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FORMATION OF DIOXINS AND FURANS DURING MUNICIPAL SOLID WASTE GASIFICATION

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Abstract - Thermal treatment is an interesting strategy to dispose of municipal solid waste: it reduces the volume and weight of the material dumped in landfills and generates alternative energy. However, the process emits pollutants, such as dioxins and furans. The present study evaluated MSW gasification-combustion integrated technologies in terms of dioxin and furan emission; and compared the obtained data with literature results on incineration, to point out which operational features differentiate the release of pollutants by these two processes. The results show that the process of integrated gasification and combustion emitted 0.28 ng N^{-1} m^{-3}, expressed in TEQ (Total Equivalent Toxicity), of PCDD/F, less than the maximum limits allowed by local and international laws, whereas incineration normally affords values above these limits and requires a gas treatment system. The distinct operational conditions of the two thermal processes, especially those related to temperature and the presence of oxygen and fixed carbon, led to a lower PCDD/F emission in gasification.
Keywords: Gasification; Municipal Solid Waste; Pollutants; Dioxins; Furans.

INTRODUCTION

The dibenzo-p-dioxins (PCDDs) and the polychlorinated dibenzofurans (PCDFs) constitute a group of persistent pollutants that inexorably originate from thermal and combustion operations (Altarawneh *et al.*, 2009). The chemical and toxicological properties of these compounds rely primarily on the number and position of chlorine atoms bound to the two aromatic rings (Altarawneh *et al.*, 2009). Certain dioxin and furan isomers are well known for their toxicological features—they exert carcinogenic and mutagenic effects. One classic example is the dioxin isomer with chlorine substituents in positions 2, 3, 7, and 8, or 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), which is among the world's most toxic substances (Huang and Buekens, 1996; Assunção and Pesquero, 1999).

PCDD/PCDF emissions from incineration processes were first detected in 1977 (Olie *et al*., 1977). Since then, scientists have assessed this type of emission by an array of thermal processes that also involve integrated gasification and combustion processes (Huang and Buekens, 1996). The release of dioxins, furans, and other pollutants during waste incineration accounts for its environmentally negative reputation (Cunliffe and Williams, 2009). Once PCDDs and PCDFs enter the atmosphere, they are subject to chemical, physical, and biological transformations, ultimately contaminating the soil, water bodies, and sediments (Martens *et al*., 1998).

In Brazil, where the present study takes place, the

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organization which is responsible for establishing national norms and standards of pollution control is CONAMA ("Conselho Nacional do Meio Ambiente" – National Council of the Environment). It established that dioxin and furan emissions can not exceed 0,5 ng TEQ/Nm^3 during thermal treatment of waste.

The present paper assessed the municipal solid waste (MSW) gasification in a horizontal chamber, with post-combustion of the generated gases, in terms of the dioxins and furans emitted along with combustion gases. To this end, the MSW will be transported through a mobile grit gasifier coupled to a torsional combustion chamber. We will compare the results with literature data on the incineration process, to find out which operational features differentiate dioxin and furan emission by these two processes, incineration technology and gasification-combustion technologies.

Incineration and Gasification

Industrialized nations generally employ incineration/combustion and gasification to generate energy and to treat waste (Tabasová *et al*., 2012). The current lack of landfills or even their closure has made solid waste treatment by thermal processes an attractive strategy. Moreover, both gasification and incineration reduce waste mass and volume, destroy hazardous residues, and recover energy (Martens *et al*., 1998).

It is possible to achieve energy recovery by reusing heat, producing electric energy, or generating alternative fuels by the Fisher-Tropsch process (Tabasová *et al.*, 2012). Nevertheless, thermal MSW treatment poses some drawbacks: it releases air pollutants together with the combustion gases, the ashes contain hazardous compounds, and the water used in some specific points of the equipment becomes contaminated.

Incinerators and gasifiers designed to treat waste have to meet the restrictive requirements of environmental agencies and are always subject to intense monitoring. It is sometimes necessary to install gas treatment systems, which require high investment (Alencar Júnior and Gabaí, 2001).

Gasification technology has been widely applied to produce chemicals and fuels. Current trends in the chemical and oil industry point to the growing use of this process to obtain synthesis gas. This is happening for two main reasons: (1) gasification furnishes a consistent and high-quality gas, and (2) a large variety of materials can feed the system (Orr and Maxwell, 2000).

During gasification, partial oxidation at high temperature (between 773 and 1673 K) and variable pressure (from 10^5 to 33.10^5 Pa) convert biomass, or any solid or liquid carbonaceous fuel, into a high-energy gas (Morrin *et al.*, 2011); most of the feedstock thermally decomposes into the gas. Unfortunately, small amounts of sub-products also originate during the process, including tar, coal, and ash (Cohce *et al*., 2011). Gasification involves endothermic chemical reactions that demand heat and generate carbon monoxide (CO), hydrogen (H_2) and other compounds. Depending on the reactor design and operational conditions, the process also affords methane and hydrocarbons (Singh *et al.*, 2011).

There are two types of gasification processes, a direct one and another indirect. In direct gasification, also known as auto-thermic, the process occurs in a single reactor, where the exothermal oxidation of the carbon takes place. Direct gasifiers normally operate using air or oxygen as oxidizing agents. In this case the heat necessary for the process is produced inside the reactor (Vitasar *et al.*, 2011), since the oxidation reactions provide the energy to maintain the high temperature of the process (Belgiorno *et al.*, 2003). In the indirect process, known as allothermic, the gasification occurs with an external energy source. Water vapour is used as the most common gasifying agent; it is easily produced and increases the amount of hydrogen in the produced gas by reforming (Singh *et al.*, 2011).

The gasifiers, in which the gasification process occurs, are classified according to the following factors (Moura, 2012):

I. Calorific heat of the product gas (low – up to 5 MJ/Nm^3; medium – from 5 to 10 MJ/Nm^3; or high – from 10 to 40 MJ/Nm^3);

II. Type of gasifying agent (air, steam, oxygen or hydrogen);

III. Movement direction of the feeding material and gasifying agent (updraft, downdraft; cross-draft or fluidized bed);

IV. Operational pressure (atmospheric or pressurized – up to 6 MPa);

V. Feeding material (industrial waste, municipal solid waste, biomass/wood).

Usually the gasifiers are internally made from refractory material, covering the combustion zone or even the whole gasification chamber, to protect the metallic parts and avoid the loss of energy by heat exchange. The most used and known gasifiers are the fluidized bed reactor and the fixed bed reactor.

During incineration, solid waste burns and directly generates thermal energy. As for gasification, the waste is first transformed into a gaseous product with enough heat power to produce thermal, me-

chanical (engines), or electric energy (Tanigaki *et al*., 2012).

Waste incineration is one of the most frequently employed technologies to process waste thermally and it can be applied to several types of materials. This process occurs under an excess of oxygen, to ensure complete oxidation. MSW incineration can reduce up to 90 and 75% of the initial waste volume and weight, respectively (Tabasová *et al*., 2012).

Research into dioxin and furan formation has targeted MSW incinerators—elevated dioxin concentrations occur in the fly ash and gas flow during the incineration process (Huang and Buekens, 1996).

Dioxin and Furan Formation

Dioxin and furan generation is a complex phenomenon that involves multiple solid- and gas-phase reactions between minimum amounts of reagents. During thermal waste destruction, dioxins and furans are known to arise together with combustion gases, fly ash, and even slag (McKay, 2002).

Researchers have examined two main hypotheses regarding the mechanism of PCDD and PCDF formation during combustion, namely the "De Novo Synthesis" (PCDD/PCDF production from elemental carbon) and dioxin and furan generation from precursors. These hypotheses are not exclusive; indeed, they may take place simultaneously during burning of the carbonaceous material (A.J. Chandler and Associates Ltd., 2006).

The mechanisms of PCDD/PCDF generation during combustion remain unclear—their concentration is low, so their quantification requires complex analytical instruments and a continuous analytical method that provides real-time information (Cunliffe and Williams, 2009). What is known is that dioxins and furans originate via not yet clarified homogeneous and heterogeneous routes.

The homogeneous route is the most probable source of these pollutants inside the combustion chamber; this route involves gas-phase reactions of chlorinated organic precursors like chlorobenzenes and chlorophenols, at higher temperatures (between 673 and 1073 K) (Stanmore, 2002). Even though it is known that dioxins and furans emerge during combustion, researchers used to believe that the high temperatures of the incineration oven destroyed them. However, PCDDs and PCDFs might arise after the gas flow leaves the combustion chamber; that is, when the gas goes through an air pollution control device that operates at lower temperatures (between 473 and 763 K) (Düwel *et al*., 1990; Reis, 2009).

Heterogeneous reactions account for dioxin and furan formation in the post-combustion region. They comprise two reaction pathways: (1) The *de novo* synthesis, in which the carbonaceous matrix burns with simultaneous oxidation and chlorination. Low oxygen concentrations (less than 2%) may diminish the rate of PCDD/PCDF production via the *de novo* synthesis (Stanmore, 2002). (2) Assisted catalytic coupling of the precursors—incomplete organic waste combustion in the incinerators culminates in organic fragments that can further serve as precursors of dioxin and furan molecules on the fly ash surface (McKay, 2002).

Transition metal species, especially copper and iron, exert a strong catalytic effect on PCDD/PCDF formation via the two heterogeneous routes (Altarawneh *et al*., 2009; Cunliffe and Williams, 2009). Experiments on a lab scale and process modeling have aided researchers in understanding the mechanisms of dioxin and furan production (Ruuskanen *et al*., 1994; Shao *et al*., 2010; Li *et al*., 2012).

Briefly, thermal processes produce PCDDs/PCDFs if the following conditions apply (Huang and Buekens, 1996; Cabrita *et al*., 2003; Suzuki *et al*., 2004; Altarawneh *et al*., 2009):

1. Presence of a fixed carbon source, fly ash, to enable the *de novo* synthesis in the post-combustion or cooling region;
2. Presence of chlorinated compounds, formation precursors, during combustion and after cooling of the exhaust gases;
3. Presence of catalysts (e.g., copper and/or iron) in the fly ash;
4. Oxidizing atmosphere, between 10 and 15% oxygen, in the cooling region;
5. Process temperatures around 473 and 873 K, with pollution control equipment operating between 473 and 773 K.

EXPERIMENTAL SECTION

A moving grit gasifier was employed to evaluate dioxin and furan emission during gasification (Figure 1) (Lopes *et al*., 2011). The equipment was fed with municipal solid waste (MSW), to generate and subsequently burn the synthesis gas. The device was fed manually; the combustion system was controlled manually, as well. The gasified MSW was provided by a landfill that receives waste collected from 14 small municipalities of the Brazilian states of Santa Catarina and Paraná, and air was used as gasifying agent.

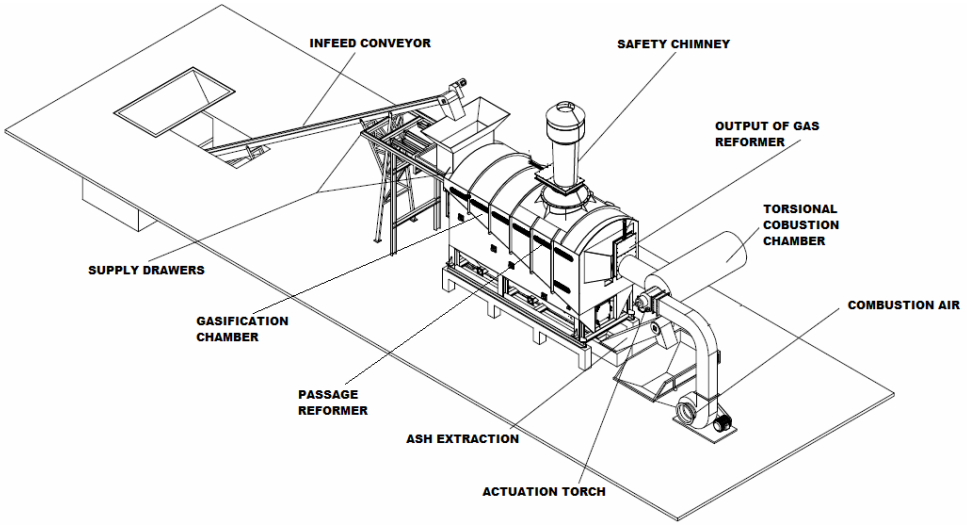

Figure 1: Scheme of the equipment (gasifier with the combustion chamber) used in the process of MSW gasification.

To obtain a syngas with combustible properties capable of maintaining an auto-sufficient combustible system, rigid control of pyrolysis, gasification and reforming reactions is necessary. The optimization of each step of the process is made in real time, according to the responses of the remote sensors, which are located according to their specificity in strategic points, where the external interventions can immediately act on the distortions and interferences caused mainly by the heterogeneity of the feeding material.

A gasification system with a horizontal chamber moved by grits, which presents a differentiated morphology adequate for each function, was designed for this study in order to reconcile the availability of reagents and energy in each step. It contemplated surface area, physical condition, size distribution, rate of homogeneous scattering, chamber area, pressure run, directed flow, pressure drop, turbulence, gas velocity, retention time and chamber volume.

The working process conditions are the following:

- Sub-stoichiometric environment: Control the addition of gasifying agent punctually according to local demand in the reactor, informed by temperature sensors and strategically arranged pressure sensors.
- Temperature range: A gradient of 630 to 680 ºC, distributed homogeneously in the processed material.
- Working pressures: all gas produced by the processes of drying, pyrolysis and gasification are immediately pulled into the posterior chambers by the difference of pressure.
- Carriage rate: Different speeds in the material movement in each step guarantee a better use of the internal conditions of the reactor.

In this process there is no storage or treatment of the combustible gases, because once already in the gas and superheated state, they can be consumed in the downstream output of the generator or reactor where they were produced.

Characterization of Municipal Solid Waste

The MSW fed into the gasifier was grossly shredded, and no adicional treatment was done. The gravimetric composition of the MSW is presented in Table 1 and the characterization of the MSW is demonstrated in Table 2.

Table 1: Gravimetric composition of MSW gasified in a moving grit gasifier.

Components	Gravimetric composition %
Organic residues	47.9
Paper and cardboard	16.6
Carton packaging	1.9
Plastics	16.1
PET	1.7
PEAD	0.7
PVC	0.4
PEBD	8.6
PP	3.3
PS	1.2
Other plastics	0.2
Diapers and absorbents	5.4
Leather, textiles and wood	4.7
Rubber, tires, etc.	0.6
Total of combustible waste	93.2
Total of inorganic waste (not combustible)	6.8

Table 2: Characteristics of the municipal solid waste gasified.

Characteristics of MSW	% mass MSW
C	25.95
H	3.21
S	0.15
N	0.10
O	18.11
Cl	0.03
H_2O	49.08
Ashes	3.36

The UCV (upper calorific value) of the MSW used in the gasification was 10149 $kJ.kg^{-1}$ and the LCV (low calorific value) was 8693 $kJ.kg^{-1}$.

Ash Analysis

The characterization and classification of the ash produced during gasification were performed according to the standards referenced by the Brazilian Association of Technical Standards (ABNT) and the Standard methods.

The NBR 10004:2004 (ABNT, 2004a) was used for the classification of the waste analyzed. For the solubilized and leached extract experiments NBR 10005 (ABNT, 2004b) and 10006 (ABNT, 2004c), respectively, were applied.

For analysis of the extracts the Standard Methods for the Examination of Water and Wastewater (APHA *et al*., 2005) were employed.

Sample Collection

The method 023 of the United States Environmental Protection Agency (USEPA, 1991) was used for sample collection and analysis, to determine polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from municipal waste combustors.

Combustion gas samples for analysis of dioxins and furans were collected from the exhaust stack of gases originated in the synthesis gas combustion chamber, without any previous treatment.

A total of three samplings were performed; each sample of exhaustion gases was bubbled in the impingers with different content for approximately 3 hours. The sampling equipment (Figure 2) contained a glass fiber filter, a condenser, a trap, and four impingers — the first and the second impingers contained distilled water, the third was empty, and the fourth contained silica gel. The impingers were replaced before each sampling. The samplings were performed using a system for isokinetic sampling with dry gas meter, orifice plate and calibrated s-pitot tube.

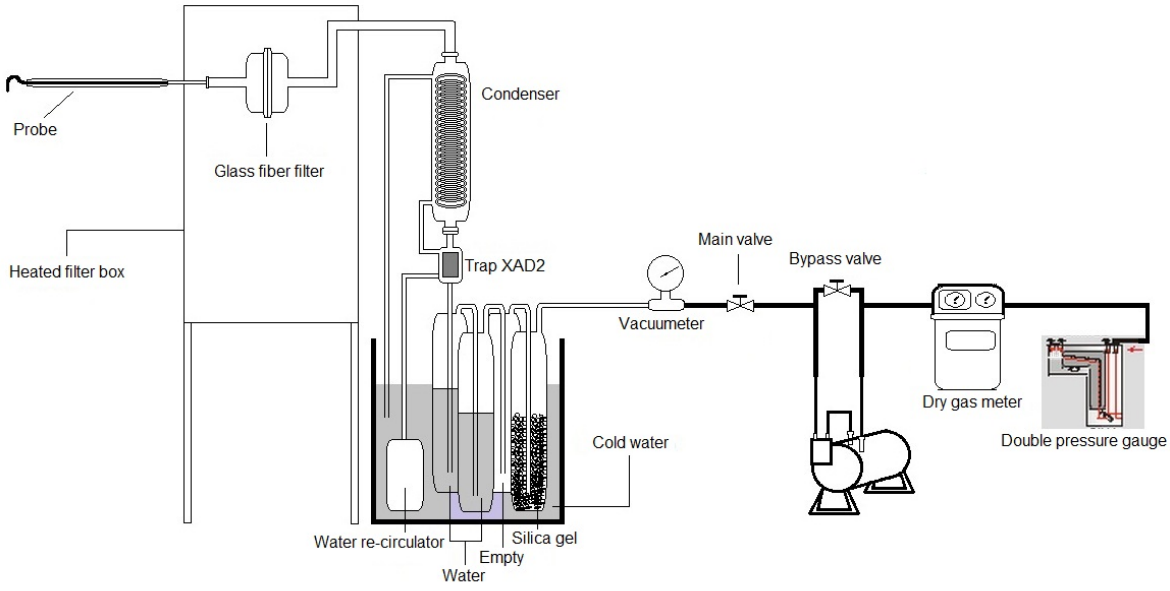

Figure 2: Schematic representation of the sampling device used during analysis of dioxins and furans.

The impingers were weighed before and after sampling, to obtain the mass of condensed water (combustion gas moisture). To sample dioxins and furans, a trap was used with 40 g of XAD-2 resin. A glass fiber filter was also used at the beginning of the experimental setup, to retain particulates.

Sample Extraction

The extraction of the samples containing dioxins and furans followed the procedures of the EPA method 23 (USEPA, 1991). The sample recovery and extraction were performed as described in Table 3.

Dioxin and Furan Analyses

Dioxins and furans were analyzed according to the method EPA-023 (USEPA, 1991), using Gas Chromatography coupled with High-Resolution Mass Spectrometry (resolution of 1:10000 with a stability of +5 ppm). Immediately prior to analysis, a 20:l (v/v) aliquot of the recovery standard solution (from Table 1 of method 23 - USEPA, 1991) was added to each sample. A 2:1 (v/v) sample of the extract was injected into the gas chromatograph. Sample extracts were first analyzed using the DB-5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's. When tetrachlorinated dibenzofurans were detected in this analysis, another aliquot of the sample was analyzed in a separate run, using the DB-225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. The same analysis was conducted for a reference solution containing known concentrations of dioxins and furans, for comparison purposes.

Table 3: Description of the sample recovery and extraction for the dioxin and furan analyses.

Container (storage)	Part of the sampling apparatus	Sample recovery	Sample extraction
Container 1	Filter	The filter, the particulate matter and the filter fibers which adhere to the filter holder gasket were carefully transferred to a soxhlet apparatus, along with the resin.	Sample was added 100:l of the internal standard solution (a stock standard solution containing the isotopically labeled PCDD's and PCDF's – concentration according to Table 23-1 of USEPA method 23) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of container 1, and the concentrate from container 2. Cover the contents of the extraction thimble with a cleaned glass wool plug to prevent the XAD-2 resin from floating into the solvent reservoir of the extractor. The extraction was carried out with toluene for 16 hours. The temperature was adjusted to cycle 3 times per hour. After cooling the system, the toluene extract and 3 rinses of 10 mL were concentrated (until 10 mL) on a rotary evaporator. The remaining solution was used to perform the chromatographic analysis.
Absorbent module	XAD-2 resin	The module with the resin was removed from the train, tightly sealed at both ends and later transferred to the soxhlet extractor.	
Container 2	Probe and cyclone	The probe and cyclone were washed with a solution of methanol and methylene chloride, and the solution was stored. The solution was concentrated (at temperature less than 310.15K), then it was added to the soxhlet apparatus along with the resin and filter.	
Container 3	Probe and cyclone	Both were also washed with toluene, and the solution stored.	Sample was added 100:1 of internal standard solution* to the solution, then concentrated to a volume of about 3-5 mL (on a rotary evaporator with temperature less than 310.15K); the container 3 was rinsed 3 times with toluene, and the rinse solution was added to the rotary evaporator and concentrated to near dryness. The extraction was separately analyzed.

* isotopically labeled PCDD's and PCDF's at known concentrations under the heading "Internal Standards" in 10 mL of nonane.

The gas chromatography operational conditions are described in Table 4.

Table 4: Operational conditions during the chromatography and spectrometry analysis.

Parameters	Conditions
Gas Chromatograph	
Carrier gas	Helium 1-1-2.10^{-8} $m^3.s^{-1}$
Oven	Initially at 423 K Raised to 463 K and then up to 573 K
High resolution mass spectrometer	
Resolution	10000 m/e
Ionization mode	Electron impact
Source Temperature	523 K

Toxicity Equivalence Factors (TEQFs) have been used to correlate the toxicity of various compounds belonging to the group of dioxins and furans; the most toxic compound in this class is 2,3,7,8-TCDD, which has a TEQF equal 1. Therefore, each compound must have its concentration multiplied by its respective equivalence factor. The sum of these final values constitutes the total toxicity relative to 2,3,7,8-TCDD (Equation (1)).

$$\text{Total Equivalent Toxicity (TEQ)} = \sum_{n=1}^{k} C_n \times TEF_n \quad (1)$$

Toxicity Equivalence Factors (TEQF) established by the local legislation, CONAMA – Conselho Nacional do Meio Ambiente - resolution 316 (CONAMA, 2002), were employed; these factors agree with internationally accepted values established by NATO - North Atlantic Treaty Organization (NATO, 1988).

RESULTS

Ash Characterization

The characterization analysis of the ash produced in the gasification of MSW showed that the lixiviated extract of ash presents concentrations of substances indicated in Annex F of the NBR 10004 (ABNT, 2004a) that are below the established limits, so the ash from the gasification process can be classified as non-hazardous waste. However, the solubilized extract presented higher concentrations of some substances, demonstrated in Table 5, which makes the ash a non-inert waste, that must be properly disposed.

Dioxins and Furans

The dioxins and furans were sampled in the combustion gas flow. The conditions of the samplings are presented in Table 6.

Table 5: Analysis results of the solubilized extract of ashes.

Determinated compound	Results (mg/L)	Maximum content in mg/L in the solubilized extract
Aluminum	27.5	0.2
Barium	1.1	0.7
Chlorides	2734.0	250.0
Phenol	0.04	0.01
Sulfate	262.0	250.0
Sodium	1069.7	200.0

Table 6: Parameter during sampling of dioxins and furans.

Parameter	Sampling			mean
	1	2	3	
Sampling time	2h48min	2h48min	2h50min	-
Gas flow rate - normal dry basis ($mg.N^{-1}m^{-3}$)	2071	2078	2086	2078
Gas flow rate – chimney conditions ($m^3.h^{-1}$)	7980	8146	8229	8118
Gas temperature (K)	872.15	881.15	880.15	877.82
Average isokinetic (%)	105	104	104	104
Average gas velocity ($m.s^{-1}$)	5.76	5.88	5.94	5.86
Gas humidity	8.61	9.28	9.91	9.27
Content of carbon dioxide (%)	11.6	9.00	10.2	10.3
Content of oxygen (%)	3.40	5.00	3.00	3.80
Content of nitrogen (%)	85.0	86.0	86.8	85.9

The chromatographic assays conducted for three samplings of municipal solid waste gasification in a mobile grit gasifier furnished the mass of dioxins and furans generated in each case. Application of the TEQFs afforded the results depicted in Table 7.

The results in Table 7 revealed that the third sampling contained the largest mass of dioxins and furans. This was a consequence of alterations in operational conditions along gasification. System feeding and combustion were controlled manually; the process was stable during the first two collection stages. Changes that occurred during gasification—excess air present in the chamber during combustion and variations in the amount of atmospheric air that entered the gasification chamber—modified the process temperature. This culminated in different conditions over time, favoring dioxin and furan formation. Higher pollutant generation during the process demonstrated that manual control caused instability. Fortunately, it is easy to overcome this drawback by automating the equipment operational controls:

combustion gas sensors can control excess air in the combustion chamber; in the gasification chamber, remote-controlled pressure and temperature sensors can elicit a response that promptly equalizes the process in terms of feedstock variations (the feedstock is MSW in this case). In other words, it is possible to optimize the process as indicated in the literature, so as to avoid the conditions that facilitate dioxin and furan production. This control system is applicable in plants that are not experimental or pilot, which is the case of the plant of the present study.

Accounting for the volume employed during the assay, one can obtain the emission of dioxin and furan analogs, corrected with 7% oxygen (for comparison with the limits established by the Emission Standards). Table 8 lists such data.

Even considering the third sampling, the dioxin and furan emissions lay below the maximum value allowed by the current legislation. The mean dioxin and furan emission from the gasification in the mobile grit reactor was 0.28 ng N^{-1} m^{-3}, expressed in TEQ (Total Equivalent Toxicity), which lay below

Table 7: Mass of dioxins and furans obtained for samplings 1, 2, and 3.

Dioxins and furans	Analytical result (in pg)					
	Samplings			$\bar{x}$	σ	CI
	1	2	3			
2,3,7,8-TCDD (tetrachloro-dibenzo-p-dioxin)	73.00	76.90	287.50	145.80	122.73	145.80 ± 138.88
1,2,3,7,8-PeCDD (pentachloro-dibenzo-p-dioxin)	42.10	74.60	140.90	85.87	50.35	85.87 ± 56.98
1,2,3,4,7,8 – HxCDD (hexachloro-dibenzo-p-dioxin)	4.42	5.08	9.52	6.34	2.77	6.34 ± 3.14
1,2,3,6,7,8 – HxCDD (hexachloro-dibenzo-p-dioxin)	2.33	3.23	5.01	3.52	1.36	3.52 ± 1.54
1,2,3,7,8,9 – HxCDD (hexachloro-dibenzo-p-dioxin)	2.57	3.27	5.38	3.74	1.46	3.74 ± 1.66
1,2,3,4,6,7,8 – HpCDD (heptachloro-dibenzo-p-dioxin)	1.70	1.83	2.33	1.95	0.33	1.95 ± 0.38
OCDD (octachloro-dibenzo-p-dioxin)	0.24	0.26	0.28	0.26	0.02	0.26 ± 0.02
2,3,7,8 – TCDF (tetrachloro-dibenzofuran)	69.80	34.34	117.23	73.79	41.59	73.79 ± 47.06
1,2,3,7,8 – PeCDF (pentachloro-dibenzofuran)	35.61	33.17	109.53	59.44	43.40	59.44 ± 49.11
2,3,4,7,8 – PeCDF (pentachloro-dibenzofuran)	281.35	259.50	673.40	404.75	232.91	404.75 ± 263.56
1,2,3,4,7,8 – HxCDF (hexachloro-dibenzofuran)	56.09	49.65	113.97	73.24	35.42	73.24 ± 40.08
1,2,3,6,7,8 – HxCDF (hexachloro-dibenzofuran)	60.13	53.21	89.50	67.61	19.27	67.61 ± 21.80
1,2,3,7,8,9 – HxCDF (hexachloro-dibenzofuran)	5.11	5.37	11.19	7.22	3.44	7.22 ± 3.89
2,3,4,6,7,8 – HxCDF (hexachloro-dibenzofuran)	35.28	28.77	57.89	40.65	15.28	40.65 ± 17.29
1,2,3,4,6,7,8 – HpCDF (heptachloro-dibenzofuran)	8.08	7.13	11.56	8.92	2.33	8.92 ± 2.64
1,2,3,4,7,8,9 – HpCDF (heptachloro-dibenzofuran)	1.50	1.26	2.00	1.59	0.38	1.59 ± 0.43
OCDF (octachloro-dibenzofuran)	0.38	0.50	0.73	0.54	0.18	0.54 ± 0.20

$\bar{x}$ – mean; σ - standard deviation; CI - Confidence Intervals

Table 8: Dioxin and furan emission for samplings 1, 2, and 3 corrected with 7% O_2.

Dioxinas e furanos	Analytical result (in ng N^{-1} m^{-3})					
	Samplings			$\bar{x}$	σ	CI
	1	2	3			
2,3,7,8-TCDD (tetrahcloro-dibenzo-p-dioxin)	0.0208	0.0241	0.0804	0.0418	0.0335	0.0418 ± 0.0379
1,2,3,7,8-PeCDD (pentachloro-dibenzo-p-dioxin)	0.0120	0.0234	0.0394	0.0249	0.0138	0.0249 ± 0.0156
1,2,3,4,7,8 – HxCDD (hexachloro-dibenzo-p-dioxin)	0.0013	0.0016	0.0027	0.0018	0.0007	0.0012 ± 0.0008
1,2,3,6,7,8 – HxCDD (hexachloro-dibenzo-p-dioxin)	0.0006	0.0010	0.0014	0.0010	0.0004	0.0010 ± 0.0004
1,2,3,7,8,9 – HxCDD (hexachloro-dibenzo-p-dioxin)	0.0007	0.0010	0.0015	0.0011	0.0004	0.0011 ± 0.0004
1,2,3,4,6,7,8 – HpCDD (heptachloro-dibenzo-p-dioxin)	0.0005	0.0006	0.0006	0.0006	0.0001	0.0005 ± 0.0001
OCDD (octachloro-dibenzo-p-dioxin)	0.0001	0.0001	0.0001	0.0001	0.00001	0.0001 ± 0.00001
2,3,7,8 – TCDF (tetrachloro-dibenzofuran)	0.0199	0.0108	0.0328	0.0211	0.0111	0.0211 ± 0.0125
1,2,3,7,8 – PeCDF (pentachloro-dibenzofuran)	0.0101	0.0104	0.0306	0.0171	0.0118	0.0171 ± 0.0133
2,3,4,7,8 – PeCDF (pentachloro-dibenzofuran)	0.0802	0.0813	0.1883	0.1166	0.0621	0.1166 ± 0.0703
1,2,3,4,7,8 – HxCDF (hexachloro-dibenzofuran)	0.0160	0.0156	0.0318	0.0211	0.0093	0.0211 ± 0.0105
1,2,3,6,7,8 – HxCDF (hexachloro-dibenzofuran)	0.0171	0.0167	0.0250	0.0196	0.0047	0.0196 ± 0.0053
1,2,3,7,8,9 – HxCDF (hexachloro-dibenzofuran)	0.0015	0.0017	0.0031	0.0021	0.0009	0.0021 ± 0.0010
2,3,4,6,7,8 – HxCDF (hexachloro-dibenzofuran)	0.0101	0.0090	0.0162	0.0118	0.0039	0.0118 ± 0.0044
1,2,3,4,6,7,8 – HpCDF (heptachloro-dibenzofuran)	0.0023	0.0022	0.0032	0.0026	0.0006	0.0026 ± 0.0006
1,2,3,4,7,8,9 – HpCDF (heptachloro-dibenzofuran)	0.0004	0.0004	0.0006	0.0005	0.0001	0.0005 ± 0.0001
OCDF (octachloro-dibenzofuran)	0.0001	0.0002	0.0002	0.0002	0.00005	0.0002 ± 0.00005
Total dioxins and furans (ng N^{-1} m^{-3})	0.1938	0.1999	0.4581	0.2839	0.1509	0.2839 ± 0.1707

$\bar{x}$ – mean; σ - standard deviation; CI - Confidence Intervals

the maximum value allowed by the Brazilian legislation (0.5 ng TEQ m^{-3}) and the limits established in other countries like the USA (0.1 to 0.3 ng TEQ m^{-3} for new plants and 0.3 to 0.8 ng TEQ m^{-3} for existing plants), Canada (0.5 ng TEQ m^{-3}), and Japan (0.1 to 0.5 ng TEQ m^{-3}) (Caponi *et al.*, 1998).

Incinerators working under controlled conditions, in the absence of a gas treatment system, furnish results above this value (Chang *et al*., 2009).

In incinerators with a simple gas cleaning system consisting of only an electrostatic precipitator, Abad *et al*. (2003) found levels between 44 and 111 ng TEQ/m^3 of PCDD/F. They also noticed that emissions of dioxins and furans decreased, around 15 ng TEQ/m^3, when a semi-dry scrubber began to operate, but only with the installation of the fabric filter were levels around 0.3–0.4 ng TEQ/m^3 achieved (ABAD *et al*., 2003).

Dioxin and furan emission after combustion of the synthesis gas was low: the system probably did not reach the conditions necessary for the *de novo* synthesis to take place or for the precursors to form.

Gasification improves combustion conditions. During the process, a fuel gas is formed prior to combustion, elevating the temperature to 950-1050 °C. In this temperature range, the synthesis gas undergoes stable and complete combustion, avoiding the generation of chlorinated precursors. The carbon conversion rate is also higher, providing the ideal conditions for fuel burning. This prevents the production of carbonized material; i.e., fixed carbon, another precursor of dioxins and furans (Tanigaki *et al*., 2012). This happens because the gasification process occurs in distinct, individually controlled stages—the reactions that transform MSW into the synthesis gas are not restricted to the same temperature conditions or the highly oxidizing incineration environment.

The exhaust gases temperature also affects dioxin and furan formation in the post-combustion region. Maximum and minimum formation occurs around 350 °C and outside the 200-450 °C range, respectively. Nevertheless, even if the optimal temperature conditions occur in the post-combustion region, the lack of fly ash and fixed carbon in this stage diminishes dioxin and furan production.

CONCLUSION

The mechanisms and models of dioxin and furan formation described in the literature, as well as the results of the analyses conducted in the gasifier, allowed us to verify that gasification followed by combustion releases significantly less PCDDs and PCDFs than the usual MSW incineration.

According to Suzuki *et al*. (2004), the presence of molecular oxygen in the gas flow is essential to generate dioxin and furan; during the gasification process, an oxygen deficit must exist, so that the feedstock undergoes partial oxidation only, to produce synthesis gas, which do not allow the formation of dioxins and furans.

Chemicals like calcium oxide (CaO), sulfur, and nitrogen compounds can also inhibit PCDD and PCDF formation (Cheng and Hu, 2010). During MSW gasification, it is likely that sulfur and nitrogen compounds arising from the organic matter present in the waste contribute to suppressing dioxin and furan formation.

The gases were collected without any treatment; that is, they were directly taken from the exhaust gas outlet. Therefore, the implementation of simple gas treatment systems can further reduce the values reported in this paper.

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