ARTICLE

EFFECT OF PYROLYSIS HEATING RATE ON THE CHEMICAL COMPOSITION OF WOOD VINEGAR FROM *Eucalyptus urograndis* AND *Mimosa tenuiflora*

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ABSTRACT – Among the parameters used in the biomass carbonization process, the heating rate is one of the most important. The objective of the present work was to assess the influence of different heating rates on the chemical composition of wood vinegar (WV) from two wood species. Dried disks of Eucalyptus grandis and Mimosa tenuiflora wood were used as raw material. Carbonization runs were carried out in a laboratory muffle furnace at three heating rates (0.7, 1.0 and 1.4 °C/min), with 10 runs at each heating rate, reaching 450 °C. Yields of charcoal, pyrolysis liquids and gases were determined for all carbonization conditions. Crude pyrolysis liquid from each wood species and each heating rate was bi-distilled, yielding purified WV samples. These samples were extracted with ethyl acetate and the organic fraction was analyzed by gas chromatography-mass spectrometry to obtain qualitative and semi-quantitative data. Results showed that lower heating rates produce higher yields of charcoal, while higher heating rates lead to higher yields of pyrolysis liquids and gases. Totals of 57 and 42 chemical compounds were identified in the WV of *Eucalyptus* and *Mimosa*, respectively, divided into the following groups: alcohols, ketones, furans and pyrans, and phenolic compounds. In general, higher heating rates led to greater contents of furans and pyrans and lower concentrations of phenolic compounds.

Keywords: Wood vinegar; Heating rate; Phenolic compounds.

EFEITO DA TAXA DE AQUECIMENTO DE PIRÓLISE NA COMPOSIÇÃO QUÍMICA DO EXTRATO PIROLENHOSO DE *Eucalyptus urograndis E Mimosa tenuiflora*

RESUMO – Dentre os parâmetros do processo de carbonização, a taxa de aquecimento é um dos mais importantes. O objetivo do presente trabalho foi avaliar a influência de diferentes taxas de aquecimento na composição química do extrato pirolenhoso (EP) de duas espécies de madeira. Discos secos de madeira de Eucalyptus grandis e Mimosa tenuiflora foram utilizados como matéria prima. As carbonizações foram conduzidas em mufla de laboratório em três taxas de aquecimento (0,7, 1,0 e 1,4 °C min^{-1}), com 10 repetições para cada taxa de aquecimento, atingindo temperatura final de 450 °C. Rendimentos gravimétricos em carvão, líquidos e gases de foram obtidas para todas as carbonizações. Os respectivos líquidos brutos da pirólise para cada espécie e taxa de aquecimento foram bidestilados, obtendo-se as amostras de EP purificado. As amostras foram extraídas com acetato de etila e a fração orgânica foi analisada por cromatografia gasosa/espectrometria de massas obtendo-se dados qualitativos e semi-quantitativos. Um total de 57 e 42 compostos químicos foram identificados nos EP's de ***Eucalyptus*** *e* ***Mimosa****, respectivamente, divididos nos principais grupos: álcoois, cetonas, furanos, piranos e compostos fenólicos. Para as duas espécies, altas taxas de aquecimento favorecem a formação de furanos e piranos e acarretam baixas concentrações de compostos fenólicos.*

Palavras-Chave: Extrato pirolenhoso; Taxa de aquecimento; Compostos fenólicos

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1.INTRODUCTION

In Brazil, about 7.8 million hectares are occupied by planted forests, of which almost 5.6 million hectares are eucalyptus forests. Of this total, 1.1 million hectares are dedicated exclusively to the production of wood for making charcoal (Indústria Brasileira de Árvores, 2017). Brazil produced 4.5 million metric tons of charcoal in 2016, and the country is unique in the world in having sustainable production by using wood from planted forests. About 85% of this output was consumed in metallurgy, including the production of pig iron, steel, iron alloys, and silicon. Most of the industrial charcoal plants use large or small masonry kilns that do not recover the byproduct gases and condensable fractions. In this production technology, mass and energy yields are very low in relation to the initial mass of dry wood. Yields of 33 and 50% in mass and energy, respectively, are common, since smoke byproducts are not recovered. In industrial wood carbonization, the losses as smoke, based on the initial dry wood mass, amount to 50-55% of original carbon, 75-52% of hydrogen and 87-90% of oxygen. Carbonization gases from industrial plants are released to the surrounding environment without any treatment, constituting a major source of air pollution. As a result, every year in Brazil millions of tons of usable chemicals are virtually lost to the atmosphere as smoke without recycling.

Since about 70% of carbonization byproducts are released as volatiles, it is desirable to use technologies able to recycle or convert these substances into usable products or heat by burning them, thus reducing the air pollution generated by the charcoal making. Besides the environmental advantages, recovery of byproducts can increase the profitability of charcoal making. These byproducts are gases, tar, and wood vinegar acid (WV). Usually liquid byproducts are recovered from charcoal kilns by trapping the carbonization gases in a condensing unit or even simple metal pipes. After a certain time (which can vary from hours or days to weeks), wood tar, which is a heavy black oily fraction, decants at the bottom of the container and separates from the WV.

Among the wood species suitable for industrial charcoal making, Eucalyptus urograndis clones and Mimosa tenuiflora have special importance. Hereafter, these wood species will be referred to simply as Eucalyptus and Mimosa. Eucalyptus clones stand out in Brazil due to their rusticity, high productivity and the characteristic of having straight trunks and good wood density, which are important qualities for charcoal making. In turn, Mimosa is a species found in the Brazilian Northeast. Its wood is considered excellent for the production of charcoal because of its high density (Gariglio et al., 2010; Formiga et al., 2011). Since the carbonization process has a low mass yield, one of the main ways to increase profitability is to recover liquids. After pyrolysis gas is trapped, a liquid portion called pyroligneous acid is recovered and can be separated into two portions, an aqueous fraction, called wood vinegar (WV), and an oily fraction, called wood tar. WV is commonly a yellowish or reddish liquid. Its chemical composition is very complex, with more than 200 components already identified (Wu et al., 2015), among which are organic acids, alcohols, ketones, aldehydes, and several other lignin derivatives (Schnitzer et al., 2015). Due to its complex chemical composition and depending on its water concentration, WV has a wide range of applications, e.g., as pest repellents, plant growth promoters, plant fertilizers and additives for animal feed (Tiilikkala et al., 2010). Other uses of WV are as antifungal and antibacterial agents (Souza et al., 2012; Araújo et al., 2017; Souza et al., 2018; Yang et al., 2018) and as herbicides (Zefferino et al., 2016).

Several authors have investigated the effect of the final temperature and heating rate on the yields of charcoal and liquids from carbonization (Oliveira et al. 2006; Paes et al., 2012; Pereira et al. 2013), but reports giving specific information about variation in the chemical composition of liquids from pyrolysis related to process parameters are scarce. Commonly, higher pyrolysis temperature is related to greater concentration of phenolic compounds in the chemical composition of WV (Wu et al., 2015). Those researchers found the highest yields of WV in the range of 350 – 450 °C. Differences in the chemical composition of wood vinegar from Eucalyptus wood were reported by Almeida et al. (2018), but only a qualitative analysis was presented in the study and no precise information about differences in the concentration of components was provided. In order to better design the carbonization process to obtain specific qualities of WV for different uses (e.g., feed additives, fertilizers alternative antibiotics), it is important to know how the heating rate influences the chemical composition of the product, not only from a qualitative standpoint but also to understand how concentrations of compounds are affected by heating rate. The present work had the objective of assessing the influence of different heating rates on the chemical composition of wood vinegar (WV) obtained from wood of two species carbonized at three different heating rates.

2. MATERIAL AND METHODS

2.1. Carbonization and WV production

The Mimosa tenuiflora wood was obtained from natural forests of the Agricultural Sciences Unit of Rio Grande do Norte Federal University, Macaíba, state of Rio Grande do Norte, at 05º 51' 30" S and 35º 21' 14". The Eucalyptus wood (clone of a hybrid of Eucalyptus urogphylla x Eucalyptus grandis, in Brazil named Eucalyptus urograndis) was collected from planted forests located in the same place. Procedures for log collection and wood sampling were carried out following the method described by Santos et al. (2013). Wood samples consisted of 3 cm thick disks, each divided into four wedges. These wedges were oven dried for 48 hours at 103±1 °C until reaching dry condition. Both wood species were characterized by proximate analysis as described by the American Society for Testing and Materials, respectively, ASTM standards E871-82, E872-85 and E1755-01 (ASTM 2006, 2007), to determine moisture, volatile matter, fixed carbon and ash contents. Likewise, the chemical composition was determined, respectively, of cellulose, hemicellulose and lignin, according to the standard procedures described by the National Renewable Energy Laboratory (NREL, 2008). Biomass densities were determined by following the procedures described in ASTM Standard D2395-17 (ASTM, 2006).

After placement in a metal container, batches of about 500 g of wood wedges were carbonized in a muffle furnace. The furnace was equipped with a device designed to trap products from pyrolysis gases, and during all carbonization runs, the condenser was water cooled to maintain temperature of 25 °C. Wood samples were carbonized at heating rates of 0.7, 1.0 and 1.4 ºC, values equivalent to total processing times of about 8, 6 and 4 hours, respectively. All the charring runs started at 100 °C and finished at 450 °C, followed by cooling to 30 °C. The carbonized samples were separated into six experimental treatments, each one related to wood type combined with heating rate used.

For each combination of wood species and heating rate, liquids collected were put in in a labeled container, forming six composite samples. After collection, these samples were immediately stored under refrigeration at 2 °C for further analysis. From the experimental data, gravimetric yields of charcoal, total liquids and gases were determined. These parameters were calculated based on the initial mass of dry wood, according to equations 1, 2 and 3, respectively. Yields of gases were obtained by weight difference

$$CY\ (\%) = (C_m/DW_m) \times 100 \qquad (1)$$

$$LY\ (\%) = (L_m/DW_m) \times 100 \qquad (2)$$

$$GY\ (\%) = 100 - (CY + LY) \qquad (3)$$

Where:

C_m = charcoal mass (g)

DW_m = dry wood mass (g)

L_m = pyrolysis liquids mass (g)

CY = gravimetric yield of charcoal (%)

LY = gravimetric yield of pyrolysis liquids

GY = gravimetric yield of gases

Then, composite samples of condensed liquids from Mimosa and Eucalyptus were bi-distilled under a 20.0 mmHg vacuum at 100 °C to obtain the respective purified WV. The distillation was interrupted as soon as the aqueous fraction was entirely distilled, which coincided with temperature of about 103 – 105 °C. Wood tar and heavy oil wastes from each distillation were properly discarded. The goal of the bi-distillation step was to obtain wood vinegar free of pitch and tar residues and ready for GC/MS analysis.

2.2. GC/MS Analysis

The samples were prepared for GC/MS analysis according to the following procedures. In the first step, 1.5 mL of a concentrated solution of ammonium hydroxide (Merck, Brazil) was added to 5 mL aliquots of the aqueous samples of WV until pH reached 5. Then extractions were carried out by adding 3 mL of HPLC grade ethyl acetate (Merck, Brazil). Three extracts were produced for each type of wood, corresponding to a different heating rate, for a total of six extracts. After liquid-liquid extraction, 1 mL of the organic fraction was transferred to a GC vial and was analyzed by GC/MS using a Varian 3900 gas chromatograph coupled to a Varian Saturn 2100T mass spectrometer. The separation was performed in a VF–5ms column (Agilent, USA, 30 m length x 0.25 mm diameter x 0.25 µm film thickness). The injector was kept at 250 °C. Samples with about 1 µL volume were injected in a split ratio of 1:10. The oven temperature program was 50 °C for 2 min, followed by 2 °C min−1 from 50 to 240 °C, maintained for 2 min. Helium was used as carrier gas at a constant flow rate of 1 mL min-1. Major (>20% area) and minor compounds (~0.02%) were detected and identified based on their typical mass spectra by comparison with the NIST library. All the chemical compounds listed in the present work had mass spectrum similarity with NIST data above 80%. Experimental data from charring runs and vacuum distillations were submitted to normality and Shapiro-Wilk tests, and the means were compared by the Tukey test at 5% significance, by using the Statistica software (Statsoft, USA, 2015 – available at http://www.statsoft.com/Products/STATISTICA-Features)

3. RESULTS

Table 1 reports the results obtained to characterize both wood species, as follows: proximate composition (moisture, volatile matter, fixed carbon and ash contents), and chemical composition (cellulose, hemicellulose and lignin contents). Mimosa showed higher contents of fixed carbon and lignin as well as higher wood density. In contrast, Eucalyptus showed higher contents of volatile matter, ashes, cellulose and hemicellulose.

Figure 1 shows the mean gravimetric yields of charcoal, pyrolysis liquids and gases obtained from the carbonization runs of Eucalyptus and Mimosa wood.

Tables 2 and 3 list the chemical compounds identified in the WV of each wood species.

Concerning to the percentage variation of the chemical compounds of both types of WV according to the heating rate, Figure 2 shows that higher heating rates were associated with greater concentrations of furans and pyrans, while the concentration of phenolic compounds tended to be lower. Indeed, for both wood species, the concentrations of the other classes of components did not present such a clear trend in response to variations in the heating rate, especially for ketones, which had different concentrations for each species.

4. DISCUSSION

As can be observed, higher heating rates were associated with lower yield of charcoal and higher yields of pyrolysis liquids and gases, which is a pattern widely cited in the literature (Oliveira et al., 2006; Pereira et al., 2013; Müller-Hagedorn et al. 2003). The experimental results showed higher lignin content and greater density for Mimosa wood in comparison to Eucalyptus wood, which explains the higher average yield of charcoal from Mimosa, as shown in Figure 1. On the other hand, Eucalyptus wood yielded higher amounts of liquids and gases. In general, high density of woody raw material is a physical property that usually increases gravimetric yields of charcoal (Brito, 1993; Oliveira et al., 2006; Pereira et al., 2013). Also, greater lignin content results in higher charcoal yields, since lignin is more resistant to thermal decomposition and remains as a solid residue during and after pyrolysis, as pointed out by Müller-Hagedorn et al. (2003).

For Eucalyptus, charcoal yields were in the range of 29 to 36%, depending on the heating rate, values similar to those obtained by Vieira et al. (2013), who charred Eucalyptus microcorys wood with a heating rate of 0.5 °C min-1 and final pyrolysis temperatures in the range of 500 to 900 °C. They reported gravimetric yields of charcoal in the range of 29 to 34%. In general, considering the heating rate, the yields of liquids and gases are inversely related to the charcoal yield, as described by Protásio et al. (2013). Therefore, the higher the heating rate, the lower will be the charcoal

Table 1 – Chemical and physical characterization of *Eucalyptus urograndis* and *Mimosa tenuiflora* wood.
***Tabela 1** – Propriedades físicas e químicas das madeiras de **Eucalyptus urograndis** e **Mimosa tenuiflora**.*

		PROXIMATE ANALYSIS (%)			CHEMICAL COMPOSITION (%)		WOOD DENSITY ($g\ cm^{-3}$)
WOOD SPECIES	VM	FC	ASHES	LIGNIN	CEL	HEM	
Eucalyptus urograndis	81.72	8.25	2.39	14.58	48.54	28.36	0.51
Mimosa tenuiflora	73.61	18.18	1.96	32.92	32.02	15.52	0.98

VM = volatile matter; FC = fixed carbon; CEL = cellulose, HEM = hemicellulose.

*Means followed by the same letter in parentheses, within each group of three columns, are statistically equal by the Tukey test at 5% significance.

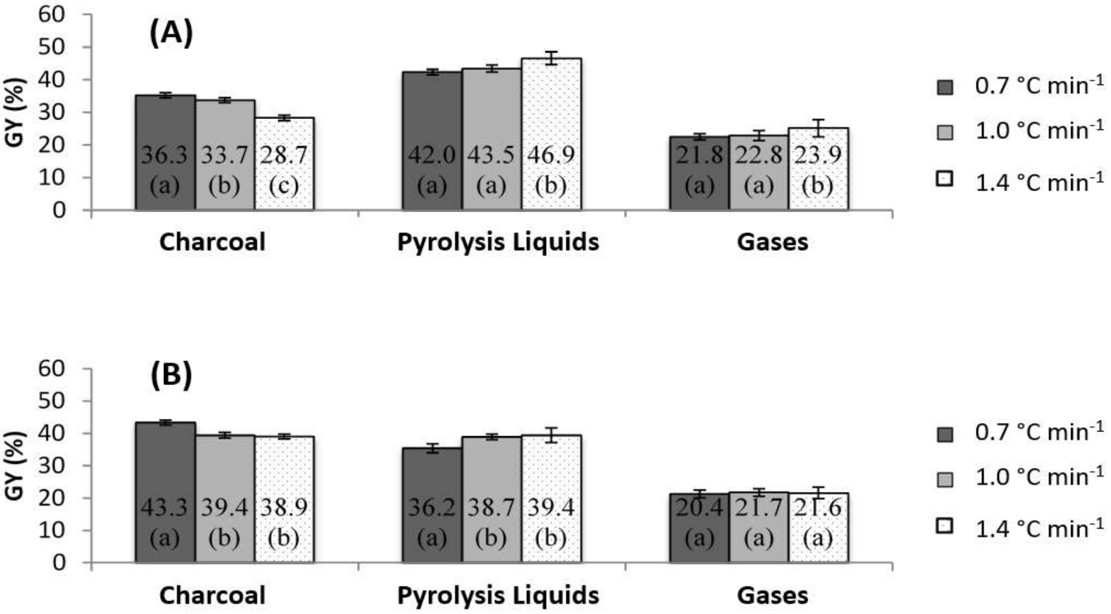

Figure 1 – Mean gravimetric yields of charcoal, pyrolysis liquids and gases obtained from the carbonization of *Eucalyptus urograndis* and *Mimosa tenuiflora* wood.

Figura 1 – *Médias dos rendimentos gravimétricos em carvão vegetal, líquidos e gases obtidos da carbonização de (A)* ***Eucalyptus urograndis*** *e (B)* ***Mimosa tenuiflora.***

yield. The yields of liquids obtained in the present work were close for the two species but higher than those reported by those authors, while the gas yields were lower. The possibility of manipulating the heating rate in carbonization is very important because by doing this, it is possible to design the process for optimal industrial conditions. Lower heating rates imply lower atmospheric emissions of smoke and higher amounts of charcoal, which adds value to the carbonization.

The gravimetric carbonization yields of Mimosa wood were similar to those for Eucalyptus, meaning that higher charcoal yields were observed with lower heating rates. However, for Mimosa carbonization, the gravimetric yields of charcoal were clearly higher, with values in the range of 39 to 43%. These values are similar to those reported by Oliveira et al. (2006), who studied the same two species with a heating rate of 0.9 °C min-1 and final temperature of 450 °C, obtaining charcoal yields in the range of 37.82 to 41.06%. Our results are also close to those reported by Carneiro et al. (2013), who found average charcoal yield of 40.7% using the same two wood species, heating rate of 1.0 °C min-1 and final pyrolysis temperature of 450 °C. In turn, yields of pyrolysis liquids and gases found here were higher and lower, respectively, than the results reported by Paes et al. (2012). Those authors employed the same raw materials, heating rate of 1.36 °C min-1 and final pyrolysis temperature of 450 °C, respectively obtaining yields of 32.77% for pyrolysis liquids and 27.81% for gases. Despite working with the same wood species and similar pyrolysis conditions, none of the authors cited here reported experimental data on the chemical composition of the resulting wood vinegar, only its yield.

A total 57 compounds were identified for Eucalyptus and 42 for Mimosa, as shown in Tables 2 and 3. The number of compounds identified for Eucalyptus here is lower than the total reported by Pimenta et al. (2018), who worked with the same species in similar pyrolysis conditions and reported 65 chemical compounds in Eucalyptus WV. Similarly, the number of compounds identified in the Mimosa WV is lower than the number reported by Araújo et al. (2017), who identified 97 chemical compounds working with the same experimental conditions for chromatographic

Table 2 – Groups of chemical compounds identified in wood vinegar of *Eucalyptus urograndis* wood obtained at three heating rates.
Tabela 2 *– Grupos de compostos químicos identificados no extrato pirolenhoso de* ***Eucalyptus urograndis*** *em função da taxa de aquecimento.*

			HEATING RATE (ºC min^{-1})					
			0.7		1.0		1.4	
ELUTION ORDER	COMPOUND	MOLECULAR FORMULA	RT (min)	Area (%)	RT (min)	Area (%)	RT (min)	Area (%)
	ALCOHOLS							
5	5-Hexen-3-ol-2.3-dimethyl	$C_8H_{16}O$	4.383	0.49	*	*	*	*
19	1,6-Heptadien-4-ol	$C_7H_{12}O$	*	*	*	*	9.641	0.29
	KETONES							
1	2-Butanone	C_4H_8O	2.874	0.78	2.875	0.77	2.873	0.47
4	3-Penten-2-one	C_5H_8O	4.117	0.11	4.104	0.41	4.119	0.09
7	2-Butanone, 3-hydroxy	$C_4H_8O_2$	4.902	0.11	*	*	4.897	0.23
9	2-methylcyclobutanone	C_5H_8O	*	*	6.659	0.32	6.549	0.63
13	2-Methyl-2-cyclopentenone	C_6H_8O	7.308	2.05	7.288	4.13	7.3	2.39
18	3-Methylcyclopentanone	$C_6H_{10}O$	9.317	0.46	*	*	9.314	0.29
34	2-Cyclopenten-2-one, 3,4-dimethyl	$C_7H_{10}O$	16.185	0.23	*	*	15.06	0.89
35	4,4-Dimethyl-2-cyclopenten-1-one	$C_7H_{10}O$	15.086	0.49	*	*	*	*
36	2-Cyclopenten-1-one, 2,3-dimethyl	$C_7H_{10}O$	15.29	0.83	*	*	*	*
44	2-Cyclohexen-1-one, 4,5-dimethyl	$C_8H_{12}O$	19.503	0.44	19.468	0.24	*	*
56	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	$C_7H_{10}O_2$	26.712	2.18	*	*	26.667	1.31
	FURANS E PYRANS							
11	Furan, 2-butyltetrahydro	$C_8H_{16}O$	*	*	*	*	6.113	0.18
12	2-Furanol, Tetrahydro-2-methyl	$C_5H_{10}O_2$	6.114	0.45	*	*	*	*
15	2-(methoxymethyl)-furan	$C_6H_8O_2$	*	*	8.659	0.14	*	*
16	Furfural	$C_5H_4O_2$	8.972	8.36	8.959	12.00	8.94	4.43
20	Furan, Tetrahydro-3,5dimethoxy	$C_6H_{12}O_3$	*	*	10.595	0.46	*	*
21	Furan, tetrahydro-2,4-dimethoxy	$C_6H_{12}O_3$	*	*	*	*	10.608	0.19
22	Furan, Tetrahydro-2,5dimethoxy	$C_6H_{12}O_3$	10.605	0.34	11.192	0.26	11.231	0.93
23	Ethanone, 2-(2-furanyl)	$C_6H_6O_2$	*	*	*	*	11.451	0.51
25	2-acetylfuran	$C_6H_6O_2$	11.895	3.77	11.837	2.81	11.843	4.89
28	2-furancarboxaldehyde, hydrazide	$C_5H_6N_2O_2$	13.152	0.53	*	*	*	*
29	2-Furancarboxaldehyde, 5-methyl	$C_6H_6O_2$	13.987	4.97	13.96	4.38	13.653	0.67
30	3-Furancarboxaldehyde, 5-methyl	$C_6H_6O_2$	*	*	*	*	13.951	6.47
31	3-Furancarboxylic acid, ethyl ester	$C_6H_6O_3$	*	*	*	*	14.184	0.32
32	2-ethyl-5-methyl-furan	$C_7H_{10}O$	14.441	2.12	14.402	1.89	14.404	2.06
37	2-Furanone, 2,5-dihydro-3.5-dimethyl	$C_6H_8O_2$	*	*	*	*	15.437	0.68
40	Ethanone, 2,2-dihydroxy-1-phenyl	$C_8H_8O_3$	*	*	*	*	18.028	0.25
	PHENOLIC COMPOUNDS							
24	Phenol	C_6H_6O	11.659	5.70	11.616	3.43	11.624	6.09
39	Phenol. 3-methyl	C_7H_8O	*	*	*	*	17.388	0.20
41	Phenol, 4-methyl	C_7H_8O	18.762	0.26	*	*	*	*
42	Phenol, 2-methyl	C_7H_8O	17.898	0.62	17.97	1.43	18.653	0.78
43	2-Methoxyphenol (guaiacol)	$C_7H_8O_2$	19.158	15.82	19.121	22.74	19093	5.23
45	Phenol. 2,3-dimethyl	$C_8H_{10}O$	19.66	0.41	*	*	19622	0.53
46	1,3-Dimethylphenol	$C_8H_{10}O$	*	*	20.491	1.38	*	*
47	2,4-Dimethylphenol	$C_8H_{10}O$	*	*	21.516	1.59	21.351	0.97
48	Phenol, 2-methoxy-4-methyl	$C_8H_{10}O_2$	*	*	22.365	1.46	22.352	1.78
49	Phenol, 4-methoxy-3-methyl	$C_8H_{10}O_2$	22.976	4.43	27.171	1.11	22.663	0.22
50	2,6-dimethoxy-phenol (syringol)	$C_9H_{12}O_3$	23.276	13.93	23.358	20.40	23.214	1.63
51	Phenol, 2,3,6-trimethyl	$C_9H_{12}O$	*	*	24.195	2.76	23.338	0.12

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Table 2...
Tabela 2...

52	Phenol, 3-methoxy-4-methyl	$C_8H_{10}O_2$	22.379	1.37	24.353	2.82	*	*
54	Phenol, 4-ethyl-2-methoxy	$C_9H_{12}O_2$	26.034	6.92	26.037	2.36	26.006	5.02
55	Phenol, 3-ethyl-2-methoxy	$C_9H_{12}O_2$	26.27	11.16	*	*	26.227	8.49
57	Phenol, 4-ethyl-3-methoxy	$C_9H_{12}O_2$	26.902	2.19	26.682	2.29	*	*
	OTHER COMPOUNDS							
2	Methyl-propionate	$C_4H_8O_2$	3.361	1.50	3.364	1.98	3.373	1.06
3	CyclobutylamineC4H9N	*	*	*	*	3.902	0.29	
6	Propanoic acid, 2-methyl-methyl ester	$C_5H_{10}O_2$	*	*	4.386	0.25	4.384	0.33
8	Butanoic acid, methyl ester	$C_5H_{10}O_2$	5.265	0.58	5.254	0.36	5.273	0.60
10	Tetrachloroethylene	C_2C_{14}	7.949	0.32	7.95	0.22	7.954	0.32
14	4-Hydroxy-pyridine	C_5H_5NO	8.468	0.08	*	*	8.236	2.05
17	2-methyl-1-pyrrole	C_5H_7N	9.129	0.37	9.101	0.70	9.111	0.71
26	1.3-Pentadiene, 3-methyl	C_6H_{10}	12.869	1.00	12.861	0.59	*	*
27	1-isopropyl-1-cyclopentene	C_8H_{14}	16.955	1.41	16.916	3.12	12.592	0.18
33	Pentanoic acid, 4-oxo, methyl ester	$C_6H_{10}O_3$	*	*	14.858	0.31	*	*
38	1-Methylcycloheptene	C_8H_{14}	*	*	15.266	0.89	16.936	2.44
53	Benzene, 1,2-dimethoxy	$C_9H_{12}O_2$	24.411	3.23	*	*	24.371	2.77

RT = retention time.

(*) compounds with concentration under detection limit.

analysis. Such differences are very likely due to the different type of chromatographic columns employed in the present work, which did not enable identification of compounds with retention times longer than 28 minutes.

Compounds identified in the WV were divided into the following groups, according to Figure 2: alcohols, ketones, furans and pyrans, phenolic compounds, and other compounds. Among these groups, the phenolic group is the most important because of its higher proportion and principally its noteworthy biological effects (Araújo et al. 2017; Schnitzer et al. 2015; Yang et al., 2018). The main products in the chemical composition of WV of both wood species, not considering the heating rate, were in descending order 2-methoxy-phenol (guaiacol), 2,6-dimethoxy-phenol, furfural, 3-ethyl-2-methoxy-phenol and phenol. Together, they represented on average 59.75 and 69.93% of the whole chemical composition of WV from Eucalyptus and Mimosa, respectively. The high contents of guaiacol, furfural, phenol and cresols present in the WV composition are responsible for its biological and antibacterial/antifungal activities (Myasaka et al., 1999; Kook and Kim, 2002; Kook et al., 2003). Besides that, phenolic compounds present in WV have preservative properties when used in the food industry (Cadwallader, 2007; Montazeri et al., 2013; Budaraga et al., 2016). Furfural, for example, is found in all kind of spices as a flavor ingredient and also can act as a fungicide (Abdel-Kahr et al., 2015; EPA 2018). However, as pointed out by Yang et al. (2018), antibacterial and antifungal activity of WV from different sources cannot be attributed to a single compound, but instead to a combination of several, mainly phenolic ones.

Some authors, such as Almeida et al. (2018), have reported acetic acid as one of the main compounds present in the chemical composition of WV, which did not occur in the present work. That absence of acetic acid can be explained by the addition of ammonium hydroxide before organic extraction, which neutralized WV and its acid acetic content, as reported by Araújo et al. (2017). According those authors, the addition of ammonium hydroxide also increases the ionic strength of the solution and makes organic compounds less soluble in the aqueous phase, therefore enhancing the efficiency of liquid-liquid extraction with ethyl acetate and allowing detection of compounds even at low levels. The high levels of phenolic compounds reported here are consistent with the values reported in the literature. Souza et al. (2012) determined a concentration of 60% phenolic compounds in the chemical composition of WV used in agricultural implements. In turn, Yang et al. (2018) found a concentration of 83.96% phenolic compounds, associating that high concentration with efficient cleavage of the lignin ether and carbon-carbon bonds in the woody biomass. The higher concentration of lignin in the chemical composition of Mimosa wood can possibly explain the higher concentration of phenolic compounds in its WV.

Table 3 – Groups of chemical compounds identified in wood vinegar of *Mimosa tenuiflora* wood obtained at three heating rates.

Tabela 3** – Grupos de compostos químicos identificados no extrato pirolenhoso* ***Mimosa tenuiflora *em função da taxa de aquecimento.*

			HEATING RATE ($^{\circ}C\ min^{-1}$)					
			0.7		1.0		1.4	
ELUTION ORDER	COMPOUND	MOLECULAR FORMULA	RT (min)	Area (%)	RT (min)	Area (%)	RT (min)	Area (%)
	ALCOHOL							
13	1,6-Heptadien-4-ol	$C_7H_{12}O$	*	*	9.589	0.21	11.949	0.28
	KETONES							
5	Cyclopentanone	C_5H_8O	7.259	0.95	7.255	1.19	7.282	1.03
10	Cyclohexanone	$C_6H_{10}O$	*	*	*	*	11.099	0.27
15	2-Heptene-4-one	$C_7H_{10}O$	*	*	12.845	0.60	13.137	0.26
20	2-Cyclopenten-1-one, 2,3-dimethyl	$C_7H_{10}O$	16.852	1.26	15.291	0.35	15.299	0.89
	FURANS AND PYRANS							
11	Furfural	$C_5H_4O_2$	11.546	8.13	11.574	8.34	11.604	11.33
12	Ethanone, 1-(2-furanyl)	$C_6H_6O_2$	11.75	3.42	11.78	2.60	11.792	2.72
16	2-Furancarboxaldehyde, 5-methyl	$C_6H_6O_2$	13.84	2.46	13.865	3.03	13.887	2.36
17	3-Furancarboxylic acid, methyl ester	$C_6H_6O_3$	14.343	0.84	14.351	0.75	14.371	0.91
28	1-Propanone, 1-(5-methyl-2-furanyl)	$C_8H_{10}O_2$	*	*	20.58	0.39	20.488	0.13
	PHENOLIC COMPOUNDS							
18	Phenol	C_6H_6O	14.482	3.17	14.586	4.18	14.655	2.98
21	Phenol, 2-methyl	C_7H_8O	17.418	2.38	17.505	2.15	17.552	2.12
22	Phenol, 3-methyl	C_7H_8O	*	*	18.368	4.64	*	*
23	Phenol, 4-methyl	C_7H_8O	18.234	4.72	*	*	18.416	3.75
24	2-Methoxyphenol (guaiacol)	$C_7H_8O_2$	18.925	39.92	19.059	38.32	19.108	32.07
26	Phenol, 2,3-dimethyl	$C_8H_{10}O$	*	*	19.56	2.07	*	*
27	Phenol, 2,6-dimethyl	$C_8H_{10}O$	*	*	*	*	19.593	0.55
29	Phenol, 2,5-dimethyl	$C_8H_{10}O$	21.029	1.83	*	*	*	*
30	Phenol, 3.4-dimethyl	$C_8H_{10}O$	*	*	21.894	0.26	21.132	2.43
31	Phenol, 2-methoxy-4-methyl	$C_8H_{10}O_2$	*	*	22.315	1.24	*	*
32	Phenol. 3-methoxy-4-methyl	$C_8H_{10}O_2$	*	*	*	*	22.327	1.67
33	Phenol, 4-methoxy-3-methyl	$C_8H_{10}O_2$	*	*	22.597	1.14	*	*
34	2-Methoxy-5-methylphenol	$C_8H_{10}O_2$	22.285	2.21	*	*	22.61	1.19
35	2,6-dimethoxy-phenol (syringol)	$C_8H_{10}O_3$	22.819	15.56	22.911	14.74	22.942	18.46
38	Phenol, 4-ethyl-2-methoxy	$C_9H_{12}O_2$	25.915	4.18	25.961	2.90	25.982	5.52
39	Phenol, 3,4-dimethoxy	$C_8H_{10}O_3$	*	*	28.391	0.81	*	*
41	Phenol, 2,6-dimethoxy	$C_8H_{10}O_3$	*	*	*	*	28.402	0.39
42	Phenol, 2-methoxy-4-propyl	$C_{10}H_{14}O_2$	*	*	28.954	0.43	28.982	0.52
	OTHER COMPOUNDS							
1	Methyl propionate	$C_4H_8O_2$	3.346	0.96	3.347	0.67	3.36	0.40
2	Propanoic acid, 2-methyl, methyl ester	$C_5H_{10}O_2$	*	*	4.366	0.21	4.394	0.14
3	Butanoic acid, methyl ester	$C_5H_{10}O_2$	11.899	0.75	5.253	0.26	5.272	0.22
4	Pyridine	C_5H_5N	5.812	0.59	5.799	0.56	5.822	0.32
6	4-Hydroxy-pyridine	C_5H_5NO	8.768	3.31	8.808	3.02	8.823	2.92
7	3-Methyl-3-hexene	C_7H_{14}	*	*	*	*	9.293	0.10
8	Propanoyl chloride, 2-methyl	$C_4H_7C_1O$	*	*	*	*	9.608	0.15
9	3-Hexyne, 2-methyl	C_7H_{12}	*	*	*	*	10.127	0.12
14	1-Methylcycloheptene	C_8H_{14}	*	*	*	*	12.855	0.22
20	1H-Pyrrole-2-carboxaldehyde, 5-methyl	C_6H_7NO	*	*	15.574	0.23	*	*
25	Cis-1.4-dimethyl-2-methylenecyclohexane	C_9H_{16}	*	*	19.451	0.19	19.485	0.36
37	1H-Pyrrole, 3-methyl-	C_5H_7N	24.107	0.60	24.151	0.77	24.167	0.41
36	Benzene, 1,2-dimethoxy-	$C_8H_{10}O_2$	23.023	2.76	23.084	3.18	23.114	3.21
40	3,4-Dimethoxytoluene	$C_9H_{12}O_2$	*	*	24.433	0.24	24.448	0.37

RT = retention time

(*) compounds with concentration under detection limit

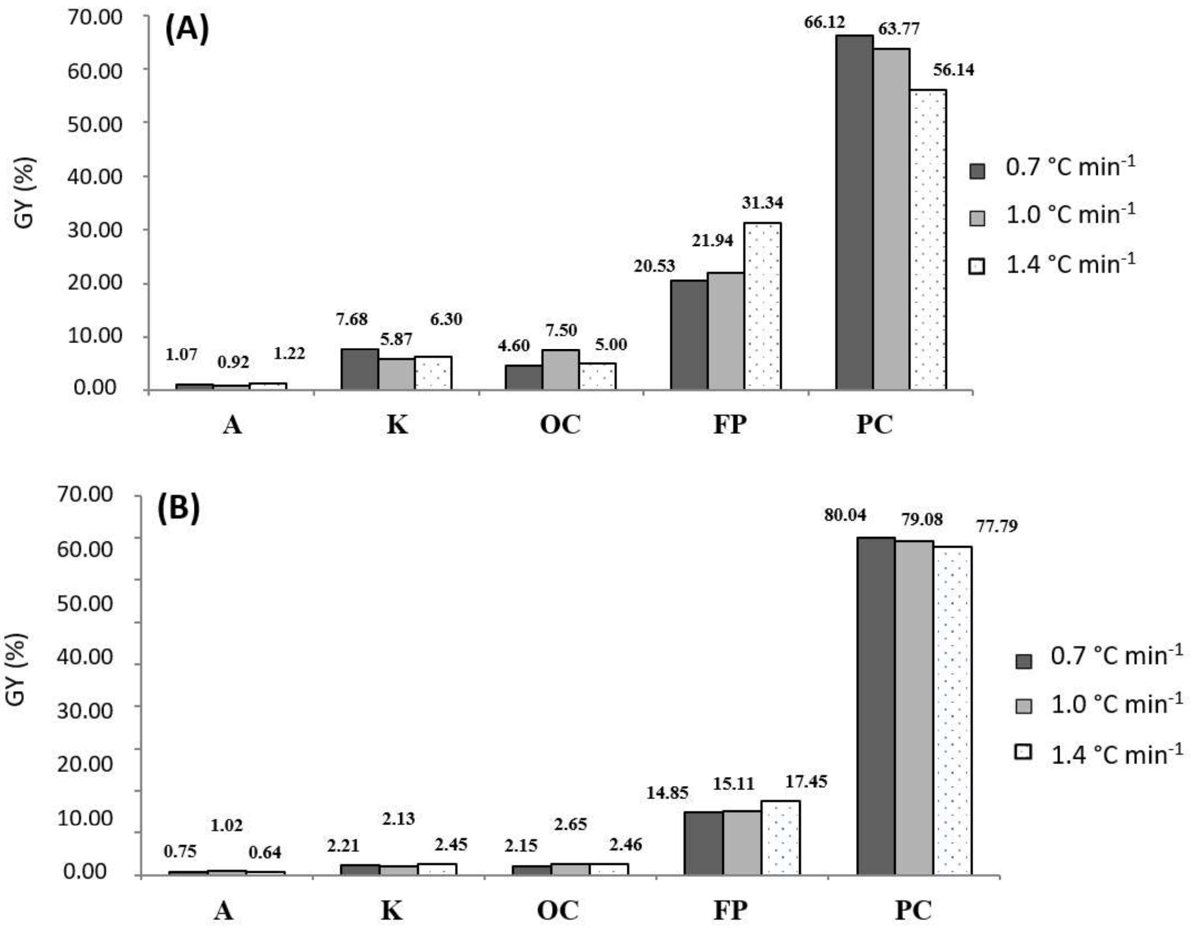

Figure 2 – Variation in chemical composition of wood vinegar according the heating rate. (A) *Eucalyptus urograndis* and (B) Mimosa tenuiflora.

Figura 2 – *Variação da composição química do extrato pirolenhoso em função da taxa de aquecimento (A)* ***Eucalyptus urograndis*** *e (B) Mimosa tenuiflora.*

The concentrations of furans and pyrans were also consistent compared to values reported by Pimenta et al. (2018), who worked with both wood species in similar pyrolysis conditions and reported that that group was the second most abundant in the chemical composition of WV. The increase in the concentration of furans and pyrans as the heating rate increased, according Galaverna and Pastre (2017), is related to the fact that those compounds come mainly from the thermal degradation of cellulose and hemicellulose, followed by a higher amount of pyrolysis liquids. Therefore, the higher concentration of furans and pyrans in Eucalyptus WV can be explained by that pattern, since that species showed higher percentage of cellulose and hemicellulose than Mimosa wood. Lastly, the low amounts of alcohols and ketones are also in accordance with values reported in the literature (Araújo et al., 2017). Since furfural and phenols are the most important compounds in the chemical composition of WV, heating rates that favor their yields should be used. In other words, lower pyrolysis heating rates are related with higher yields of furfural and phenols.

5. CONCLUSIONS

Heating rate was the main factor determining the chemical composition of WV of both Eucalyptus and Mimosa, and a higher heating rate was associated with larger yields of charcoal and lower yields of liquids and gases. If the idea is to maximize the yields of furfural and phenolic compounds, lower pyrolysis heating rates are recommended, with the added advantage of producing higher yields of charcoal.

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7. REFERENCES

Abdel-Kahr MM, Hamman MMA, El-Mougy NS, Abd-Elgawad MMM. Pesticide alternatives for controlling root and root knot of cucumber under plastic house conditions. International Journal of Innovations Research Science, Engineering and Technology. 2015;4(11):25-31.

American Society for Testing and Materials - ASTM. Standard E871-82: standard test method for moisture analysis of particulate wood fuels. Philadelphia-PA: USA; 2006.

American Society for Testing and Materials - ASTM. Standard E872-85: standard test method for volatile matter in the analysis of particulate wood fuels. Philadelphia-PA: USA; 2006.

American Society for Testing and Materials - ASTM. Standard D2395-17: standard test methods for density and specific gravity (Relative Density) of wood and wood-based materials. Philadelphia-PA: USA; 2006.

American Society for Testing and Materials - ASTM. Standard E1755-01: standard test method for ash in biomass. Philadelphia-PA: USA; 2007.

Almeida RSR, Taccini MM, Moura LF, Ceribelli UL, Brito JO. Chemical Composition and Purification of Pyroligneous Liquor from Eucalyptus Wood. Modern Concepts & Developments in Agronomy. Crimson Publishers. 2018;1(4):68-72. http://dx.doi.org/10.31031/mcda.2018.01.000518.

Araújo ES, Feijó FMC, Pimenta AS, Castro RVO, Fasciotti M, Monteiro TVC, Lima KMG. Antibacterial and antifungal activities of pyroligneous acid from wood of Eucalyptus urograndis and Mimosa tenuiflora. Journal of Applied Microbiology. 2017;124(1):85-96. http://dx.doi.org/10.1111/jam.13626.

Brito JO. Reflexões sobre qualidade do carvão vegetal para uso siderúrgico. Piracicaba-SP: IPEF - (Forest Science and Research Institute); 1993. Technical Report 181.

Budaraga IK, Arnim YM, Bulanin U. Analysis of liquid smoke chemical components with GC MS from different raw materials variation production and pyrolysis temperature level. Int. J. ChemTech Res. 2016;9(6):694–708.

Cadwallader KR. Wood smoke flavor. In: Nollet LML, Boylston T, Chen F, Coggins PC, Gloria MB, et al. (eds). Handbook of meat, poultry & seafood quality. New Jersey, USA: Blackwell Publishing Ltd; 2007. p. 201-209.

Carneiro ACO, Santos RC, Castro RVO, Castro AFNM, Pimenta AS, Pinto EM, et al. Estudo da decomposição térmica da madeira de oito espécies da região do seridó, Rio Grande do Norte. Revista Árvore. 2013;37(6):1153-1163.

EPA - U.S. Environmental Protection Agency. Office of Pesticide Programs (2018). Available at: http://www.ipmcenters.org/Ecotox/index.cfmand (accessed on March 5, 2019).

Formiga LDAS, Pereira Filho JM, Nascimento Júnior NG, Sobral FES, Brito ICA, Santos JRS, et al. Diâmetro do caule sobre a desidratação, composição química e produção do feno de Jurema preta (*Mimosa tenuiflora* Wild. Poir.). Revista Brasileira de Saúde e Produção Animal. 2011;12(1):22-31.

Galaverna R, Pastre JC. Production of 5-(hydroxymethyl)-furfural from biomass: synthetic challenges and applications as building block in polymers and liquid fuel production. Revista Virtual de Química. 2017;9(1):248-273. doi: http://dx.doi.org/10.21577/1984-6835.20170017.

Gariglio MA, Sampaio EVSB, Cestaro LA, Kageyama PY (Org.). Uso sustentável e conservação dos recursos florestais da caatinga. Brasília: Serviço Florestal Brasileiro; 2010, 368 p. Relatório Técnico.

Indústria Brasileira de Árvores – IBA. Relatório Técnico 2017. Available at: www.iba.org (accessed on March 7, 2019).

Kook K, Kim JE, Jung KH, Kim JP, Koh HB, Lee JI, et al. Effect of supplemental bamboo vinegar on production and meat quality of meat-type ducks. Korean Journal of Poultry Science. 2002;29(4):293-300.

Kook K, Kim KH. The effects of supplemental levels of bamboo vinegar on growth performance, serum profile and meat quality in fattening Hanwoo cow. Korean J Anim Sci Technol. 2003;45(1):57-68.

Montazeri N, Oliveira ACM, Himelbloom BH, Leigh MB, Crapo CA. Chemical characterization of commercial liquid smoke products. Food Sci. Nutr. 2013;1(1):102–115.

Müller-Hagedorn M, Bockhorn H, Krebs L, Müller U. A comparative kinetic study on the pyrolysis of three different wood species. Journal of Analytical and Applied Pyrolysis. 2003; 68-69(1):231-249.

Miyasaka S, Ohkawara T, Utsumi B. Ácido Pirolenhoso: uso e fabricação. Boletim Agroecológico, nº 14, 1999.

National Renewable Energy Laboratory – NREL. CAT Task Laboratory Analytical Procedure 002 – Two Stage Sulfuric Acid Hydrolysis for Determination of Carbohydrates, 2008.

Oliveira E, Vital BR, Pimenta AS, Lucia RMD, Ladeira AMM, Carneiro ACO. Estrutura anatômica da madeira e qualidade do carvão de *Mimosa tenuiflora* (Willd.) Poir. Revista Árvore. 2006;30(2):311-318.

Paes JB, Lima CR, Oliveira E, Santos HCM. Rendimento e caracterização do carvão vegetal de três espécies de ocorrência no semiárido brasileiro. Ciência da Madeira. 2012;3(1):1-10.

Pereira BLC, Carneiro ACO, Carvalho AMML, Trugilho PF, Melo ICNA, Oliveira AC. Study of thermal degradation of Eucalyptus wood by thermogravimetry and calorimetry. Revista Árvore. 2013;37(3):567-576.

Pimenta AS, Fasciotti M, Monteiro TVC, Lima KMG. Chemical Composition of Pyroligneous Acid Obtained from Eucalyptus GG100 Clone. Molecules. 2018;23(2):426-438. doi: http://dx.doi.org/10.3390/molecules23020426.

Protásio TP, Couto AM, Reis AA, Trugilho PF, Godinho TP. Potencial siderúrgico e energético do carvão vegetal de clones de Eucalyptus spp aos 42 meses de idade. Pesquisa Florestal Brasileira. 2013;33(74):137-149. doi: http://dx.doi.org/10.4336/2013.pfb.33.74.448.

Schnitzer JA, Su MJ, Ventura MU, Faria RT. Doses de extrato pirolenhoso no cultivo de orquídea. Revista Ceres. 2015;62(1):101-106. doi: http://dx.doi.org/10.1590/0034-737x201562010013.

Santos RC, Carneiro ACO, Pimenta AS, Castro RVO, Marinho I, Trugilho PF, et al. Energy potential of species from forest management plan for the Rio Grande do Norte State. Ciência Florestal. 2013;23(2):493-504.

Souza JBG, Re-Poppi N, Raposo Junior JL. Characterization of pyroligneous acid used in agriculture by gas chromatography mass spectrometry. Journal of the Brazilian Chemical Society. 2012;23(4):610-617.

Souza JLS, Guimarães VBS, Campos AD, Lund RG. Antimicrobial potential of pyroligneous extracts – a systematic review and technological prospecting. Brazilian Journal of Microbiology. 2018;49(Supl.1):128-139.

Tiilikkala K, Fagernäs L, Tiilikkala J. History and Use of Wood Pyrolysis Liquids as Biocide and Plant Protection Product. Open Agric. J. 2010;4:111–118.

Vieira RS, Lima JT, Monteiro TC, Selvatti TS, Barauna EEP, Napoli Adi. Influência da temperatura no rendimento dos produtos da carbonização de Eucalyptus microcorys. Cerne. 2013;19(1):59-64.

Wu Q, Zhang S, Hou B, Zheng H, Deng W, Liu D, et al. Study on the preparation of wood vinegar from biomass residues by carbonization process. Bioresource Technology. 2015;179:98-103. doi: http://dx.doi.org/10.1016/j.biortech.2014.12.026.

Yang JF, Yang CH, Liang MT, Gao ZJ, Wu YW, Chuang LY. Chemical Composition, Antioxidant, and Antibacterial Activity of Wood Vinegar from Litchi chinensis. Molecules. 2016;21(9):1-10. doi: http://dx.doi.org/10.3390/molecules21091150.

Zefferino I, Lima EA, Vieira ESN. Uso de extrato pirolenhoso em mistura com herbicida no controle da germinação de plantas daninhas. In: Embrapa Floresta; 2016. p. 50-51.