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Addition of *Eucalyptus* sp wood to urban wood waste as a strategy for energetic use

Adição da madeira de Eucalyptus sp aos resíduos madeireiros urbanos como estratégia para a geração de energia

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Abstract

This study analyzed the effect of adding *Eucalyptus* sp. wood to urban wood waste (UWW) as a strategy for improving the material for energy use. The UWW was collected at a recycling plant in the town of Piracicaba and the wood of *Eucalyptus* sp. came from a seven years old plantation. Five proportions (%) of WWU and eucalyptus wood were tested: T1 = 100/0, T2 = 75/25, T3 = 50/50, T4 = 25/75 and T5 = 0/100. Physical, chemical and immediate properties were evaluated. In addition the mineral contaminants content and the presence of heavy metals in the wood and in ashes of T1 and T5 were determined. The results showed lignin, fixed carbon and ash content higher in treatments with greater amounts of UWW. Heavy metals were detected in both treatments. T4 treatment stood out as the best strategy to the use of UWW, related to its energy potential combined with low ash content and lower contamination of minerals.

Keywords: Biomass and energy; Wood waste use; *Eucalyptus* wood; Heavy metals.

Resumo

Este trabalho analisou o efeito da adição de madeira de *Eucalyptus* sp aos resíduos madeireiros de origem urbana (RMOU) como estratégia para geração de energia. Os RMOU foram coletados em uma Usina de Reciclagem no município de Piracicaba, SP e a madeira de *Eucalyptus* sp foi obtida a partir de um plantio de sete anos de idade. Foram analisadas cinco proporções (%) de RMOU e madeira de *Eucalyptus* sp., sendo T1 = 100/0, T2 = 75/25, T3 = 50/50, T4 = 25/75 e T5 = 0/100. Analisaram-se as características físicas, químicas e composição imediata. Determinaram-se ainda, os teores de contaminantes minerais e a ocorrência de metais pesados nos materiais *in natura* e nas cinzas dos tratamentos T1 e T5. Os resultados evidenciaram teores de lignina, de carbono fixo e de cinzas mais elevados nos tratamentos com maiores proporções de RMOU. Foram detectados metais pesados em dois tratamentos. O tratamento T4 destacou-se como melhor estratégia para utilização de RMOU, visto seu potencial energético, aliado a baixos teores de cinzas e a menor taxa de contaminação por minerais.

Palavras-chave: Biomassa e energia; Aproveitamento de resíduos madeireiro; Madeira de *Eucalyptus*; Metais pesados.

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1. INTRODUCTION

The increase in generation of urban wood wastes in Brazil and their improper disposal have aroused concerns on environmental problems that they may cause. In most cases, these residues are allocated without any prior treatment and the common destinations are construction and demolition landfills, municipal solid waste landfills, specific landfill for inert materials, recycling stations and illegal deposition (Brasil, 2009). It is estimated that the construction sector and the urban areas (urban pruning) together are responsible for the generation of 2.85 million tons of wooden waste in Brazil, corresponding to approximately 11% of the national total (Wiecheteck, 2009). In general, urban solid wastes are represented mainly by paper, glass, wood, plastics and organic materials. Among the different types, one of the main ones is wooden waste, consisting mainly of rest of pallets, construction timbers and other woods mixed with municipal solid waste (Atkins & Donovan, 1996). Often other materials are found adhered to the wood waste such as additives, preservatives, ink, resins, cement, mortar, metallic materials (nails, hinges, etc.), paper, cardboard, waxes and adhesives (Scotland, 2004; Wiecheteck, 2009). Aside from the mentioned contaminants, there is the possibility of the contamination of urban wood waste (UWW) by hazardous substances such as heavy metals coming from preservative treatments of wood (Bouslamti et al., 2012).

Among the possibilities of reuse of the wood residues the energy generation stands out, since it has a renewable potential as biomass. However, greater knowledge of the material is needed given the possibility of its contamination, which requires characterization studies for an appropriate destination (Krook et al., 2006). The energy features of UWW vary wildly and often are unfavorable for its use, mainly because of the diversity of materials in its composition. In addition, pollution problems such as contamination of soil, atmosphere and groundwater may hinder the recycling of materials and can compromise the use of by-products (Reijnders, 2000; Kovacs et al., 2016). The UWW presents a potential feedstock for energetic use, because they are easy to obtain and have virtually no cost. The use for this purpose can represent a minimization of environmental problems which, with a proper destination also creates a chain use for these products, generating new jobs, new revenues and increased tax collection, with positive environmental, social and economic results (Wiecheteck, 2009).

According to Reis (2015) studies for better understanding the energy features of UWW can guide them to promising uses, e.g. for electricity generation. Currently, however, this application has been restricted but should gradually increase over time and may become an important and complementary source of energy instead of hydroelectricity and fossil fuel from thermal power plants. In Sweden, for example, solid wastes are already responsible for generating almost 60% of the electricity used in heating systems of urban buildings (Krook et al., 2006). The uses of UWW in boiler furnaces for steam generation, distillation furnaces, forging and potteries, also are potential alternatives and are used (Dias Júnior et al., 2014). Brazil, in spite of generating large amounts of wood residues, stands out in the cultivation of eucalyptus, the most planted forest tree. Eucalypt species occupy approximately 5.7 million hectares (Indústria Brasileira de Árvores, 2017). The fast growth of this renewable biomass associated with its multiple use with emphasis on the energy destination, given that wood provided 8% of the domestic energy supply in 2016 (Brasil, 2017), makes eucalyptus wood attractive to be added to other materials aiming at improving the characteristics of the mixture. In addition, it is a widely studied genus with regard to characterization and properties.

Hence, it has been hypothesized that the addition of homogeneous material, as from a single species, to UWW will provide improvement in the characteristics for thermal purpose. Thus, this research aimed to study the characteristics of UWW and the addition of *Eucalyptus* spp. wood in different proportions. Therefore, the physical, chemical and immediate features, mineral contaminants and heavy metals contents were analyzed.

2. MATERIALS AND METHODS

The collection site was a construction waste recycling plant that additionally receives wood from other sectors collected by the dump services of the town of Piracicaba, SP/Brazil (Figure 1). The sampling was done according to the Brazilian standard NBR 10.007 (Associação Brasileira de Normas Técnicas, 2004). The wood of *Eucalyptus* (hybrid of *Eucalyptus grandis x Eucalyptus urophylla*) came from a seven years old plantation.

In the plant the collected UWW material passed through a conveyor belt containing a magnetic plate for metal removal. Then, the materials were chipped and homogenized in a 30 mm sieve. The UWW chips sieved at 30 mm (approximately 340 kg) were taken to the Laboratory of Chemistry, Pulp and Energy - LQCE ESALQ/USP, where the analyzes were carried out. For better description of the studied material, UWW chips were manually separated and identified in 56% of solid wood and 44% reconstituted wood panels. The logs of *Eucalyptus* sp. were also chipped and sieved at 30 mm. The materials remained in the oven at 103 ± 2 °C for drying to constant weight and five treatments were defined:

- T1: 100% chips of UWW.
- T2: 75% chips of UWW and 25% of *Eucalyptus* sp.
- T3: 50% chips of UWW and 50% of *Eucalyptus* sp.
- T4: 25% chips of UWW and 75% of *Eucalyptus* sp.
- T5: 100% chips of *Eucalyptus* sp. wood.

2.1 Assays

The extractive content was determined according to the standard Tappi T-12 05-75 (Technical Association of the Pulp and Paper Industry, 1975), and the lignin content was defined following the Tappi standard 222 05-74 (Technical Association of the Pulp and Paper Industry, 1974). The holocellulose content was obtained indirectly, being given by the total minus the contents of lignin and ashes. The immediate analysis was done to determine the volatile matter, the ash and the fixed carbon contents, according to the standard NBR 8112 (Associação Brasileira de Normas Técnicas, 1986). The higher heating value was determined using a digital calorimeter Ika C-2000, according to NBR 8633 (Associação Brasileira de Normas Técnicas, 1984) and the lower heating value; that is the result of combustion under constant pressure in the open air discounting the condensation of water formed, was calculated according to Brand (2010), using the Equation 1 below.

$$LHV = HHV - 600\frac{9H}{100} \quad (1)$$

Where: LHV = lower heating value (MJ kg^{-1}); HHV = higher Heating Value (MJ kg^{-1}); H = theoretical hydrogen content: assumed as 6%.

To ascertain the mineral contaminant content the protocol described by Brito & Ceribelli (2012) was adapted. This analysis assists in the estimation of minerals coming from external contamination, non-woody components. A composite sample for each treatment was made, and ten grams sieved between 20 and 40, placed in a beaker of 250 ml, previously filled with 200 ml of distilled water was used. The suspension was stirred for a minute and left to rest for five minutes. In a next step, the supernatant material in solution was collected and dried till constant weight. By this methodology it is accepted that the supernatant wood is free of contaminating minerals due to their decantation.

The material ashes, free from external contaminants, were obtained according to the standard NBR 8112 (Associação Brasileira de Normas Técnicas, 1986). All procedures were done in three replicates. The contamination rate was determined using the Equation 2 (Dias Júnior et al., 2017).

$$CR(\%) = \frac{ASt - ASm}{ASt} x100 \quad (2)$$

Where: CR = contamination rate; ASt = total ashes content (wood ash + contaminant ashes) (%); ASm = material ash content (free of external contaminant - %).

The analysis of the heavy metals was performed by plasma mass spectrometry technique (*ICP-MS*) following the standard EPA (U.S. Environmental Protection Agency, 2000, 2007). This method proposed to determine the elements: Arsenic (As), Lead (Pb), Mercury (Hg), Chromium (Cr), Copper (Cu), Cadmium (Cd), Zinc (Zn) and Iron (Fe). This analysis was conducted in the raw materials as collected (minced and sifted wood) and in the ashes of treatments T1 (100% UWW) and T5 (100% *Eucalyptus* sp.). This procedure was adopted due to the intermediate treatments consisting of a blend of these two extremes, probably showing intermediate characteristics in accordance to the percentage of each material.

2.2 Data analysis

The data were tested for their variances (Levene) and normality (Shapiro-Wilk) test before an analysis of variance was performed. The ANOVA was done in a completely randomized design, composed of five treatments (described in Section 2.1) and five replications. When the hypothesis *H0* (equal population means) was rejected, the Scott-Knott test for multiple comparison of mean values of treatments was applied. The analyses were conducted at a 95% confidence interval.

Beyond the multivariate analyses of principal component was performed in order to inform the proximity between the treatments. Thus, only the average of each variable except for the chemicals heavy metals was considered; where the analysis was conducted based on the data correlation matrix. For better accuracy, the data were first standardized with mean 0 and variance 1 (Mingoti, 2005). Then, it was possible to determine the scores of the principal components of interest for classification and clusters formation to the analyzed treatments. The principal components analysis (PCA), allows to indirectly identify the best compositions for the energetic use of better efficiency. By PCA it is possible to explain the variance and covariance structure of a random vector (composed of random p-variables) by constructing linear combinations of the original variables, with p original variables and p principal components obtained. In general, by the use of PCA, it is desired to decrease the number of variables to be evaluated and to facilitate the interpretation of the linear combinations constructed. The obtaining of the main components involves the decomposition of the covariance matrix of the random vector of interest. Once the main components were determined, their scores (values) were calculated for each sample element. This method allows to determine, from the characteristics of the treatments, subsets in which each unit belongs only to one subset, and that the units grouped in the same subset are similar to each other and different from the units of other subsets (Sgarbossa et al., 2015; Strandberg et al., 2017).

3. RESULTS AND DISCUSSION

3.1 Chemical composition and immediate

Table 1 show the difference between treatments of basic chemical components and each result of immediate analysis.

The addition of *Eucalyptus* sp. did not influence the extractive content since only the treatment composed exclusively of eucalyptus wood (T5) showed lower content. It is possible that the solvents used in the assay to remove the extractives also removed other type of components adhered to wood, such as paints, varnishes and adhesives, that can have increased the extractive content in treatments containing UWW. The higher amount of extractives in the treatments containing UWW may also be explained by the fact that in their composition are reconstituted materials (panels, boards, etc.); often produced from coniferous wood (Iwakiri et al., 2005), which usually have a higher amount of extractives than hardwood, as observed by Yamamoto et al. (2014).

Table 1. Chemical composition and immediate.

Treatment	EX	LIG	HOL	VM	FC	AS
T1	17.84^{a} (3.13)	28.23^{a} (9.50)	53.93^{c} (5.62)	83.32^{b} (8.97)	18.54^{a} (11.27)	1.36^{a} (7.65)
T2	17.87^{a} (4.40)	28.42^{a} (2.92)	55.70^{c} (2.39)	81.32^{b} (2.56)	17.58^{a} (12.44)	1.10^{a} (9.13)
T3	17.20^{a} (6.76)	24.85^{b} (0.79)	61.59^{b} (8.13)	83.37^{b} (2.79)	16.06^{b} (14.15)	0.56^{b} (10.79)
T4	17.48^{a} (12.57)	22.95^{b} (7.34)	59.72^{b} (5.05)	82.68^{b} (0.42)	16.90^{b} (2.88)	0.42^{b} (42.87)
T5	7.75^{b} (26.84)	23.18^{b} (6.12)	69.07^{a} (10.33)	86.08^{a} (3.92)	14.20^{c} (16.88)	0.29^{b} (1.75)

Where: EX = extractive content (%); LIG = lignin content (%); HOL = holocellulose content (%); VM = volatile matter content (%); FC = fixed carbon content (%); AS = ash content (%). Averages followed by the same letters do not differ in the same column by test Scott-Knott at 5% of significance (p value > 0.05). Values between brackets are the coefficient of variation.

The treatments having greater amount of UWW (T1 and T2) showed the highest levels of lignin content. It is assumed that this behavior may be related mainly to the presence of wood panels, originally produced with wood of *Pinus* spp; according to Carvalho et al. (2009) softwoods have higher lignin content than hardwoods. In addition, wood panels are produced largely with mixed young trees, coming from short-rotation plantations, where the percentage of juvenile wood is higher than mature wood (Pecho et al., 2004) and commonly have a higher lignin content (Rowell et al., 2000). Another possibility is that the resins, glues and paints usually present in these panels, could be diluted in acidic solutions and thus might have been mistaken as lignin. The holocellulose content showed the opposite behavior to lignin: it was lower in T1 and T2, intermediate in T3 and T4, and higher in T5. The holocellulose, extractives, lignin and minerals vary, among other factors, according to the species and age of the wood; these chemical components are related to the energy potential of the material, when they are correlated to the higher heating value (Quirino et al., 2004). This is also corroborated by the fact that coniferous wood, most used for the manufacture of wooden panels, have the lowest content of holocellulose (Yamamoto et al., 2014), as presented in T1 and T2.

The immediate analysis determines the volatile matter, ash and fixed carbon contents; important in the characterization of fuels and correct indication for use. T5 showed the higher content of volatile matter. The panels and other reconstituted materials present in the UWW are previously pressed and dried (particles and fibers) under high temperature, partially removing some of the more volatile components. This fact is possibly associated with lower VM values obtained for treatments with greater amount of UWW in their composition, since the heating, even if moderate, removes some more volatile components from the wood (Aquino et al., 2005).

T1 and T2 showed higher, T5 lower, and T3 and T4 intermediate fixed carbon content. There was an increasing trend of fixed carbon content with the increase of the percentage of UWW in the compositions. None of the treatments was heat treated for carbon concentration, it is believed that this observation emphasizes the hypothesis that UWW have in their composition greater quantities of wood from conifers, since they have lager carbon content than the hardwoods. Fuels with high carbon content burn more slowly, resulting in longer residence time in the combustion and requires less refueling (Dias Júnior et al., 2014).

Regarding the ashes, T1 and T2 presented the highest levels. As found for the fixed carbon content; there is an increasing trend with an increase in the proportion of UWW. Ashes are inorganic compounds (minerals), which are used in paints, adhesives and varnishes; they are usually found in reconstituted wood panels, possibly increasing the ash content in UWW. Furthermore, UWW were sampled from a stack of wood displaced on the ground and with constant input and output of material, therefore, they could be contaminated with mineral soil material. The higher the ash content the higher is the wastage and maintenance of equipment (chippers, mills and crushers). Thus, the lower the ash content the lower is the cost of processing and disposal of UWW (Souza et al., 2009; Farage et al., 2013).

3.2 Higher heating value (HHV)

The higher heating value and lower heating value showed no differences among the different treatments, for the same variable. The HHV ranged from 18.95 MJ kg^{-1} (T2) to 19.15 MJ kg^{-1} (T4) with a difference of only 2% between these levels. The LHV showed a variation of 17.56 MJ kg^{-1} (T3 treatment) to 17.79 MJ kg^{-1} (T4 treatment). These results indicate that there were no significant responses to heat energy when there was added *Eucalyptus* sp. to UWW.

3.3 External mineral contaminants

Treatment T3 showed the highest contamination level, followed by treatment T2, possibly due to contamination by substances adhered to UWW or coming from the contact with the ground in the stockyard, showing in values of 55.17% and 33.37%, respectively (Figure 1).

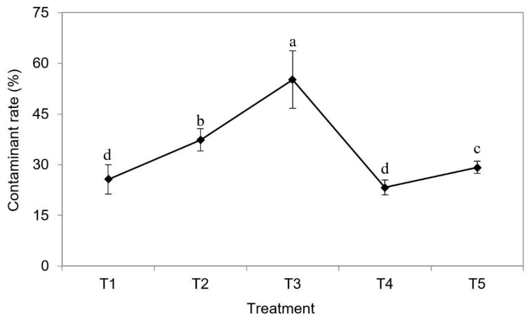

Figure 1. External mineral contamination content of the treatments. *Equal letters do not differ by the Scott-Knott test at 5% significance (p > 0.05).

The UWW, especially from the construction sector, may contain several minerals adhered to waste such as cements, mortars and other contaminants (Figure 1). In this case, even when in equal proportions of UWW and *Eucalyptus* sp. (treatment T3); there was a higher contamination rate, displaying no proportional behavior. This fact highlights the complexity of UWW and the necessity of studies to better understanding, treating and using these materials.

Beyond equipment wear, high content of minerals, inherent of material or from contamination, implies in greater accumulation at the site of combustion, requiring more frequent removals and also being abrasive and often leading to corrosion and fouling of equipment. Knowledge of this fact enables the planning of systems for their collection and disposal (Brand, 2010).

3.4 Detection of heavy metals

Among the heavy metal analyzed, described in Table 2, only mercury (Hg) was lower than the detection limit (DL), which did not allow quantification.

Table 2. Heavy metal content.

Treatment	T1			T5		
Element	Wood	Ash	Variation (%)	Wood	Ash	Variation (%)
Arsenic	3.03	5.54	45.30	2.54	1.70	-33.13
Chromium	2.57	139.10	98.11	2.17	3.88	44.00
Copper	6.61	244.61	97.23	4.85	41.31	88.21
Cadmium	0.10	1.55	93.50	0.04	0.22	81.81
Zinc	29.84	4300.24	99.34	20.10	70.97	71.67
Iron	364.50	12408.33	97.12	127.60	2009.62	93.64
Lead	11.49	353.55	96.70	0.85	0.85	-2.31
Mercury	< DL	< DL	-	< DL	< DL	-

Where: As = Arsenic (mg kg^{-1}); Cr = Chromium (mg kg^{-1}); Cu = Copper (mg kg^{-1}); Cd = Cadmium (mg kg^{-1}); Zn = Zinc (mg kg^{-1}); Fe = Iron (mg kg^{-1}); Pb = Lead (mg kg^{-1}); Hg = Mercury (mg kg^{-1}). DL = detection limit.

The concentration of heavy metals was higher in T1 (UWW) than in T5 (*Eucalyptus* sp.), both in wood and ashes (Table 2). In the woods, Lead in T1 was the only element greater than the maximum established values, ranging from 7.0 to 10 for As, Cr, Cu, Cd and Pb in wood and leaves of eucalyptus, according to Gonçalves et al. (1997) and Velasco Molina et al. (2006). Thus, the treatment containing only *Eucalyptus* sp. (T5) showed lower values and within the established limits, corroborating the idea that its addition to UWW can reduce the percentages of these elements. The concentrations of metals in *Eucalyptus* wood may be due to the fact that eucalyptus has a high absorption capacity of nutrients as well as heavy metals available in the soil (Soares et al., 2000). The higher content of elements analyzed was found in UWW (T1) and can be linked to the use of chemical solutions in surface finish and industrial preservatives such as Ar, Cr, Cu, Zn, Hg and Pb (Nilsson & Jermer, 1999). Atkins & Donovan (1996) also reported the presence of aluminum, titanium, iron and manganese in wood waste from urban origin. Also Silva (2006) and Vidal et al. (2015) argue that the higher levels of Ar, Cr and Cu, as presented in T1, can be derived from preservative solutions, traditionally used in the treatment of wood, in order to remain in contact with the soil, against xylophagous agents.

The heavy metals for T1 and T5 were higher in the ashes than in the wood, as observed by Hoffman et al. (1997), except for Arsenic in T5, which may be explained by his elemental boiling temperature of 614 °C. This temperature is lower than the temperature used to transform the wood into ashes (750 °C). This might be a hindrance in the use of this material, since heavy metal analysis in treatments for energy purposes are based on aspects that indicate the possibility of contamination by combustion; because emissions occur depending on the burning temperature and due to the different properties of the elements. Studies of quantification of the emissions may predict more specifically the potential of contamination by the UWW (Kovacs et al., 2016). For instance, the minimum temperature for incineration chamber of UWW is approximately 1000 °C (Kovacs et al., 2016), with a recommendation by Brunner & Brown (1988) that the gas emitted by the incinerator be filtered. This indicates that, overall, there was a concentration of these elements after combustion in ash formation.

The wood waste containing heavy metals are considered polluters (Hasan et al., 2011), negatively impacting the environment and human health in greater or lesser degree, depending on the concentration and use (Townsend et al., 2005; Kovacs et al., 2016). The higher values of the element concentrations in the ash show that care should be taken in discarding such materials without treatment, once the presence of heavy metals is in the materials, woods or ashes can contaminate the environment (soil, ground water, waterways, air, etc.), especially if they are deposited in the open sites or even in landfills and able to leach and/or solubilize (Krook et al., 2004, 2006; Kovacs et al., 2016; Hla et al., 2016).

3.5 Multivariate analysis

Table 3 shows that the first two principal components explain about 87% of the total variance of the data analyzed, and from these components, there were no major changes in the variances.

Table 3. Eigenvectors of the first two principal components.

Variable	Component 1	Component 2
Extractives content - EXT (%)	0.177	0.446
Lignin content - LIG (%)	0.462	0.056
Holocellulose content - HOL (%)	-0.476	-0.005
Higher heating value - HHV (kcal kg^{-1})	0.420	-0.253
Lower heating value - HLV (kcal kg^{-1})	0.420	-0.253
Volatile matter content - VM (%)	0.177	0.487
Fixed Carbon content - FC (%)	-0.168	-0.441
Ash content - AS (%)	-0.024	0.468
Contamination Rate - CR (%)	-0.335	0.130
Eigenvalue	4.39	3.40
Variance (%)	48.77	37.80
Accumulated variance (%)	48.61	86.67

The first principal component basically represents the global performance index of feasibility analysis of the energy use of biomass (Protásio et al., 2013). The highest coefficients of the first principal component (Table 2) in module are related to holocellulose and lignin contents and also to the higher and lower heating values. It was noted that the higher heating value of the component (score), and the inverse was observed for ash content, contamination rate and fixed carbon content. As a strategy for energy generation these aspects unite the main features necessary for selecting UWW and *Eucalyptus* sp. compositions. The second principal component showed the contrast between the fixed carbon content and volatile matters, ash and extractives contents; in other words, it may reflect problems for the proposed energy use; since high values of this component (score) are associated with the generation of large amount of ash that leads to corrosion and fusion in equipment, and also lager elimination of gases, associated with high levels of volatile matters.

Figure 2 shows an ordering diagram of the variables and the scores of the first two principal components.

The values calculated of the first principal component score showed that the T4 treatment stands out due to its heating values (HHC and LHV) and lignin content, pointing to its energy use. The lowest scores of the second main component were observed for the T1 and T2, mainly because of the high ash contents (Figure 2). The T5 treatment had the highest score of the second principal component, because it's high holocellulose and fixed carbon contents. Treatment T3 showed a value close to zero due to the high contamination rate and high holocellulose content.

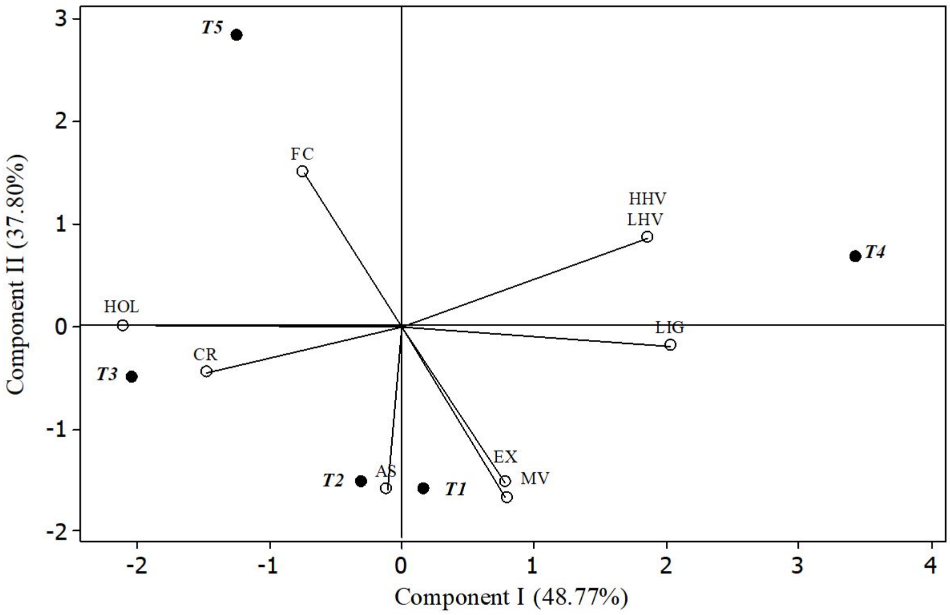

Figure 2. Ordination diagram of treatments considering the scores and eigenvectors of the principal components I and II. Where: EX = extractives content (%); LIG = lignin content (%); HOL = holocellulose content (%); HHV = higher heating value (MJ kg^{-1}); LHV = lower heating value (MJ); VM = volatile matter content (%); FC = fixed carbon content (%); ASH = ash content (%); CR = contamination rate (%).

4. CONCLUSIONS

The higher contamination rate was observed in the treatment with the same proportion of urban wood waste and *Eucalyptus* sp., demonstrating the difficulty of homogenizing this kind of material. The highest concentration of heavy metals was in the treatment consisting only of urban wood waste. Treatment T4 presented the best strategy to use urban wood waste, based on its lower ash content and lower contamination rate.

The principal component analysis was an effective tool in the evaluation and selection of treatment strategy. However, according to the ordination diagram T3, T4 and T5 formed distinct groups and T1 and T2 were grouped into a different group, since they had similar characteristics.

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