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Analysis of Arithmetic Models for Predicting Calorific Values of Landfilled Municipal Solid Waste

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ABSTRACT

Arithmetic models have been used for predicting the calorific value of fresh municipal solid wastes (MSW) based on their gravimetric and elemental compositions. However, the use of these models for landfilled MSW is still recent, although the calorific value of landfilled MSW is very important for landfill mining projects. Landfill mining, a technique used to mine MSW from sanitary landfills and dumps, aims to recover materials and mitigate environmental impacts. The present research aimed to determine and apply experimental data of landfilled MSW to arithmetic mathematical models which predict Higher Heating Value (HHV) and Lower Heating Value (LHV) to validate these models by comparing theoretical and experimental values. A representative MSW sample aged approximately 8 years was mined from a sanitary landfill of Campinas city, south-eastern Brazil. Five compound samples (Plastics, Rubbers, Easily Degradable (ED), Diapers and Textiles, and the landfilled MSW without Fines and Dangerous categories (LMSW)) were submitted to HHV, LHV, elemental composition and gravimetric composition tests. Data from elemental composition and gravimetric composition tests were used to predict theoretical HHV and LHV values through four arithmetical mathematical models from the technical-scientific literature. Results showed that elemental and caloric values of landfilled MSW categories were in accordance with the values reported in the literature, indicating potential to be used in incineration plants and generate energy. A model based only on element C predicted better the calorific value of compound samples of landfilled MSW categories, such as Rubbers, and Plastics. On the other hand, gravimetric composition models predicted better the calorific value of the LMSW. A model based on elements C, H, S, and O did not predict appropriately the calorific value of the LMSW compound sample, however, predicted the calorific value of the rubber and ED compound samples with excellent accuracy according to the Mean Absolute Percentage Error (MAPE) classification.

Keywords: Arithmetic Mathematic Models, Municipal Solid Waste, Landfill Mining, Higher Heating Value, Lower Heating Value

1 INTRODUCTION

Proper Municipal Solid Waste (MSW) management is a challenge worldwide. In several countries, such as in Brazil, solid waste management is deemed in this order: non-generation, reduction, reuse, recycling, and treatment (i.e. biological, thermal) (Brasil, 2010). Once MSW is generated, recycling appears as an interesting option to reuse it before disposing of in landfill. However, currently in Brazil, this is not a reality yet since just 38% of the Brazilian urban population have access to the selective collection program (ANCAT, 2020), this condition leads to the increase of recyclable materials being disposed of in sanitary landfills and open dumps. In 2022, ABRELPE (2022) reported that around 46.40 million tonnes of MSW were disposed of in sanitary landfills, whereas open dumps and unsuitable landfills received 29.71 million tons of MSW. Note that unsuitable landfills in Brazil differ from the open dumps only because the MSW are covered with daily soil as explained by Nascimento et al. (2019). ABRELPE (2020) also reported that the MSW that has been disposed of in landfills and open dumps are constituted by organic matter (45.30%), fabric, leather, and rubber (5.60%), metals (2.30%), glass (2.70%), plastic (16.80%), paper/cardboard (10.40%), long-life cartons (1.40%), non-recyclable solid waste (14.10%) and others (1.40%). In this context, the landfill mining seems to be an option to recover landfilled MSW and re-insert them into the production chain. This is a technique that has attracted much attention in the last decades and comprises the process of excavating wastes with the aim of reusing landfilled materials (Rotheut & Quicker, 2017). Two potential reusing routes of landfilled MSW can be considered as a source of energy by thermal process (incineration, gasification, pyrolysis), and biological treatment process (anaerobic digestion), or as a source of material. Recycling these solid wastes as renewable material is not recommended in some cases especially because they presented aggregated fine material attached in their surfaces (Canopoli et al., 2020), thus, biological, or thermal treatment is proposed for reusing several categories of landfilled MSW (Zhou et al., 2014). Other benefits of landfill mining are the reduction of fugitive emission of methane (CH_4) into the atmosphere (Kaartinen et al., 2013), as well as the prevention/remediation of soil and bodies of water contamination near the landfill site (Hogland et al., 2004).

When planning thermal treatment plants or during the operation stage of them, the information of calorific values (Higher Heating Value (HHV) and/or Lower Heating Value (LHV)) is essential. Nonetheless, the high cost of the calorific tests, which involve skilled labour and a bomb calorimeter, often makes these treatments unfeasible (Drudi, 2017). As an interesting option for predicting the MSW calorific value is the use of arithmetic mathematical models that are widely available in technical-scientific literature, some of which employ gravimetric composition and/or so-called elemental composition data. Gravimetric composition refers to the percentage in mass of MSW constituents, such as plastics, paper, organic matter, metals, glass etc., whereas elemental composition refers to the percentage of the main constituent atoms of the samples (Carbon (C), Hydrogen (H), Oxygen (O), etc.) (Kathiravale et al., 2003). These data are easy to obtain, and the costs of their tests are relatively low compared to the bomb calorimeter costs. (Khan & Abu-Gharara, 1991; Wang et al., 2021).

Most of the arithmetic mathematical models have been applied for fresh MSW, and few models have been elaborated and applied for landfilled wastes. There are three main differences between fresh and landfilled wastes in terms of calorific value: a) degradation rate, b) presence of the aggregate fine material, and c) gravimetric composition, due to mainly the organic matter degradation. Thus, firstly it is necessary to validate the models that predict the calorific value of fresh MSW before applying them to landfilled waste, as the results may not be realistic with their characteristics.

In this context, this research aimed to predict the calorific values of landfilled MSW using four arithmetic mathematical models, formulated to predict calorific values of fresh MSW. Experimental data of elemental and gravimetric composition of the landfilled MSW were obtained and used to apply in the models. Theoretical calorific values were compared with the experimental ones, obtained for the same landfilled MSW, in order to validate these models.

2 MATERIALS AND METHODS

2.1 MSW excavation, sample preparation and analyses

A representative sample of 248.23 kg of landfilled MSW of 8 years was mined on December 16, 2019, from the deactivated Sanitary Landfill Delta A, located in Campinas, South-eastern Brazil. This landfill received solid wastes considered non-inert and non-hazardous, such as household wastes, tree pruning and weeding services wastes, and health services solid wastes after submitting them to microwave treatment, during its operation time. The representative sample of landfilled MSW of 8 years was transported to the laboratory and was segregated in 25 categories. The sorting process consisted of sieving the sample using a 19 mm sieve and segregating tactile and visually the material greater than 19 mm. In this case, the solid waste that passed through the sieve was defined as Fines (D < 19 mm). On the other hand, the solid waste retained in the sieve was manually sorted in the following 24 categories: Hard Plastic, Soft Plastic, Bags and Plastic Bags, Magnetic Metal, Non-Magnetic Metal, Glass, Porcelain, Long-Life Cartons, Styrofoam, Rubber, Construction and Demolition Waste (RCD), Leather, Foam, Composite (materials composed by more than one type of category), Miscellaneous (materials that could not be classified in the other categories), Organic Matter, Paper, Cardboard, Wood, Pruning, Diapers and Sanitary Pads, Fabric, Hazardous Waste, and Soil. Additionally, the moisture contents, on dry basis, of the representative sample of MSW (non-segregated) and each of these 25 categories were determined by drying them at 60ºC in a laboratory oven. Leme et al. (2021) presented a more detailed explanation of these steps.

From the gravimetric composition of landfilled MSW of 8 years obtained by Leme et al. (2021), it was determined a new gravimetric composition that does not account the Fines and Dangerous categories in order to apply the arithmetical mathematical models and to predict calorific values. The Fines category was excluded because usually studies reported in the technical-scientific literature did not consider this category for energy generation as it has low calorific value and a large amount of soil-like material, which results in significant ash generation and various operational problems in thermal reactors. The Dangerous category was not used due to safety concerns for the researchers. It is impossible to guarantee that this category is free of pathogenic organisms. As the research group manually handled the waste, it was decided not to manipulate this category. The Fines category is expressive in landfilled MSW composition comprising 35.65% on wet basis and 35.56% on dry basis, and the Dangerous category comprises only 0.99% on dry basis and 0.71% on wet basis according to Leme et al. (2021). The gravimetric composition of the landfilled MSW of 8 years, on dry and wet weight, without the Fines and Dangerous categories, and the moisture content of each of the 23 categories adapted by Leme et al. (2021) were presented in (Table 1).

Table 1. *Gravimetric composition of landfilled MSW without Fines and Dangerous (LMSW) and Easily Degradable (ED) of 8 years*

Categories	Moisture content (%)	Gravimetric composition (%)		
		LMSW		ED
	Wet basis[a]	Wet basis[b]	Dry basis[b]	Wet basis[b]
Plastic Bags	39.15	18.47	16.75	-
CDW	8.22	14.78	20.21	-
Paper	53.41	13.93	9.67	38.27
Organic Matter	42.23	8.93	7.69	24.54
Hard Plastic	15.60	7.13	8.97	-
Wood	44.63	5.58	4.61	15.34
Pruning	46.01	4.82	3.88	13.25
Fabric	46.62	3.55	2.88	-
Composite	22.40	3.95	4.57	-
Glass	0.40	2.94	4.36	-
Soft Plastic	18.53	2.87	3.49	-
DS[c]	43.44	2.49	2.10	-
Cardboard	59.56	3.13	1.89	8.60
Soil	18.17	2.07	2.53	-
Magnetic Metal	5.18	1.42	2.01	-
LLC[d]	45.74	0.91	0.74	-
Porcelain	4.04	0.70	1.00	-
Rubber	17.29	0.62	0.77	-
Styrofoam	20.38	0.53	0.63	-
NMM[e]	43.39	0.42	0.36	-
Foam	17.43	0.37	0.46	-
Miscellaneous	19.72	0.37	0.44	-
Leather	39.53	0.00	0.00	-

Note: [a]Data obtained by Leme et al. (2021); [b]Data adapted from Leme et al. (2021); [c]DS: Diapers and Sanitary Pads; [d]LLC: Long Life Cartons; and [e]NMM: Non-Magnetic Metal.

Five compound samples of the landfilled MSW with 8 years were prepared to be used in this research. These compound samples were: (a) Rubbers: comprising all types of rubbers; (b) Diapers and Textiles (DT): comprising Diaper, Sanitary Pad, Fabric and Leather categories; (c) Easily Degradable (ED): comprising Organic Matter, Paper, Cardboard, Wood, and Pruning categories (Table 1), (d) Plastics: comprising all types of plastics – Hard Plastic, Soft Plastic, and Plastic Bags categories; (e) landfilled MSW (LMSW): comprising all the categories of landfilled MSW without the Fines and Dangerous categories. The preparation of these five compound samples consisted of drying them at 40ºC until their mass became constant. Afterwards, each of the dried samples was crushed individually in different granulator mills or an industrial blander (for DS category), or manually cut with the aim turquoise and sanded using metal sandpaper (for Metals and Composite categories). The crushing process was done until all categories had a diameter equal or smaller than 3 mm. The proportions of individual categories used in the compound samples were determined based on the gravimetric composition of the landfilled MSW. It was utilised a proportional reasoning according to Equation 1.

$$X_n = (100 - I_n)/P \qquad (1)$$

Where X_n is the percentage of each category included in the compound samples, I_n is the percentage of the category present in the whole landfilled MSW, P is the sum of the percentages of each category that compose the compound sample in the whole landfilled MSW. All variables are on dry basis.

All the compound samples were submitted to elemental composition, HHV and LHV analyses in triplicate. The elemental composition was determined by using an elemental analyser, series 2400 II CNHS/O – Perkin Elmer®. The oxygen content was calculated by Equation (2) (Fanslau et al., 2020).

$$O\ (\%) = 100 - (S\% + H\% + N\% + C\%) \qquad (2)$$

Where O (%), S%, H%, N%, and C% are the percentage value of elemental composition of Oxygen, Sulphur, Hydrogen, Nitrogen, and Carbon, respectively.

The HHV was determined based on D5865 (ASTM, 2010), and a calorimetric bomb (model C200, Ika) was used for this purpose. The LHV was calculated by substituting the HHV result on Equation (3) proposed by Doat (1997).

$$LHV\ (J/g) = HHV - 600\ (9H/100)\ 4.184 \qquad (3)$$

Where LHV is the Lower Heating Value on constant pressure (J/g), HHV is the Higher Heating Value on constant pressure (J/g), and H is the mass percentage of Hydrogen atoms on the sample (%).

The average value (AV), standard deviation (SD), and coefficient of variation (CV) of elemental composition, HHV and LHV were calculated. Note that the coefficient of variation is defined as the ratio between standard deviation and the average value multiplied by 100.

2.2 Mathematical models and MAPE statistical analysis

The HHV was predicted using two mathematical models, one of them was the classic arithmetic mathematical Model of Steuer (Liu et al., 1996; Ready et al., 2005; Choi et al., 2008) (Equation (4)). The other one was the Model nº12 of Choi et al. (2014) (Equation (5)).

$$HHV_{db}\ (J/g) = (81C - 30.375O + 21.375O + 345H - 21.5625O + 25S)\ 4.1868 \qquad (4)$$

$$HHV_{db}\ (J/g) = 410.18\ (2.71828^{0.0373C}) \qquad (5)$$

Where HHV_{db} is the Higher Heating Value on dry basis; C, O, H and S are the percentages of Carbon, Oxygen, Hydrogen, and Sulphur atoms on dry basis present on the samples.

Abu-Qudais & Abu-Qdais's (2000) model and Wang et al.'s (2021) model, as described in Equations (6) and (7), respectively, were used to predict the LHV.

$$LHV_{db}\ (J/g) = (267(Pla/Pa) + 2285.7)\ 4.1868 \qquad (6)$$

$$LHV_{wb}\ (J/g) = -\ 72.42Fo + 83.20Pa + 67.90Pla + 7669.08 \qquad (7)$$

Where LHV_{db} and LHV_{wb} are the Lower Heating Value on dry basis and on wet basis, respectively, and Pla, Pa and Fo are the percentages of Plastics, Papers, and Food, respectively. Note that, in Equation (7), the parameter Pla and Pa are referred to gravimetric composition on wet basis, whereas the same parameters in Equation (6) are on dry basis. Food usually is not found in landfilled MSW composition because its degradation occurs very quickly. Thus, in this case, the value of Fo was considered 0.

For predicting the LHV of LMSW by applying the Equations (6) and (7), it was considered the variable "Pla" (plastics) being the sum of the percentages of Soft Plastic, Hard Plastic, Plastic Bags, Rubber and Styrofoam categories (Table 1), whereas the variable "Pa" (papers) defined as the sum of the percentages of Paper, Cardboard and Long-Life Cartons categories (Table 1). On the other hand, for applying the Equation (7) to predict the LHV of ED, the percentage of Paper considered was the sum of the cardboard and paper in relation to the compound sample composition (Table 1). Note that in this last case, the Long-Life Cartons were not included in the definition of “Pa”, since they were not included in the definition of ED (Table 1).

The mathematical model proposed by Wang et al. (2021) (Equation (7)) to predict the LHV presents a result on wet basis. However, in this research, the LHV of all composed samples were determined on dry basis since they were dried in a laboratory oven at 40ºC before submitting them to the calorific tests. Thus, it was not possible to compare the experimental results with the calculated LHV by Equation (7). Therefore, the Equation (8) presented by Hla & Roberts (2015) was used to convert the experimental LHV_{db} to LHV_{wb}.

$$LHV_{wb}\ (J/g) = LHV_{db}\,(1 - MC0{,}01) - 2.443MC/100 \qquad (8)$$

Where LHV_{wb} and LHV_{db} are the Lower Heating Value on wet basis and on dry basis, respectively, and MC is the percentage of Moisture Content. The Moisture Content of the LMSW and ED considered were 29.90% and 48.87% on wet basis, respectively. These values were obtained by calculating the average Moisture Content of the categories that comprise each compound sample (Table 1).

The Mean Absolute Percentage Error (MAPE) was calculated to assess the precision of the mathematical models used to predict the calorific values. The MAPE is defined by the Equation (9), adapted from Lin et al. (2013).

$$MAPE\ (\%) = (|Xt - Xm|/Xm)\ 100 \qquad (9)$$

Where MAPE is the Mean Absolute Percentage Error, Xt is the theoretical value and Xm is the measured value. The MAPE value classifies the relation between theoretical and measured data as: excellent (MAPE < 10%), good (MAPE = 10% to 20%), acceptable (MAPE = 20% to 50%), and unacceptable (MAPE > 50%).

3 RESULTS AND DISCUSSION

3.1 Elemental composition and calorific value

Overall, landfilled plastics, rubbers, and DT had high C and H contents in relation to LMSW and ED (Table 2). Hla and Roberts (2015) explained that the higher C and H contents, the higher the calorific value. Therefore, LMSW and ED had an HHV, on dry basis, lower than other categories (Table 2). The HHV, on dry basis, of landfilled rubbers and DT were higher than the average values of HHV, on dry basis, of non-landfilled diapers and sanitary pads (19780.00 J/g), and textiles (20830.00 J/g) studied by Drudi et al. (2019) (Table 2). The HHV, on dry basis, of landfilled plastics (28828.00 J/g) was higher than the minimum HHV found for non-landfilled plastics by Drudi et al. (2019), which ranged from 24350.00 J/g to 40600.00 J/g. The HHV of landfilled plastics were also higher than the one determined by Quaghebeur et al. (2013) for landfilled plastics for 14 and 29 years, which varied from 19000.00 J/g to 28000.00 J/g, on dry basis. Zhou et al. (2014) stated that the calorific value of landfilled plastics was similar to the one determined for non-landfilled plastics. These results suggest that the calorific value of hardly degradable solid wastes does not change significantly over the years of landfilling.

The HHV of ED, on dry basis (12181.00 J/g), was lower than the average value determined for non-landfilled paper (17630.00 J/g) and organic waste (food/yard wastes) (15780.00 J/g) studied by Drudi et al. (2019). This result might be due to the degradation process of the ED along the time. The C content of ED (34.87%) was slightly lower than the non-landfilled cardboard (45.50%), office paper (37.90%), tissue paper (42.90%) (Li et al., 2020), newspaper (39.50%), and branches (44.30%) (Zhou et al., 2021). Singh and Chandel (2020) and Wang et al. (2021) reported that calorific value tended to reduce as long as the solid waste got older.

The LHV of LMSW, on dry basis, was a value higher than the one found for LMSW of 3 years (9468.00 J/g) and lower than the LHV of LMSW of 1 year (20103.00 J/g) (Wang et al., 2021). The LMSW ageing between 1 to 10 years studied by Singh and Chandel (2021) presented an HHV, on dry basis, that ranged from 3000.00 J/g to 18000.00 J/g. Overall, the calorific values (HHV and LHV) of LMSW of the present study were in accordance with the values reported in the literature. Therefore, this type of waste has a potential to be used in incineration plants and generate energy.

Table 2. *Elemental composition, HHV and LHV of compound samples of landfilled MSW of 8 years*

Category		C (%)	N (%)	H (%)	S (%)	O (%)	HHV$_{db}$ (J/g)	LHV$_{db}$ (J/g)	LHV$_{wb}$ (J/g)
Plastics	**AV**[f]	**64.79**	**0.35**	**10.39**	**0.23**	**24.24**	**28828.00**	[e]	[e]
	SD[g]	3.99	0.06	0.80	0.07	4.81	3061	-	-
	CV[h]	6.19	17.14	7.70	30.43	19.86	10.62	-	-
Rubbers	**AV**[f]	**61.31**	**0.66**	**7.23**	**1.97**	**28.84**	**26050.00**	[e]	[e]
	SD[g]	3.42	0.15	0.20	0.25	3.67	1142	-	-
	CV[h]	5.58	22.73	2.77	12.69	12.71	4.38	-	-
LMSW[a]	**AV**[f]	**26.84**	**0.49**	**4.51**	**0.15**	**68.00**	**15021.00**	**14002.03**	**9816.76**
	SD[g]	3.56	0.07	0.62	0.02	4.26	1205	1276.03	648.61
	CV[h]	13.26	14.29	13.75	13.33	6.27	8.02	11.64	11.64
ED[c]	**AV**[f]	**34.87**[b]	**0.76**[b]	**5.39**[b]	**0.27**	**58.71**	**12181.00**	**10963.21**	**5571.62**
	SD[g]	2.48	0.01	0.52	0.04	2.97	1276	1204.97	844.80
	CV[h]	7.11	1.32	9.65	14.63	5.05	10.48	8.61	8.61
DT[d]	**AV**[f]	**63.64**	**2.68**	**8.70**	**0.18**	**24.80**	**26780.00**	[e]	[e]
	SD[g]	0.88	1.23	0.98	0.01	3.08	1819	-	-
	CV[h]	1.38	45.90	11.26	5.56	12.42	6.79	-	-

Note: [a]Non-segregated landfilled MSW of 8 years without Fines and Dangerous categories; [b]Data obtained from Leme et al. (2022); [c]ED: Easily Degradable; [d]DT: Diapers and Textiles; [e]The LHV for Plastics, Rubbers and DT were not analysed because the models of LHV used are only in function of gravimetric composition that is not applicable to these categories, only for ED and LMSW categories; [f]AV: Average Value (% or J/g); [g]Standard Deviation (% or J/g); [h]Coefficient of Variation Value (%).

3.2 Theoretical calorific and MAPE values obtained from mathematical models.

The theoretical calorific value of the compound samples of landfilled MSW of 8 years predicted by the mathematical models, as well as the data obtained from experimental tests, and the MAPE values are presented in Table 3.

Model nº 12 of Choi et al. (2014) (Equation (5)) presented theoretical values of HHV close to the experimental ones for Rubbers, Plastics, and Diapers and Fabrics with MAPE values of 0.21, 4.31 and 1.18, respectively, which are deemed excellent. However, the theoretical HHV for LMSW were not accurate in this case, although MAPE value (23.92%) indicated that this result was acceptable (Table 3). One reason for the low accuracy of the Equation (5) to calculate the theoretical value of HHV of LMSW should be related to the constitution of the compound sample submitted to the elemental composition tests, in which it is required around 100 mg of the sample. Since LMSW is a heterogeneous sample constituted of 23 solid waste categories (Table 1), with different weights and percentages, it was not easy to mix proportional parts of them, on dry mass, to prepare a small representative sample, even after drying and crushing each category individually until they had a diameter smaller than 3 mm.

The Standard Deviation of elemental composition of LMSW compound sample was below 5%, and the coefficient of variation was below 15% for each element (C, N, H, S, O) (Table 2). According to Słomczyńska and Słomczyńska (2004), a coefficient of variation less than 20% means that the repeatability of the tests in the laboratory was good. Thus, the hypothesis that the 100 mg compound sample of LMSW were not prepared properly cannot be excluded. This condition may have led to underestimate the C content of LMSW and overestimated its O content (Table 2), consequently, the application of Equation (5), which predicts HHV only in function of C, indicated a low HHV of LMSW in relation to the experimental value. Other studies that calculated the calorific value of non-landfilled MSW also reported that preparing a compound sample of heterogeneous MSW was difficult, thus, the calorific value of these samples should be predicted by equations based on gravimetric composition rather than equations based on elemental composition or other parameters (Liu et al., 1996; Kathiravale et al., 2003). Hence, the gravimetric models (Equations (6) and (7)) predicted better the calorific value of the compound sample of LMSW (with MAPE values of 11.50 and 14.10, respectively).

Table 3. *Theoretical and experimental calorific values of compound samples*

Calorific value	Base of the model	Model	Eq. nº	Compound samples				
				Theoretical calorific value (J/g)				
				Rubbers	ED[a]	DT[b]	Plastics	LMSW
HHV	Elementary	Steuer	4	27751.31	12128.32	30993.99	33902.85	6931.21
		MAPE (%)[e]	-	6.35	0.43	15.74	17.60	53.86
		nº 12 of Choi et al. (2014)	5	26103.87	14847.97	27095.92	27585.55	11427.63
		MAPE (%)[e]	-	0.21	21.89	1.18	4.31	23.92
		Experimental HHV	-	**26050.00**	**12181.00**	**26780.00**	**28828.00**	**15021.00**
LHV	Gravimetric	Abu-Qudais & Abu-Qdais (2000)	6	[c]	[d]	[c]	[c]	12391.24
		MAPE (%)[e]	-	[c]	[d]	[c]	[c]	11.50
		Experimental LHV_{db}	-	[c]	[d]	[c]	[c]	**14002.03**
		Wang et al. (2021)	7	[c]	11568.41	[c]	[c]	11201.08
		MAPE (%)[e]	-	[c]	107.63	[c]	[c]	14.10
		Experimental LHV_{wb}	-	[c]	**5571.62**	[c]	[c]	**9816.76**

Note: [a]ED: Easily Degradable; [b]DT: Diapers and Textile; [c]The LHV for Plastics, Rubbers and DT were not analysed because the models of LHV used are only in function of gravimetric composition that is not applicable to these categories, only for ED and LMSW compound samples; [d]Equation (6) cannot be used for ED because this Equation uses the category Plastics as the denominator and, since the ED compound sample does not have the category Plastics (Table 1), the denominator would be 0, which would invalidate the LHV calculation. [e]The MAPE comparison scale: Excellent (MAPE < 10%), good (MAPE = 10% to 20%), acceptable (MAPE = 20% to 50%), and unacceptable (MAPE > 50%).

Additionally, the higher the percentage of O in the composition of a solid waste, the more unpredictable becomes the calorific value obtained through mathematical models that use the variable O (such as Steuer's model, Equation (4)) (Huang & Lo, 2020). The MAPE value of LMSW when applying Equation (4) was 53.86% and its percentage of O was 68.00%. However, the prediction of theoretical calorific value of ED by the Equation (4) was an exception, since it was very close to the experimental value (Table 2), and presented a MAPE value of 0.43%, and its percentage of O was 58.71%. This could be because it is possible to avoid errors during the determination of elemental composition of ED, since differently from LMSW, the ED is composited with five different categories of solid waste, thus, a compound sample that is representative of ED can be prepared easier than LMSW, that is composed by 23 categories.

Steuer's model (Equation (4)) also predicted calorific values considered excellent by MAPE value for landfilled rubbers (6.35%), and good for DT (15.74%) and plastic (17.60%) (Table 3). Nevertheless, Equation (5) predicted even better the calorific values of landfilled rubbers, plastics, and DT with MAPE values of 0.21, 4.31 and 1.18, respectively. This difference could be because Equation (4) is based on the O, C, H, and S contents, whereas Equation (5) is only in function of C. The coefficient of variation of C content was below 7% for all these compound samples, meaning that these data were more homogeneous, consequently, its content did not significantly affect the prediction of the theoretical calorific value when applying Equation (5). On the other hand, the coefficient variation of the S, O and H contents of these samples were higher than 7% in some cases (Table 2) due to different types of plastics (hard plastics, soft plastics, and plastic bags), rubbers, diapers and fabrics that can be found on the landfill, and it might be interfered on the prediction of calorific values applying Equation (4). These results suggest that simplistic mathematical models, such as Equation (5), are recommended for predicting the calorific value of hydrocarbon-rich categories.

The Steuer's models (Equation (4)) have been applied to predict HHV of fresh MSW compound samples (Chang et al., 1997; Reddy et al., 2005; Choi et al., 2008; Khuriati et al., 2017), but sometimes do not predict the calorific value of this category with great precision. In this research, the MAPE value for the application of Steuer's model for LMSW was 53.86%, which is unacceptable. Some elementary models formulated specifically for fresh MSW, such as those developed by Amen et al. (2021) and Liu et al. (1996), do not consider the value of H in their formulations. Liu et al. (1996) reported that H did not contribute to the heating value of their samples of MSW from Kaohsiung City, Taiwan. The authors argued that, on the contrary, classical elementary models such as Steuer's (Equation (4)), consider the value of H, however, this model was initially elaborated for coal that is more homogeneous, rich in H and poor in O than MSW compound samples. The percentage of H in LMSW compound sample had the lowest value (4.51%) in comparison with the other four compound samples (Table 2). This indicates that the H element is not very relevant for the HHV determination of the LMSW of this study, indicating that it is probable that a model not considering the value of H in its formulation can better predict the calorific value of this compound sample. Furthermore, the H value does not contribute or negatively contribute to the calorific value in some elementary models developed to predict calorific value of MSW compound samples from developing countries as also observed in Taiwan by Liu et al. (1996). This may be since H in solid wastes from developing countries may be associated with moisture content because of the large quantity of organics commonly found in these wastes, while in developed countries the H may be associated with the large quantity of plastics and papers, available in large quantities in this MSW.

Many authors (Khan & Abu-Gharara (1991); Chang et al. (2007); Drudi et al. (2019)) considered that the calorific value of MSW is determined mainly by the presence of papers and plastics in its composition. Equations (6) and (7) are basically in function of the percentages of Plastics and Papers (except for Equation (6), which considers food percentage, but, for landfilled wastes, this value was considered 0), and they predicted well the calorific value of LMSW compound sample. Thus, it suggests that Plastics and Papers are the main categories responsible for the calorific value not only in fresh wastes but in landfilled wastes either. Moreover, plastics have low degradation rate, and their percentage inside landfills is huge (Table 1). The calorific values of landfilled plastics remain practically unchanged compared to fresh wastes (Ahmed, 2019).

The model of Wang et al. (2021) (Equation (7)), based on gravimetric composition, was the model that predicted the theoretical calorific value of ED with the lowest accuracy, with a MAPE value of 107.63%, proving not to be adequate to this compound sample. This result should be because the model was formulated for MSW compound samples and not for ED compound samples, and considered 3 variables: Food, Plastic and Paper, of which the ED compound sample lacks two of them (Food and Plastic). Therefore, using only the ED compound sample paper percentage in Equation 6 may result in low accuracy.

The prediction of calorific value of LMSW by the model of Wang et al. (2021) (Equation (7)) (MAPE value of 14.10%) was better than those predicted from the classic model of Steuer (Equation (4)) and nº 12 of Choi et al. (2014) (Equation (5)), which resulted in MAPE values of 53.86% and 23.92%, respectively (Table 3). One reason for this result is that the model (Equation (7)) was specifically developed for MSW and with data of solid wastes from many regions around the Globe, thus, it can be used more universally than many other models from the literature. Sheng & Azevedo (2005) also inferred that the larger the database used to build the model, the greater the accuracy of the estimate when using solid waste with different characteristics. Furthermore, Wang et al. (2021) reported that most of the data used for their model formulation came from developing countries in Asia. The similarity of MSW from developing countries such as Asia and Brazil favoured the application of Wang et al. 's (2021) model to the landfilled MSW.

4 CONCLUSION

The HHV and LHV of landfilled rubbers, plastics, DT, ED and LMSW were predicted using four different arithmetic mathematical models, two of them were based on elemental composition and the others on the gravimetric composition. Overall, the comparison of the theoretical calorific values of these landfilled MSW samples with their experimental calorific values suggested that different mathematical models were suitable for each case. In this research, a model based only on element C predicted better the calorific value of landfilled rubbers, plastics, and DT with MAPE values of 0.21, 4.31 and 1.18, respectively. Thus, simplistic mathematical models are recommended for predicting the calorific value of landfilled hydrocarbon-rich categories. On the other hand, both gravimetric composition models predicted better the calorific value of the LMSW compound sample (with MAPE values of 11.50 and

14.10, respectively). Although ED was constituted by five different landfilled waste categories, and it is not a hydrocarbon-rich waste, the elemental composition model predicted its calorific value better than gravimetric composition model.

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