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METHANE PRODUCTION AND BROMATOLOGICAL CHARACTERISTICS OF THE DIFFERENT FRACTIONS OF ORGANIC MUNICIPAL SOLID WASTE

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ABSTRACT
In some countries, garden trimmings are not considered part of urban solid wastes. Lignocellulosic substances contribute to heterogeneity, complicating the analysis of the organic fraction of municipal solid waste (OFMSW) and, subsequently, for methane production. Some of the substances contained in OFMSW are readily biodegradable, and others are not. This work analyses OFMSW from Mexico City and the methane production from its separate components. From OFMSW, nine fractions were visually identified and separated. Including bromatological and fibre analysis, the characterisation of OFMSW and its components was made to determine how the different substances influence methane production. Together, branches, dry leaves, fresh garden trimmings, unsorted wastes (mainly garden trimmings), kitchen paper, and waste vegetables represent 56% of OFMSW in weight. Fruit waste and unsorted organics contribute to 60% of the total methane production. Except for branches and dry leaves, methane production increases inversely with the content of lignocellulosic compounds. Animal waste, having the highest concentrations of proteins and lipids and the lowest in lignocellulosic substances, is characterised by the highest level of methane production. Fibre-rich fractions in OFMSW contributed with little or no methane production. Higher concentrations of lignocellulosic substances in the fractions resulted in lower methane production rates.

1. INTRODUCTION

By 2050, the world is expected to increase waste generation by 70 percent, from 2.01 billion tonnes of waste in 2016 to 3.40 billion tonnes of waste annually (Hoornweg et al., 2013). Individuals and governments make decisions about waste management that affect the daily health and cleanliness of communities. Increasing waste trends are particularly intense in less developed countries (Kaza et al., 2018). Waste production trends not only increase resource stress but also contribute to greenhouse gases. A transformation toward resource-circular systems and sustainable municipal solid waste management is necessary (Wainaina et al., 2019). Growing environmental pressure has caused regional/national targets to divert waste from landfills and increase the recycling and recovery rate. While developed countries struggle to reach a zero MSW production through recycling, developing countries struggle to avoid open dumpsites by implementing controlled landfill sites (Kumar et al., 2019; Manjunathaa et al., 2019).

A preferred treatment method for the organic fraction of municipal solid waste (OFMSW) is anaerobic digestion (AD) because it allows the production of methane as fuel, and the resulting solids (digestate) can be used for soil improvement (Möller and Müller, 2012). The whole AD microbial degradation process is divided into four consecutive biological processes: 1) the hydrolysis of complex organic molecules to soluble monomers takes place in the first step; 2) acidogenesis or fermentation is the process by which the soluble monomers from hydrolysis are converted to alcohols, volatile fatty acids (VFA), namely acetic, propionic and butyric acids, and CO_2 and hydrogen; 3) acetogenesis is the step where several of the previously

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produced VFA and alcohols are converted into acetate, which is an essential molecule used by methanogens as substrate and 4) methanogenesis is the final step where different archaea can use acetate, CO_2 and hydrogen to produce methane as a final product (Bajpai, 2017).

Methane from the organic fraction of the municipal solid wastes (OFMSW) is a potential energy source. Results from several studies indicate that biogas produced by microbial activity does not contain only CO_2 and CH_4, but also other compounds that need consideration when using this biogas as fuel to generate electricity (Rasi et al., 2006). Papurello (2019) demonstrates efficient biogas sampling procedures and precise analytical methods. Several undesired compounds need to be removed from biogas before using it as fuel. There are several standard processes to remove CO_2, hydrogen sulphide, and other sulphur compounds from biogas, but special attention needs to be paid to organic silicon compounds that cause abrasion in the engines (Ohannessian et al., 2008).

OFMSW heterogeneity (Naroznova et al., 2016) and complex composition (VALORGAS, 2010) are limiting factors of OFMSW for biogas production. Methane potential depends on substrate characteristics and biodegradability (Campuzano and González-Martínez, 2016). According to reports from VALORGAS (2010), Kobayashi et al. (2012), Naroznova et al. (2016), and Alibardi and Cossu (2016), the knowledge of OFMSW composition and characteristics allows the improvement of urban solids waste management and subsequent methane production. Eventually, it is possible to determine which fractions or components can be considered for methane production and which ones need to be avoided during source separation. According to the classifications in different countries, the contents of fiber-rich substances can significantly vary. For example, kitchen paper and garden trimmings are accepted as organic waste in countries like the United Kingdom, Finland, and Denmark. Still, they are not allowed in other countries like Norway and Sweden (Naroznova et al., 2016).

Geographic and socioeconomic aspects affect OFMSW composition (VALORGAS, 2010). Studies have been performed to determine how much methane or hydrogen can be produced according to the bromatological and chemical characteristics of the different OFMSW fractions (Kobayashi et al., 2012; Alibardi and Cossu, 2016; Naroznova et al., 2016; Edwiges et al., 2018). Every study classifies OFMSW according to their specific objectives, and there are essential differences between selected components. In Japan, Kobayashi et al. (2012) analyzed Kyoto OFMSW, and they found, in kitchen wastes, animal rests, vegetables, paper, cereals, food wrappings, tea and coffee bags, and some garden trimmings. In Italy, in an anaerobic digestion plant, Alibardi and Cossu (2016) found meat, fish, cheese, fruits, vegetables, pasta, bread, and some unidentifiable substances. In Denmark, Naroznova et al. (2016) characterized OFMSW in the city of Halsnæs. They classified the fractions as animal food waste, vegetable food waste, kitchen paper, vegetation waste, molded fibers, animal straw, dirty paper, and dirty cardboard.

Using bromatological and physicochemical analysis, several authors found that OFMSW fractions have different influences on methane production during anaerobic digestion. One concern about fiber-rich compounds in OFMSW are lignocellulosic compounds and their relative concentration of cellulose, hemicellulose, and lignin (Teghammar et al., 2010, Triolo et al., 2011). Edwiges et al. (2018) found that the biochemical methane potential (BMP) improved when the wastes contained higher amounts of lipids while lignin negatively affected methane production. Xu et al. (2014) also noted that methane production was negatively affected when the substrate was lignin-rich. Extractable substances, such as cellulose and other compounds, are desirable because they have a positive effect on methane production. Labatut et al. (2011) observed that the highest methane productions were from substrates rich in fat and carbohydrates and that the lowest rates were obtained with lignocellulosic-rich substances.

Lignocellulosic biomass is the most important and more abundant product from photosynthesis. In vegetal biomass, hydrogen bridges, forming microfibers with hemicellulose and covered by lignin compounds (Taherzadeh and Karimi, 2008), bind cellulose chains. Hemicellulose is the essential union between lignin and cellulose fibers, providing rigidity to the cellulose-hemicellulose-lignin compounds, resulting in highly recalcitrant compounds (Hendriks and Zeeman, 2009). High fiber concentrations in organic wastes indicate low biodegradability, and lignin presence is undesired during methane production in anaerobic digestion (Alibardi and Cossu, 2016; Fonoll et al., 2016). According to Campuzano and González-Martínez (2016), lignocellulosic compounds represent approximately 40% in weight in Mexico City's OFMSW, meaning that every kilogram of OFMSW contains 225 gVS/kg, and, from them, only 135 g are biodegradable. The remaining 90 g are slowly biodegradable or not susceptible to transformation to biogas; the authors did not mention which components contain higher amounts of lignocellulosic compounds.

Even though OFMSW is a potential source of bioenergy, it is crucial to determine how its composition affects the anaerobic digestion process. Independently of the specific local legislation, there will always be different substances in OFMSW. Paper and cardboard are generally present and also are cellulose-rich compounds (Kobayashi et al., 2012; Naroznova et al., 2016; González-Miranda et al., 2016). Fruits and vegetables are cellulose and fiber-rich substances and represent almost 74% of OFMSW (Nielfa et al., 2015; Naroznova et al., 2016; Edwiges et al., 2018). Animal rests are present in OFMSW in lower quantities and are not fiber-rich (Kobayashi et al., 2012; Naroznova et al., 2016).

Considering the discrepancies observed in other published research about OFMSW classification, this work aims to determine the influence of different compounds in the identifiable OFMSW fractions on methane production. For this purpose, it was necessary to identify and quantify OFMSW components according to their physicochemical and chemical characteristics.

2. MATERIALS AND METHODS

OFMSW from Mexico City was used for this purpose, considering that garden trimmings and market wastes are allowed as part of OFMSW.

2.1 OFMSW sampling and classification

OFMSW sampling and conservation was made on one day when source-sorted organic wastes are collected. Considering that between 380 and 450 trucks discharge solid wastes every day in the Coyoacán transfer station, eleven trucks were randomly selected and, from each one, approximately 100 kg were separated and thoroughly mixed; from the resulting amount, 200 kg were set apart according to the quartering method (ASTM D5231-92, 2016). Inorganic materials and plastics were hand-separated and discarded. The sample was distributed in 2-liter freezing bags, and they were immediately frozen at -20°C.

In the laboratory, approximately 20 kg of slowly defrosted OFMSW were placed in trays, and, carefully, all components were visually identified, manually separated, and grouped according to their apparent origin. To homogenize the separated and identified fractions before analysis, they were ground using a 0.35 W electric disc mill (DelRey, Mexico).

2.2 Biochemical methane potential tests

For biochemical methane production (BMP), an AMPTS II system from Bioprocess Control AB (Sweden) was used. The inoculum was anaerobic granular sludge from the wastewater treatment plant of a large beer factory in Mexico City. The granular sludge was washed three times using tap water and concentrating it using a centrifuge to separate exogenous dissolved substances from the solids. For BMP, VDI 4630 recommendations were followed: Inoculum to substrate ratio (ISR, as volatile solids) was 4:1; temperature, 35°C and per triplicate (VDI 4630, 2016). According to experiences from previous projects, the duration of the tests was set to 21 days (Campuzano and González-Martínez, 2015). Biogas sampling and analysis were performed daily. A blank only with inoculum was used as a reference (blank).

The theoretical biochemical methane production (TBMP) is widely used to estimate methane potential. Triolo et al. (2011) calculated TBMP after modifying the method proposed by Møller et al. (2004), where they included lignin with the following empirical formula, $C_{10}H_{13}O_3$, and with it, they calculated the TBMP of lignin through the Symons and Buswell (1933) equation resulting in a value of 727.1 $NLCH_4$/kglignin. Triolo et al. (2011) propose Equation 1 to calculate TBMP. Equation 1 includes lipids ($C_{57}H_{104}O_6$), protein ($C_5H_7O_2N$), carbohydrates ($C_6H_{10}O_5$), and lignin ($C_{10}H_{13}O_3$); values expressed as g/kgVS.

$$TBMP=(C_{57}H_{104}O_6\cdot 1014+C_5H_7O_2N\cdot 496+C_6H_{10}O_5\cdot 415+C_{10}H_{13}O_3\cdot 727\cdot 0.001 \qquad (1)$$

TBMP is used to evaluate the biodegradability of a substrate using Equation 2 (Triolo et al., 2011).

$$Anaerobic\ biodegradability = BMP/TBMP \cdot 100\% \qquad (2)$$

2.3 Analytical methods

The different fractions and original OFMSW were analysed for humidity, total solids (TS), volatile solids (VS), chemical oxygen demand (COD), Kjeldahl nitrogen (KN), ammonia nitrogen (NH4-N), total phosphorus (TP), and pH. These determinations were performed according to APHA (2005). Protein, grease and fats, total carbohydrates, lignin, cellulose, and hemicellulose were determined according to Van Soest (Van Soest, 1963, Goering and Van Soest, 1970) and Official Methods of Analysis of AOAC International (AOAC, 2012). Biogas composition was determined using an SRI 8610c gas chromatograph equipped with a thermal conductivity detector and stainless steel silica gel packed column 8600-PK1A using helium gas as carrier at a flow rate of 27 mL/min.

For carbohydrates fractioning, the method proposed by the Cornell Net Carbohydrate and Protein System (CNCPS) was used. This method separates the fractions according to their degradability. Structural carbohydrates were calculated as the difference between neutral detergent fibre and non-soluble protein. Non-fibrous carbohydrates or non-structural carbohydrates are the difference between total carbohydrates and structural carbohydrates (Sniffen et al., 1992, Lanzas et al., 2007).

3. RESULTS AND DISCUSSION

Approximately 20 kg OFMSW were overnight defrosted at 4°C. The visually identified fractions were: Food waste from animal origin (animal waste), flour products, fruits, vegetables, kitchen paper, dry leaves, branches (garden cuts), fresh trimmings, and a fraction was called unsorted as these wastes could not be visually identified or separated but mainly were related to garden trimmings and dry leaves. Table 1 shows a description of the substances found in every fraction; Figure 1 shows the fractions' images.

TABLE 1: Identified components in OFMSW.

Fraction	% OFMSW	Visually identified components
Fruits	36	Rests, peelings, and seeds from oranges, lemon, pineapple, watermelon, bananas, papaya, mamey (Pouteria sapota), mango, and avocado peeling and seeds, grapes, and tamarind shells and seeds
Vegetables	13	Jicama, carrots, different types of chilies, peanuts, potato peeling and rests, red beet, peas, fresh corn grains, garlic, onions, and seeds from sunflower
Animal waste	8	Red and white eggshells, beef leftovers and bones, chicken skin and bones
Flour products	3	Tortilla (typical Mexican flatbread from maize)
Fresh trimmings	6	Bugamvilia, fresh grass, pine needles, eucalyptus, palm, and ash tree leaves
Dry leaves	7	Leaves from different unidentified trees and maize leaves.
Branches	4	Different unidentified small and thin tree branches (from trimmings)
Kitchen paper	2	Paper napkins, kitchen paper, and some wax paper
Unsorted	21	Mostly from dry leaves and trimmings, in small pieces, unidentified

FIGURE 1: The identified OFMSW fractions (branches are not shown).

3.1 Characterisation of OFMSW fractions

3.1.1 OFMSW fractions

The fraction with the highest weight percentage is fruits (36%) followed by unsorted (21%) and then vegetables (13%) (Table 1). The fractions with the lowest contribution in OFMSW are kitchen paper (2%) and cereal waste (3%). Considering unsorted, dry leaves, garden trimmings, and branches together, garden wastes amount to 37% in weight; this last value is significant compared to reports from other countries (Naroznova et al., 2016; Kobayashi et al., 2016).

Vegetables, fruits, and fresh trimmings present the lowest solids concentrations with values from 22 to 28%. In comparison, the fractions with the highest solids concentrations are branches with 55%, followed by animal wastes and flour products with 45 and 44%, respectively (compare humidity in Table 2). When comparing these results with the ones Naroznova et al. (2016) found in Denmark, similarities can be found: they report 24% for vegetables and, in this research, 23 and 22% were determined for fruits and vegetables, respectively. For wastes from animal origin, Naroznova et al. (2016) report 41% solids concentration and 45% are observed in this research.

The fraction with the lowest VS corresponds to vegetables with 192 g/kg and the highest to branches with 475 g/kg. Naroznova et al. (2016) report values similar to the ones in this research: food animal wastes, 344 g/kg, vegetables, 223 g/kg, and vegetation wastes (garden trimmings), 240 g/kg; in the case of kitchen paper, they report 491 g/kg compared to 265 g/kg in this work. The VS/TS ratio is an indicator of the organic material concentration related to total solids: The highest VS/TS ratio belongs to fruits with 0.9, followed by cereals with 0.87, branches, 0.86, and kitchen paper, 0.86; the lowest value is for animal wastes

TABLE 2: Characterization of OFMSW fractions.

	[3] Humidity%	VS/TS	[3] VS g/kg	[3] Protein	[2] Lipids	[3] Total Carbohydrates	Hemicellulose*	Cellulose*	Lignin*
				g/kg_{VS}					
Animal	55±0.6	0.70	320±2.6	373±45.6	390-396	70±7.5	3	4	39
Kitchen paper	69±0.1	0.86	265±1.3	62±2.4	202-204	970±44.3	20	207	32
Flour	56±0.4	0.87	380±3.5	123±5.3	119-122	406±16.1	232	53	32
Vegetables	78±0.4	0.84	192±2.8	121±5.5	95-97	464±25.8	63	102	65
Fruits	77±0.2	0.90	206±4.3	94±3.0	78-83	505±12.2	7	121	32
Branches	45±0.1	0.86	475±4.9	44±2.3	93-100	451±14.5	155	37	401
Fresh trimmings	72±0.2	0.81	227±1.6	130±9.3	147-155	504±12.2	51	111	69
Dry leaves	64±0.2	0.84	306±2.4	89±5.9	156-176	394±13.6	49	98	68
Unsorted	[5] 66±0.5	0.73	[5] 252±4.0	131±4.3	170-189	294±18.6	62	33	165
OFMSW	[5] 71±1.1	0.78	[5] 228±3.0	168±4.7	133-136	791±41.3	9	102	53

*[3] Three replicas; [5] Five replicas; [2] In lipids only two replicas were made; both values are reported. *Average of three replicas; no standard deviations are available.*

with 0.7, containing eggshells and bones, and unsorted materials with 0.73. Campuzano and González-Martínez (2016) report a VS/TS ratio of 0.75 for other OFMSW samples in Mexico City; VS/TS of the OFMSW sample taken for this research is 0.78.

From Table 1 and Figure 2, the following observations can be drawn:

- Wastes of animal origin is the fraction with the lowest concentration of lignocellulosic substances (46 g/kgVS) and the highest in fat and protein.
- Fruits have the third-highest concentration of carbohydrates; fat and protein concentrations are relatively low. The concentration of lignocellulosic compounds is low but, with 160 g/kgVS, it is three times higher than the amounts in wastes of animal origin.
- Dry leaves contain high hemicellulose and lignin concentrations with 49 and 68 g/kgVS, respectively. Confusing can be that fat concentration is relatively high in dry leaves; it needs to be considered that the maize leaves found in OFMSW are disposed of after being used to wrap a traditional meal called tamales (fatty).
- Vegetables present higher concentrations in protein with 121 g/kgVS, and the concentration of degradable carbohydrates is higher than the average among the fractions with 299 g/kgVS. This fraction reports lower lignin concentrations than dry leaves but higher in cellulose and hemicellulose with 102 and 63 g/kgVS, respectively.
- Fresh trimmings, as expected, have higher cellulose and lignin concentrations with 111 and 69 g/kgVS, respectively. Nevertheless, it presents lower hemicellulose concentrations and is the third in protein concentration. The relatively high lipids concentration suggests that this fraction was previously in contact with other fat-rich materials.
- Kitchen paper has the highest cellulose concentration with 207 g/kgVS and the lowest lignin concentration with 32 g/kgVS; it also has the highest degradable carbohydrates concentration and the second place in lipids with 203 g/kgVS.
- Unsorted materials have third place in lipids and protein concentrations and one of the highest lignocellulose concentrations. Lignin is the second highest with 165 g/kgVS and, after animal rests, the lowest in degradable carbohydrates.
- Flour-rich substances present higher lignocellulosic concentrations, being hemicellulose the highest with 232 g/kgVS. Protein, lipids, and degradable carbohydrates are 123, 121, and 121 g/kgVS, respectively. As no amylase was used to determine the fiber, starch could not be avoided. Most probably, the starch interferes with the determination, and hemicellulose reports slightly higher values than expected.
- Of all fractions, branches have the highest lignocellulose concentrations with 401 g/kgVS. It has the lowest concentrations of protein and lipids and relatively high concentrations of degradable carbohydrates.
- OFMSW can be considered as a general average value of all determinations shown in Table 2.

The general characteristics of Mexico City's OFMSW are similar to the organic solid wastes from other countries. Table 3 shows a comparison of the OFMSW characteristics found in several papers with the ones reported in this research. Grinsted, Prague, Lisbon, and Padua report TS above 300 g/kg; under 300 g/kg are Mexico City, Verona, Copenhagen, and Southampton. Other cities like Cadiz, Kerala, Canton and Beirut, report values under 200 g/kg. Similar values can be found for VS in these same cities. The VS/TS value reported in this research is 0.78, which is

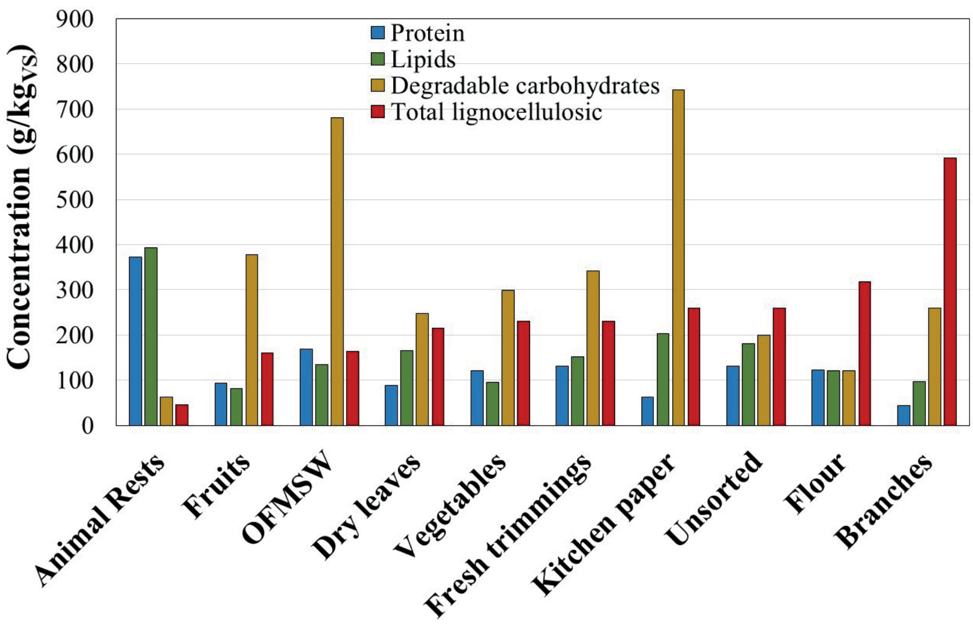

FIGURE 2: Comparison of bromatological characteristics in the separated fractions. The fractions are organized in ascending concentration of total lignocellulosic substances.

TABLE 3: Comparison of the OFMSW characteristics of this research with other countries. All values are wet based (raw OFMSW)

City	TS g/kg	VS g/kg	VS/TS -	KN g/kg	TP g/kg	COD g/kg	Reference
Kerala, India	187	169	0.91	1.04	-	-	Sajeena Beevi et al., 2015
Padua, Italy	305	281	0.92	7.7	1.16	575	Alibardi y Cossu, 2015
Verona, Italy	288	228	0.79	28	2.4	347	Bolzonella et al., 2005
Lisbon, Portugal	338	276	0.82	5.1	1.7	-	VALORGAS, 2010
Luton, UK	237	218	0.91	7.4	1.2	-	VALORGAS, 2010
Southampton, UK	277	244	0.88	8.9	1.9	-	Banks et al., 2011
Beirut, Lebanon	186	172	0.93	-	0.7	-	Ghanimeh et al., 2012
Prague, Chech Republic	325	231	0.71	4.5	0.7	-	Hanc et al., 2011
Cadiz, Spain	172	74	0.43	26.0	-	140	Forster-Carneiro et al., 2008b
Canton, China	184	113	0.62	4.2	0.4	-	Dong et al., 2010
Karlsruhe, Germany	255	225	0.88	7.8	-	350	Nayono et al., 2009
Copenhagen, Denmark	283	250	0.88	7.4	1.4	-	Davidsson et al., 2007
Grindsted, Denmark	356	307	0.86	6.3	-	431	Hartmann and Ahring, 2006
Mexico City, Mexico	297	223	0.75	5.4	1.8	304	Campuzano and González-Martínez, 2015
This research	290	228	0.78	6.1	3.9	294	

slightly lower than most of the values reported for other cities; the lowest VS/TS values of 0.43 and 0.42 correspond to Cadiz and Canton. Important differences are observed in macronutrients: KN presents values between 1.04 and 28 g/kg for Kerala and Verona, respectively. Grindsted, Copenhagen, Karlsruhe Luton, Lisbon, and Padua report similar KN to this research. TP values vary between 0.4 g/kg in Canton to 2.4 g/kg in Verona, and, surprisingly, this research reports 3.9 g/kg TP, the highest of all values. Table 3 shows that fruits, vegetables, and fresh trimmings contain elevated phosphorus concentrations. Except for Cadiz, other cities present higher COD values than the one from this research. No explanation can be offered about how COD can be related to TS because the reported values in Table 3 do not show any correlation.

3.1.2 Bromatological characteristics

According to the characteristics of the substances identified in the fractions, the following observations can be made.

Protein. As expected, animal wastes present the highest protein concentration with 373 g/kgVS and branches and paper, the lowest with 44 and 62 g/kgVS, respectively. The highest values agree with the ones reported by Kobayashi et al. (2012) for kitchen wastes and wasted animal rests. Alibardi and Cossu (2016) report higher concentrations for meat, fish, and cheese rest. Edwiges et al. (2018) report similar values as those in this work for protein in fruits and vegetables of 15.9%VS. Campuzano and González-Martínez (2016) report a total value of 152 g/kgVS for OFMSW, like the one in this research of 168 g/kgVS. From the total protein in OFMSW, animal wastes contribute with the highest value of 27%, and the lowest is for paper with less than 1% (Figure 2).

Lipids. Like protein concentration, animal wastes present the highest value with 393 g/kgVS; the lowest value is for fruits with 81 g/kgVS. Kobayashi et al. (2012) report similar results, and Alibardi and Cossu (2016) report similar results for fish, meat, and cheese wastes. For Brazil, Edwiges et al. (2018) report an average value of 4.5%VS for fruits and vegetables. From the total grease and oil in OFMSW, the highest concentration is for unsorted wastes with 25%VS and the lowest for paper with less than 2%VS (Figure 2).

Carbohydrates. Table 2 shows that the highest carbohydrate concentration is for paper with 970 g/kgVS. Coinciding with this work, Kobayashi et al. (2012) report 959 g/kgVS for wrapping paper. Alibardi and Cossu (2016), González-Miranda et al. (2016), and this work report that the lowest value for carbohydrates is for animal rests. Campuzano and González-Martínez (2016) report 529 g/kgVS for OFMSW, while this research determined a higher value with 791 g/kgVS. As a percentage of OFMSW, fruits correspond to 41% of the total carbohydrates, and animal wastes are the lowest with 2%.

Cellulose. Table 2 shows that kitchen paper has the highest cellulose concentration with 207 g/kgVS, followed by fruits with 121 g/kgVS. Kobayashi et al. (2012) and González-Miranda et al. (2016) show that paper also contains the highest cellulose concentration and Naroznova et al. (2016) indicate dirty carton with the highest cellulose followed by moulded fibres and fruits and vegetables with 120 g/kgVS. Kobayashi et al. (2012) report lower cellulose contents in wastes from animal origin with 1.6 g/kgVS, and Naroznova et al. (2016) also note lower cellulose content in waste animal origin with 2%VS. Edwiges et al. (2018) report average cellulose values in fruits and vegetables of 17.1%VS; in this research, the average cellulose concentrations in fruits and vegetables are 12.1 and 10.2%VS, respectively; from the total cellulose concentration in OFMSW, fruits contribute with 50% and wastes from animal origin with less than 1%.

Hemicellulose. Like cellulose, wastes from animal origin present the lowest concentration with 3 g/kgVS. In contrast, Kobayashi et al. (2012) found that "other kitchen wastes" have 2.7%VS and Naroznova et al. (2016) found 3%VS hemicellulose in dirty paper. González-Miranda et al. (2016) report similar values to those in this work for fruits with 1%VS. (10 g/kgVS). This work's highest values for hemicellulose are for flour (cereals) with 232 g/kgVS. Kobayashi et al. (2012) report the highest values for coffee and tea, while Naroznova et al. (2016) and Alibardi and Cossu (2016) note this for straw for pets and in vegetables. Edwiges et al. (2018) show average values in fruits and vegetables of 9.4%VS. From the total hemicellulose in OFMSW, unsorted wastes contribute 25% and animal wastes with less than 1%.

Lignin. The lowest lignin concentrations determined in this work were for paper, fruits, and flour with 32 g/kgVS, while the highest values are for branches with 401 g/kgVS, followed by unsorted wastes with 165 g/kgVS. Naroznova et al. (2016) found that, in their analysis, the lowest content was for animal rests with 2%VS and the highest for straw for domestic animals; they report the same lignin value for paper and dirty paper with 30 g/kgVS. Considering fruits, Naroznova et al. (2016) and this research agree on a lignin concentration of 4.5%VS and González-Miranda et al. (2016) and Edwiges et al. (2018) with a slightly higher value of 6.4%VS. Of the total lignin content in OFMSW, unsorted wastes contribute 37%, and paper with less than 1%.

Considering that lignocellulosic compounds are not readily biodegradable, Figure 2 compares the different OFMSW fractions according to the concentration of total lignocellulosic substances and degradable carbohydrates together with protein and lipids. Degradable carbohydrates are the difference between total carbohydrates and structural carbohydrates (cellulose and hemicellulose). The lowest values for total lignocellulosic substances are for animal wastes and the highest for branches. Degradable carbohydrates are high for kitchen paper with 743 g/kgVS, followed by OFMSW and fruits with 680 and 377 g/kgVS, respectively. Figure 2 also shows no direct relationship between carbohydrates and the concentration of lignocellulosic compounds.

3.1.3 Nutrients in OFMSW fractions

Table 4 shows COD and Kjeldahl and ammonia nitrogen, as well as total phosphorus concentrations. The highest COD corresponds to fresh trimmings with 1,395 g/kgTS, followed by fruits, animal wastes, unsorted, and flour with values between 1,287 and 1,222 g/kgTS. From the OFMSW fractions, the lowest COD is for branches with 742 g/kgTS. Considering total COD in OFMSW, fruits and unsorted together contribute 52% of the total.

Table 4 shows that values for Kjeldahl nitrogen are highest in animal rests (protein) with 42 g/kgTS. The lowest KN value was found in kitchen paper. The fractions animal rests, fruits, and unsorted contribute 72% of the total Kjeldahl nitrogen.

For ammonia nitrogen in OFMSW fractions (table 4), the highest value is for animal rests with 1.7 g/kgTS and the lowest for flour products (mainly tortilla) with 0.4 g/kgTS. All other fractions contain low NH4-N concentrations and, compared to KN, they can be considered negligible for the purpose of methane production. Like KN in OFMSW fractions, NH4-N contribution is mainly attributed to unsorted, fruits, animal, and vegetables, with a total of 77% of the total. Campuzano and González-Martínez (2016) report similar values for Kjeldahl nitrogen for OFMSW with 18.2 g/kgTS.

OFMSW is mixed at the origin, during transportation, separation, and selection of fractions; these procedures contribute to transferring fluids among the fractions and the liquids' partial homogenization. Total phosphorus concentrations in branches are lowest with 2.4 g/kgTS, which is less than 1% of OFMSW; vegetables have the highest with 18.9 g/kgTS (15% of OFMSW). Fruits follow with 15.9 g/kgTS (35% of the total in OFMSW). In contrast, González-Miranda et al. (2016) report that unsorted has the highest value with 67.6% of the total in OFMSW and paper the lowest with 0.4%.

3.2 Methane production

Except for branches, the curves in Figure 3 show diauxic behaviour. During the first three days, methane production increased rapidly, and then it slowed down and, after sever-

TABLE 4: COD, Kjeldahl nitrogen (KN), ammonia nitrogen (NH4-N), and total phosphorus (TP) in OFMSW fractions.

	COD*	KN**	NH_4-N**	TP*	COD	KN	NH_4-N	TP
	g/kg_{TS}				% OFMSW			
Fruits	1287±71.4	13.4±0.4	1.0±0.07	15.9±0.8	29	22	20	35
Vegetables	1311±90.9	16.3±0.7	1.3±0.08	18.9±0.2	10	9	11	15
Animal	1274±45.6	42.0±1.8	1.7±0.12	8.3±0.4	12	30	18	8
Flour	1222±58.4	17.1±0.7	0.4±0.03	9.0±0.1	4	4	1	3
Fresh trimmings	1395±81.0	16.5±1.2	1.1±0.09	14.0±0.4	6	5	5	6
Dry leaves	1224±72.4	12.0±0.8	1.2±0.10	10.5±0.3	8	6	8	7
Branches	742±23.4	12.8±0.6	1.3±0.01	2.4±0.3	5	3	8	1
Kitchen paper	1430±64.0	8.5±0.4	0.7±0.06	10.5±0.5	3	1	1	2
Unsorted	1265±77.2	15.3±0.5	1.4±0.12	12.9±0.6	23	20	28	23
OFMSW	1014±47.2	21.1±0.5	3.6±0.11	13.5±0.6	100	100	100	100

** Seven replicas, ** Three replicas*

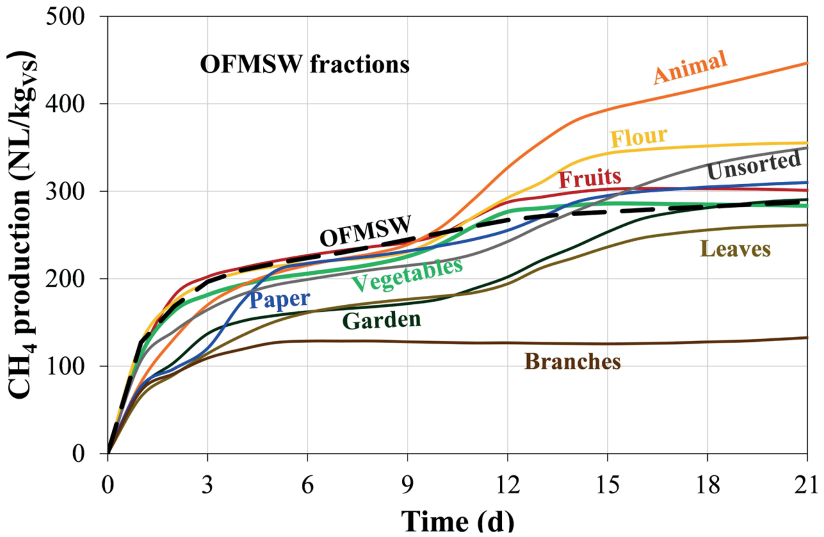

FIGURE 3: Methane production from OFMSW fractions.

al more days, it increased again to reach a point where the production became deficient until the end of the 21 days.

Animal waste and unsorted are the only fractions where low methane production continues after day 21. Branches produce methane only until day 5. On the third day, fruits and vegetables show increasing methane production, representing more than 60% of the methane produced in 21 days, indicating that these fractions contain readily biodegradable substances. From day 4 to 9, all fractions produced little methane, and, after day 10, the production increased in all fractions except in branches. After day 18, the methane production receded except for animal rests and unsorted organics. The diauxic behaviour can be related to several processes during anaerobic digestion: Readily degradable substances will be transformed first, and then other substances that require longer degradation times. Analysis of the methane production curves in Figure 3 allows determining the behaviour of the previously described sequence (Campuzano and González-Martínez, 2015).

Table 5 shows methane production and concentration in the biogas after 21 days for every fraction and OFMSW. The highest methane production belongs to animal wastes with 447 NL/kgVS, and the lowest belongs to branches with 133 NL/kgVS. This can be related to their composition: Animal waste has the highest protein and lipids concentrations and the lowest in lignocellulosic compounds; branches have the highest concentrations in lignocellulosic substances and the lowest in protein and lipids (see Figure 2). Labatut et al. (2011) conclude that they obtained the highest methane production from substrates rich in fat and carbohydrates and the lowest rates with lignocellulosic-rich substances. Kitchen paper absorbs fluids from other fractions, and because of this, it presents a relatively high methane production with 310 NL/gVS. It can be concluded that methane production decreases with increasing concentrations of lignocellulosic substances. Xu et al. (2014) also noted that methane production was "negatively affected" when the substrate was lignin-rich and that extractable substances, such as cellulose and other compounds, are desirable because they have a "positive" effect on methane production. When Xu et al. (2014) calculated the methane production based on volatile solids, they concluded that low methane

TABLE 5: Biogas and methane production after 21 days' anaerobic digestion. Because of the characteristics of this test, only one curve was determined for every substrate.

Fraction	CH_4 in biogas %	CH_4 production NL/kg$_{VS}$	TBMP NL/kg$_{VS}$	Anaerobic Biodegr. (%)	CH_4 in fraction %
Fruits	55	301	361	84	35.1
Vegetables	56	283	397	71	12.0
Animal waste	62	447	641	70	11.7
Flour	53	355	375	95	3.3
Fresh trimmings	61	291	477	61	5.5
Dry leaves	61	261	425	61	5.8
Branches	64	133	599	22	1.6
Kitchen paper	60	310	662	47	1.9
Unsorted	58	350	489	72	22.7
OFMSW	55	288	586	49	100

production is related to low VS and vice versa. Fruits represent the highest contribution to total methane production in OFMSW with 35.1%, followed by unsorted with 22.7%. Fruits, unsorted, vegetables, and animal rests together represent 81.5% of the total methane production from OFMSW. Table 5 shows that methane concentration in the biogas for OFMSW was 55% and that animal rests, fresh trimmings, dry leaves, branches, and kitchen paper had methane concentrations above 60%, indicating healthy anaerobic digestion.

Figure 4 compares experimentally determined methane production (BMP) with the theoretical one (TBMP), with and without considering the presence of lignocellulosic substances in the fractions. TMBP represents the amount of methane produced from all organic material in the sample, and it does not consider the complexity of the organic substances. Although lignocellulosic substances are considered recalcitrant to microbial degradation, several of their components, such as cellulose and hemicellulose, can be transformed under anaerobic conditions (Paul and Dutta, 2018). When these components are closely linked to lignin, they become unavailable to the microorganisms. As lignocellulosic compounds are not readily biodegradable or biodegradable, Figure 4 shows that, in all cases, TMBP has higher values than BMP.

Except for animal waste, all other fractions show that TBMP with lignocellulosic substances is higher than without them. This difference indicates that lignocellulosic substances contain biodegradable molecules, most probably hemicellulose and cellulose. Surprisingly, flour showed the highest biodegradability with 95%, followed by fruits with 84% and unsorted with 72%. As expected, branches has one of the highest TBMP and the lowest experimental BMP with 22% of the theoretical. Figure 4 also shows that TBMP, considering the presence of lignocellulosic substances, in all cases, has higher values than without them, but these differences are slight. It can be concluded that the presence of lignocellulosic substances in the different OFMSW fractions contributes little to methane production.

In fruits, vegetables, and unsorted, the TBMP without lignocellulosic substances and the experimental values are similar, meaning that BMP was produced from readily biodegradable substances. This can also mean that lignocellulosic substances have lower lignin concentrations or that the lignin clusters did not prevent biodegradable carbohydrates from biodegradation.

4. CONCLUSIONS

From Mexico City's OFMSW, nine fractions were visually identified, from which branches, dry leaves, fresh garden trimmings, unsorted wastes (primarily garden wastes), kitchen paper, and vegetable wastes together contain lignocellulosic compounds with 56% in weight. Together with fruit-waste and unsorted organics account for 60% of total methane production. Branches contain the highest concentration of lignocellulosic compounds, and it delivers the lowest methane production. Much differently, animal rests have higher protein and lipids concentrations and lower lignocellulosic substances leading to the highest level of methane production. Fibre-rich fractions in OFMSW contributed with little or no methane production. The methane production obtained in the laboratory from all fractions and OFMSW resulted in lower values than the theoretical ones.

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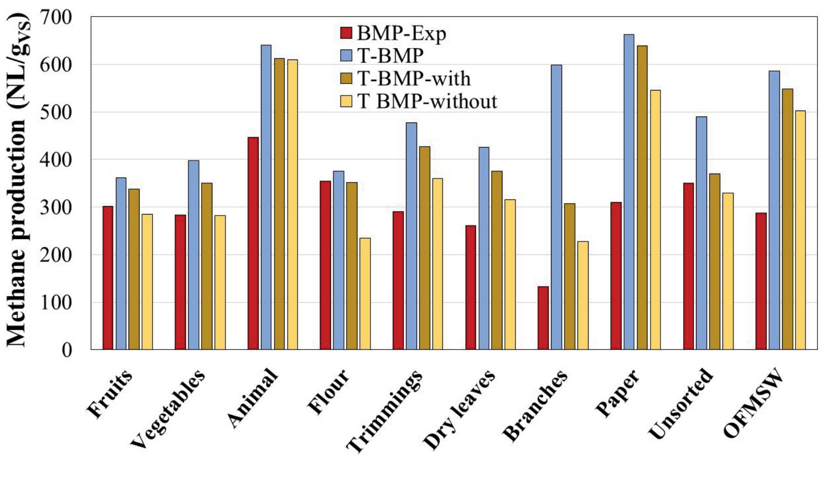

FIGURE 4: Methane production from OFMSW fractions after 21 days reaction. BMP-Exp (experimental); T-BMP (theoretical BMP); T-BMP-with (lignocellulosic substances); T-BMP-without (lignocellulosic substances).

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