidized-bed reactor system using nitrogen as a carrier gas, as described by Meng *et al.* (2012). In this system, which is different than the one used for the generation of the charcoal, the liquor (condensed liquid) was obtained in three places: two in successive condensers cooled with water at 5 °C and a third from an electrostatic precipitator. The two fractions from the condensers were combined so that only two portions remained: one with a higher water content, after the condenser, and one with a lower water content, after the electrostatic precipitator or ESP (Meng *et al.* 2012).

Pyrolysis was initiated at room temperature and conducted at 500 °C for 40 min after the system had stabilized. This temperature is considered a default limit usually applied in the industrial pyrolysis of biomass systems. The biomass feed rate was approximately 150 g/h and resulted in a sample residence time of ca. 1.5 s. Under these conditions, the wood thermal degradation is typically a fast pyrolysis.

Analyses of the bio-oil fractions were performed in duplicate on an Agilent Technologies gas chromatograph coupled with a mass spectrometer detector (GC/MS). The instrument used a HP-5MS Ui column, 30 m in length x 0.25 mm in diameter. Helium was used as the carrier gas. The temperature program of the oven ranged from 40 to 230 °C with a heating rate of 6 °C per minute. Additionally, 0.6 g of each bio-oil fraction was dissolved in 12 mL of acetone to obtain the solution to be analyzed. The extracts were injected into the GC/MS manually, and 0.4 µL volumes were utilized. Chemicals were identified qualitatively by comparing the mass spectra of the chromatographic peaks to those in the National Institute of Standards and Technology (NIST) 2012 database.

RESULTS AND DISCUSSION

Immediate Analysis of Orange Wood Charcoal

The pyrolysis process employed for this part of the study yielded 26.3% biochar, 57.6% condensable gases, and 16.0% non-condensable gases (by weight except for the non-condensable gases done by difference) and coefficients of variation of 0.99%, 1.3%, and 4.3%, respectively. These results are close to those obtained from *Eucalyptus* sp., which is the species commonly used for charcoal in Brazil: 40 to 45% yield for condensable gases, 19 to 22% for non-condensable gases, and 23 to 25% for biochar (Dias Júnior *et al.* 2015). Not surprisingly, the charcoal content obtained from the orange wood under these experimental conditions is comparable to the biochar/charcoal content obtained from other biomass species (Manya 2012; Tomczyk *et al.* 2020).

The charcoal from orange wood was found to have a 25.5% volatiles content, a 71% fixed carbon content, and a 3.5% ash content (with coefficients of variation of 3.0%, 1.0%, and 4.7%, respectively). It is possible to compare these values with those from *Eucalyptus* sp. charcoal. Santos (2010b) reported results from four clones with 11.7% to 14.3% volatiles content, 85.3% to 87.5% fixed carbon content, and 0.39% to 0.76% ash content. Generally, the fixed carbon content obtained from the orange wood is in the range of the fixed carbon contents obtained from other biomass species, especially that from Orange pomace (Tomczyk *et al.* 2020).

There is a Brazilian standard – the Carvão Vegetal Qualidade São Paulo standard – that defines characteristics of good quality charcoal for domestic use. For this designation, the fixed carbon must be higher than 73% and the ash content lower than 5% (SAA 2015). According to these parameters of quality, given the coefficients of variation, it appears that the orange wood charcoal meets the requirements of the standard. However, these are preliminary experiments and further verification work is needed. Regardless, however, the species can be used as a secondary material since the immediate analysis values are close to those required for the standard.

Bio-oil GC/MS Analysis

Table 1 shows the identifiable chemical components (and corresponding peak areas) that were collected by the condenser and ESP portions of the pyrolysis process stream. In total, at least 178 compounds in the two fractions were gas-chromatographable. However, only a portion of them (25%) are shown in Table 1. This is because not all of the compounds in the original chromatograms could be confidently identified using the NIST mass spectral database. Accordingly, only compounds with NIST library hits (probabilities) greater than approximately 75% are included in the table.

Table 1. Chemical Compounds from Orange Wood Pyrolysis ID'd by GC/MS

Chemical Compounds	Average Retention Time (Min)	Average Peak Area, Condenser*	Average Peak Area, ESP*
Acetic acid	2.27	10,275,571	5,215,876
1,2- Ethanediol	2.47	ND	138,320
2-Propanone, 1-hydroxy-	2.57	3,245,935	1,765,490
2-Propenoic acid	3.18	142,140	131,353
Pyridine	3.92	ND	76,719
Succindialdehyde	4.18	1,386,170	756,616
Propanoic acid, 2-oxo-, methyl ester	4.35	1,037,061	1,161,646
Diacetyl sulphide	4.48	ND	67,517
Furfural	5.21	753,576	974,465
2-Cyclopenten-1-one	5.34	361,980	412,530
2-Furanmethanol	5.73	296,194	568,623
5,9-Dodecadien-2-one, 6,10-dimethyl-, (E,E))-	5.81	238,234	281,209
4-Cyclopentene-1,3-dione	6.38	167,088	273,980
2-Cyclopenten-1-one, 2-methyl-	6.99	167,494	242,715
2(5H)-Furanone	7.15	411,381	850,041
2-Furancarboxaldehyde, 5-methyl-	8.33	105,616	232,881
2-Cyclopenten-1-one, 3-methyl-	8.53	125,880	328,199
2(5H)-Furanone, 3-methyl-	8.76	221,139	461,277
2-Hydroxy-gamma-butyrolactone	9.38	ND	204,746
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	10.16	373,810	1,428,292
4-Methyl-5H-furan-2-one	10.44	ND	248,571
Phenol, 2-methoxy-	11.45	244,609	703,316
Maltol	12.28	ND	269,728
2H-Pyran-3(4H)-one, dihydro-6-methyl-	12.35	106,231	428,099
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	12.43	ND	182,815
Catechol	14.22	485,594	2,802,657
1,4:3,6-Dianhydro-α-d-glucopyranose	14.53	172,680	352,018
5-Hydroxymethylfurfural	14.95	165,103	701,226
1H-Inden-1-one, 2,3-dihydro-	16.15	ND	145,728
1,2-Benzenediol, 4-methyl-	16.35	196,980	1,702,292
Phenol, 2,6-dimethoxy-	17.69	162,045	999,482
1,2,3-Benzenetriol	18.33	ND	772,278
β-D-Glucopyranose, 1,6-anhydro-	20.52	144,148	ND
Benzene, ethylpentamethyl-	21.72	ND	289,484
3,4-Dihydroxy-5-methoxybenzaldehyde	22.78	ND	324,464
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	22.89	ND	406,355
Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	24.01	ND	854,072
2-Propenal, 3-(4-hydroxy-3-methoxyphenyl)-	25.34	ND	592,645
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	25.37	ND	188,078
4-((1E)-3-Hydroxy-1-propenyl)-2-methoxyphenol	25.43	ND	704,614
1-Butanone, 1-(2,4,6-trihydroxy-3-methylphenyl)-	26.04	ND	89,747
Pentanamide, 2-(dimethylamino)-4-methyl-N-[2-methyl-1-[[3,3a,11,12,13,14,15,15a-octahydro-12,15-dioxo-13-(phenylmethyl)-	27.36	ND	58,410
Ethanethioic acid, S,S'-[thiobis(methylene)] ester	28.50	ND	113,175
3,5-Dimethoxy-4-hydroxycinnamaldehyde	29.55	ND	156,755

*ESP: Electrostatic precipitator; ND: Not detected because the quantity was below the detection limit of the instrument; Due to the lack of calibration curves for the individual compounds, only the areas in the rows should be directly compared.

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 a reasonable confidence of prediction. Of the total number of compounds shown in Table 1, approximately 55% of them were found in the condenser fraction and 98% of them were found in the electrostatic precipitator fraction. A comparison of the peak areas for the compounds reveals that, as expected, the lower boiling point chemicals – reflected by the lower retention times – are more efficiently collected in the cold-water condensers than the higher boiling point chemicals. Additionally, and not surprisingly, these chemicals are common pyrolysis products of biomass including those from pine, spruce, and corncobs (Evans and Milne 1987; Lyu *et al.* 2015).

It is worth noting that only components with boiling points lower than 230 °C were observed overall. This temperature was the final temperature used in the GC/MS oven program and thus, higher boiling point fractions were not observable. Additionally, it should be pointed out that a few compounds in the chromatograms, compounds such as acetic acid, acetone, and the larger chain carboxylic acids, might arise from the fragmentation of thermally labile compounds in the bio-oil.

Value-Added Use

Potential applications of the compounds identified in the bio-oil (Table 1) are shown in groups in Fig. 2. These groups were created by examining the published literature and other sources (National Institutes of Health 2004; Huber *et al*. 2006; Dalvand *et al.* 2018; Sigma-Aldrich 2018).

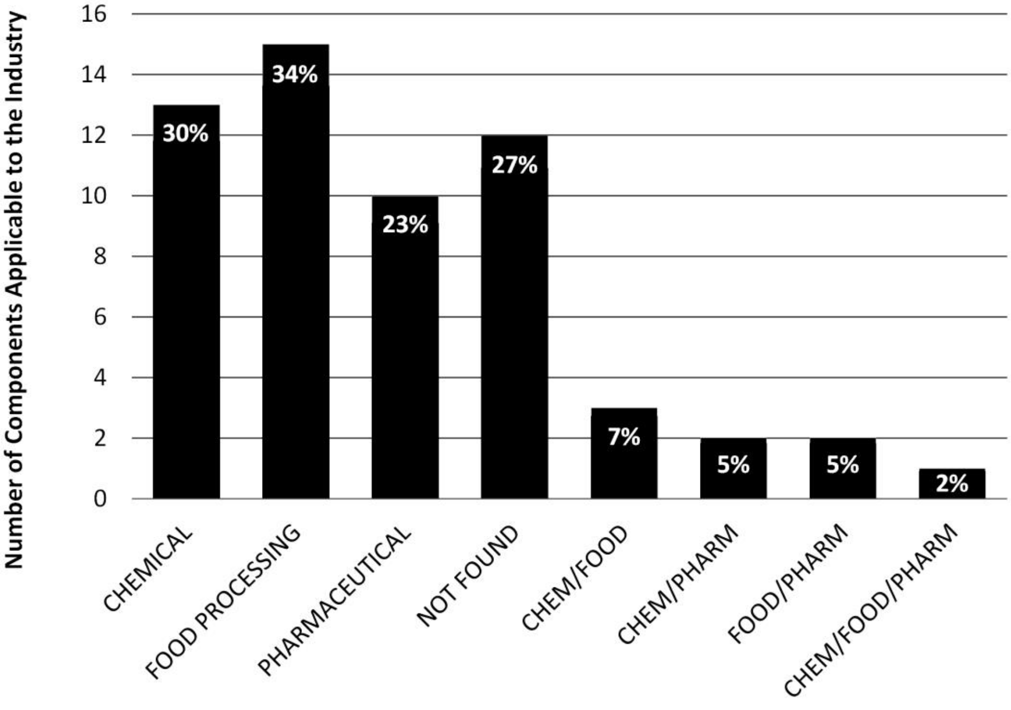

Fig. 2. Bio-oil classification according to literature (percent values are relative to the total number of identified compounds)

The groups in Table 1 may have use in chemistry, *e.g.*, as organic synthesis agents or solvents (Chem and Chemical in Fig. 2); food processing as flavoring, preservatives, or packaging (Food in Fig. 2); and in pharmaceutics as preservatives in cosmetics, aromas for perfumes, and components of medicines (Pharm and Pharmaceutical in Fig. 2). Note that many of these compounds can be used in more than one application.

As shown in Fig. 2, 73% of the identified compounds have direct application, while 27% have no current use. Clearly, as shown in this work, many of the components in the orange wood pyrolysis bio-oil are valuable and, thus, the eradicated trees do not necessarily have to be burnt/destroyed in the orchards. However, technology will be required to separate and utilize these chemicals, and both processes may involve costs. Studies are advancing in this area to overcome these limitations, so the use of these value-added compounds are a tangible possibility. Clearly, there is need for further studies to explore this potential avenue.

CONCLUSIONS

1. The pyrolysis process employed in this preliminary study yielded 26.3% charcoal, 57.6% condensable gases, and 16.0% non-condensable gases with coefficients of variation of 0.99%, 1.3%, and 4.3%, respectively. The charcoal from orange wood was found to have a 25.5% volatiles content, a 71% fixed carbon content and a 3.5% ash content with coefficients of variation of 3.0%, 1.0%, and 4.7%, respectively.
2. Orange wood charcoal produced from pyrolysis potentially meets the quality of the Carvão Vegetal Qualidade São Paulo standard. Further work is necessary to verify this. If it does not, then the charcoal may be used as a secondary material.
3. Condensable pyrolytic gases (bio-oil) have at least 178 gas-chromatographable chemical compounds. However, only 25% of those were readily identified by GC/MS in this study. These compounds were found to be similar to those obtained from the pyrolysis of other cellulosic biomass materials.
4. With regards to the added value of the identified bio-oil compounds, 73% have immediate application in the chemical, food processing, and pharmaceutical areas.

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