Supplementary data

Exergy Analysis of Waste-to-Energy Technologies for Municipal Solid Waste Management

This supporting information provides additional details for the paper "Exergy Analysis of Waste-to-Energy Technologies for Municipal Solid Waste Management." It comprises three sections: Section A offers a brief explanation of exergy and waste-to-energy technologies; section B provides further insights into the methodology; and section C includes some data and parameters used in the study.

1. Exergy and waste-to-energy technologies

1.1 Exergy

The first law of thermodynamics which states that energy can only change in form but cannot be destroyed, introduces the notions of internal energy and enthalpy both of which remain constant in a physicochemical system. The second law explains that it is not possible to fully utilise thermal energy within atmospheric conditions, and has defined entropy, free energy (Helmholtz energy) and free enthalpy (Gibbs energy) as thermodynamic energy functions that indicate the feasibility and potential for advancing irreversible processes. An energy function known as 'exergy' has been introduced to represent the quantity of usable energy, its potential for conversion into various forms, and particularly its capacity to perform useful work within a given system of energy carriers in our natural environment on Earth. The term exergy was coined by Zoran Rant in 1956; it means the amount of work that is released. The concept was first put forward by Willard Gibbs, who introduced the term 'available energy' in 1873, defined as *"the greatest amount of mechanical work which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition."*

Exergy is only defined with respect to a reference environment. The reference environment can be said to be either a restricted dead state when the process is inside a system that does not interact with the ambient (isolated system) or an unrestricted dead state when the process occurs in an open system. There has been debate in the literature about the preferred approach (see Magnanelli et al., 2018). However, it is important to clearly state the assumed reference state, as the results of exergy analysis are dependent on it.

Several exergy-based performance indicators have been used as a metric for exergy and material inputs in the literature. Exergy efficiency which is expressed as the ratio of the actual useful work or output produced by a system to the maximum possible useful work or output that could be obtained from the available exergy of the input energy or resources, is the most commonly used exergy performance indicator. According to Magnanelli et al. (2018), exergy efficiency is divided into three main groups: total exergy efficiency, task exergy efficiency, and exergy efficiency without transit exergy. However, total energy efficiency is commonly used due to its unambiguous definition, making it applicable to any well-defined system. Other performance indicators include improvement potential and exergy defects. Magnanelli et al. (2018) give a detailed description of exergy-based performance indicators and their strengths and weaknesses.

1.2 Gasification

Gasification is a technological process, a form of indirect combustion wherein an exothermic reaction takes place in a low-oxygen environment to break down MSW into its constituent molecules (Ouda et al., 2016). The process of gasification transforms MSW into a gas known as synthesis gas or syngas. Syngas primarily consists of carbon monoxide (CO), hydrogen (H_2), and nitrogen (N_2). Syngas can serve as a fuel source for electricity generation or act as a fundamental building block for various products in the petrochemical and refinery sectors such as methanol, ammonia, synthetic gasoline, etc. (Rahimpour et al., 2012).

1.3 Incineration

Incineration is one of the most prevalent techniques used to dispose of MSW. This technique involves the controlled combustion of waste in a high-temperature furnace, typically ranging between 750 and 1,100^{o}C (Tozlu et al., 2016). The primary goal of this process is to break down and eliminate the organic components present in MSW while utilizing oxygen to convert the waste into heat and energy. By employing

this technique, it is possible to decrease approximately 70% of the overall waste weight and shrink the total volume by as much as 90%. Alternatively, for solid wastes, the reduction can reach approximately 80-85% depending on the composition and the extent to which certain materials such as metals are recovered from the resulting ash for recycling purposes (Beyene et al., 2018).

1.4 Landfill

A landfill is a designated area for waste disposal where municipal waste is deposited. Landfills vary in type, ranging from uncontrolled open dumps to controlled open dumps to sanitary landfills. Uncontrolled open dumps are rudimentary and not considered a proper waste management practice. However, controlled dumps and sanitary landfills follow appropriate local health and environmental regulations, offering efficient and safe disposal methods for MSW (Reddy, 2011). The idealized sequence of waste degradation processes that occur in a landfill for a homogeneous volume of waste includes a short aerobic phase, an intermediate anaerobic phase, a methanogenesis phase and a maturation phase. It is important to note that the actual conditions within a landfill will significantly deviate from this straightforward sequence, primarily due to the heterogeneous nature of the waste mass. Different areas of the landfill will progress through these stages at various rates, and some areas may not undergo all the stages at all, leading to substantial variations in the overall trends for the landfill (Kumar, 2016). The landfill gas (LFG) can be collected and treated to remove impurities. After the purification process, the gas can be used as a source of energy, either for electricity generation, heat generation or vehicle fuel.

1.5 Anaerobic digestion

Anaerobic digestion (AD) is a biological process that breaks down organic materials, such as food waste, sewage sludge, and agricultural residues, in the absence of oxygen. During this process, microorganisms typically bacteria, break down organic matter into biogas which primarily consists of methane and carbon dioxide (Zamani, 2015). AD primarily consists of four distinct stages as shown in Figure S1.

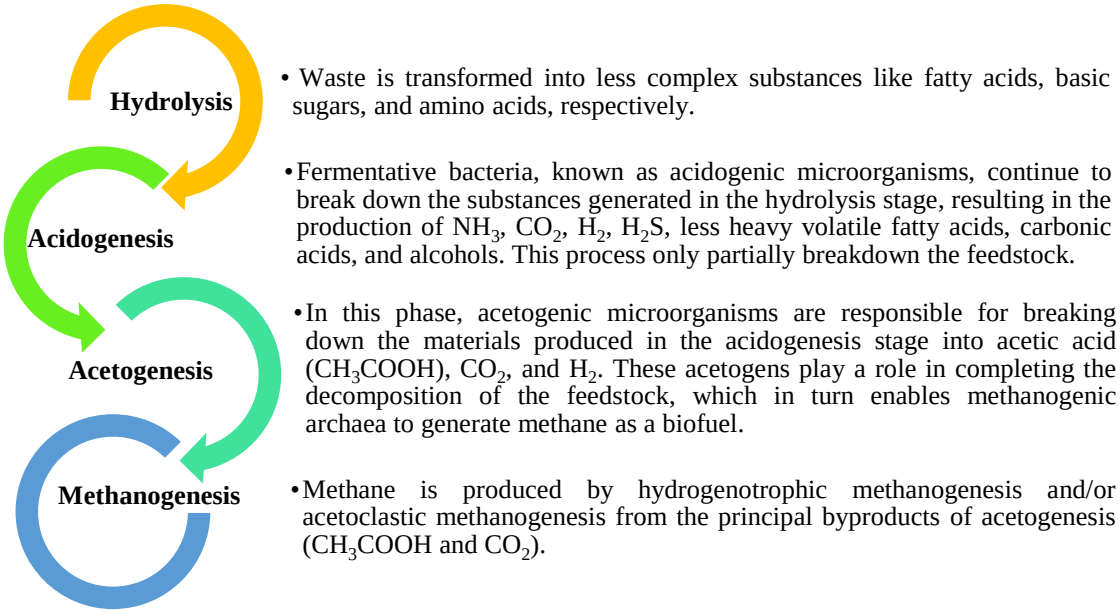

Figure S1. Primary stages in the process of anaerobic digestion

1.6 Plasma gasification

Plasma gasification is an advanced and environmentally friendly method for managing MSW and transforming it into valuable products. It is a non-incineration thermal process that operates at extremely high temperatures within an oxygen-deprived environment, leading to the complete decomposition of waste materials into very basic molecules (Mountouris

et al., 2008). The elevated temperature enables a more efficient conversion process resulting primarily in the production of syngas, slag, and ash. The significant advantage of this approach when compared to conventional gasification methods, is its effectiveness in breaking down toxic compounds into harmless chemical elements owing to the extremely high temperatures involved (Sanlisoy and Carpinlioglu, 2017). Plasma consists of high-temperature ionized gases which enable efficient heat transfer through electric discharge (Mazzoni et al., 2017). To generate thermal plasmas, there are three main methods: electric arc, plasma torch, or radio-frequency induction discharge (Bosmans et al., 2013; Ramos and Rouboa, 2022). Electric arcs can be classified as free or confined arcs. In free arcs, heat exchange with the gas occurs naturally, while confined arcs involve forced convection. Various types of electric arcs including DC, AC, plasma torches, radio frequency, high frequency and ultra-high frequency plasmas can be used. Plasma torches can be further categorized into transferred and non-transferred torches. In the transferred torch, an electric arc is created between the torch tip (typically the cathode) and a conductive surface (anode). In the non-transferred configuration, the plasma gas is heated within the torch, and the arc forms inside the torch itself as both the cathode and anode are part of the same element. The choice of torch shape and configuration depends on feedstock properties, facility equipment, desired outcome, torch components and the gas used to generate the plasma (Ramos and Rouboa, 2022). A detailed description of this process can be found in Oliveira et al. (2022) and Ramos and Rouboa (2022).

2. Methodology

2.1 Landfill gas to energy

LandGEM version 3.02 is used to estimate the amount of LFG from the landfilling process. In the absence of site-specific data, default parameters can be relied on to estimate emission rates for total LFG, methane, carbon dioxide, nonmethane organic compounds (NMOCs), and individual air pollutants from MSW landfills. The default parameters include values for methane generation rate (k), potential methane generation capacity (L_o), NMOC concentration, and methane content. The methane generation rate employed in this study is according to the IPCC classification (Pipatti et al., 2006) and was obtained from an earlier study (Amulah, 2023). Default values were used for the other parameters.

2.2 Incineration

Refer to Figure 3a in the main text. In the input stream I, the total exergy of the feed MSW is estimated from Equations 3 and 4. It is assumed that the heat exergy needed to dry the MSW feed is provided by an external source. Hence, the total exergy required for the evaporation of water from MSW, is the sum of the sensible heat associated with the quantity of water evaporated and the latent heat of vaporization as presented in Equation S1 (Jadhao et al., 2017).

$$B_t = \gamma \int_{T_0}^{T} c_p \, dT + mL \quad \text{(S1)}$$

Where; m is the mass of the water evaporated, γ is the number of moles of the evaporated water, L is the specific latent heat of vaporization of water and c_p is the specific heat of water (J/mol) expressed as (Yaws, 2003):

$$c_p = A + BT^2 + CT^3 + DT^4 \quad \text{(S2)}$$

Where; A, B, C, D are constants obtained from the Handbook of Thermodynamic and Physical Properties of Compounds (see Table S3) (Yaws, 2003). The total exergy associated with MSW after the drying operation is the sum of the physical exergy (obtained from Equation 3) and chemical exergy of the MSW. The following reactions are possible for the incineration of MSW:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \text{(S3a)}$$

$$H_{2(g)} + 0.5O_{2(g)} \longrightarrow H_2O_{(g)} \quad \text{(S3b)}$$

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)} \quad \text{(S3c)}$$

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)} \quad \text{(S3d)}$$

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)} \quad \text{(S3e)}$$

In the estimation of gas composition, it is assumed that the entire carbon content in the MSW undergoes conversion into CO_2 with no unburned carbon present in the bottom ash. The physical exergy associated with the

flue gases produced during incineration (Figure 3b) is obtained in Equation 3. Here c_p of the gases is expressed as (Yaws, 2003):

$$c_p = A + BT^2 + CT^3 + DT^4 + ET^5 \quad \text{(S4)}$$

The chemical exergy of the flue gases is given by (Jadhao et al., 2017):

$$Ex_{ch,i} = \sum \gamma_i Ex^0_{q,i} + RT_0 \sum \gamma_i \ln \gamma_i \quad \text{(S5)}$$

Where; $Ex^0_{q,k}$ is the standard chemical exergy (kJ/mol) of the gases obtained from Morris and Szargut (1986), R is gas constant and γ_k is the number of moles of the gaseous component in the mixture stream. The total exergy of the flue gases is the sum of the physical exergy and the chemical exergy. The exergy input to the steam turbine (Figure 3c) is the exergy associated with the flue gases. The exergy associated with electricity produced from incineration is estimated assuming 22% of the exergy of the flue gases is converted to electricity.

2.3 Plasma gasification

The fundamental gasification process can be described by the following reactions (Zainal et al., 2001):

$$C_{(s)} + CO_2 \rightleftarrows 2CO \quad \text{(S6)}$$
(Boudouard equilibrium reaction- endothermic)

$$C_{(s)} + H_2O \rightleftarrows CO + H_2 \quad \text{(S7)}$$
(Heterogenous water gas shift reaction- endothermic)

$$C_{(s)} + 2H_2 \rightleftarrows CH_4 \quad \text{(S8)}$$
(Hydrogenating gasification reaction- exothermic)

Equations S6 and S7 can be combined to form the water gas shift reaction (exothermic).

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad \text{(S9)}$$

The global gasification reaction considered for MSW is written in terms of the typical chemical formula of MSW based on a single atom of carbon, as shown in Equation S10 (Zainal, et al., 2001; Mountouris, et al., 2006).

$$CH_xO_y + wH_2O + mO_2 + 3.76\alpha N_2 \rightleftarrows x_1H_2 + x_2CO + x_3CO_2 + x_4H_2O + x_5CH_4 + 3.76\alpha N_2 \quad \text{(S10)}$$

Where; CH_xO_y is the chemical formula of MSW, w is the amount of water per mole of MSW, α is the amount of oxygen per mole of MSW, $x_1, x_2 \ldots, x_5$ are the coefficients of the gaseous products. Equation S10 yields six variables representing the stoichiometric coefficients of the products and the oxygen content in the reaction. Consequently, it necessitates the formulation of six equations based on the following criteria:

Carbon balance: $1 = x_2 + x_3 + x_5$ (S11)

Hydrogen balance: $2w + x = 2x_1 + 2x_4 + 4x_5$ (S12)

Oxygen balance: $w + y + 2\alpha = x_2 + 2x_3 + x_4$ (S13)

Equation S8 provides the equilibrium constant for the creation of methane as follows:

$$K_1 = \frac{[CH_4]}{[H_2]^2} = \frac{x_5}{x_1^2} \quad \text{(S14)}$$

In accordance with Equation S9, the equilibrium constant for the water gas shift reaction is expressed as:

$$K_2 = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{x_1x_3}{x_2x_4} \quad \text{(S15)}$$

The enthalpy balance equation in the plasma furnace can be written as (Mountouris, et al., 2006):

$$H^0_{f,MSW} + wH^0_{f,H_2O(l)} + \alpha H^0_{f,O_2} + 3.76\alpha H^0_{f,N_2} = x_1H^0_{f,H_2} + x_2H^0_{f,CO} + x_3H^0_{f,CO_2} + x_4H^0_{f,H_2O(g)} + x_5H^0_{f,CH_4} + \int_{T_0}^{T} \left(x_1c_{p,H_2} + x_2c_{p,CO} + x_3c_{p,CO_2} + x_4c_{p,H_2O} + x_5c_{p,CH_4} + x_1c_p + 3.76\alpha c_p, N_2 \right) dT \quad \text{(S16)}$$

Where; $H^0_{f,MSW}$ is the heat of formation of the waste material, $H^0_{f,H_2O(l)}$ is the heat of formation of liquid water, $H^0_{f,H_2O(g)}$ is the heat of formation of water vapour, H^0_{f,H_2}, $H^0_{f,CO}$, H^0_{f,CO_2}, and H^0_{f,CH_4} are the heats of formation of the gaseous products (see Table S4), c_{p,H_2}, $c_{p,CO}$, c_{p,H_2O}, c_{p,CH_4}, c_p, N_2 are the specific heats of the gaseous products (as expressed in Equation S4), and T is the gasification temperature. The composition of the syngas is predicted by solving the above system of equations (S11-S16) using the Newton-Raphson method. Further details on the equilibrium model can be obtained from Zainal et al. (2001) and Mountouris et al. (2006).

From the predicted composition of syngas, the physical exergy associated with the syngas is estimated using Equation 3, and the chemical exergy is obtained from Equation S5. Assuming a combined cycle operation (as shown in Figure 4) with a conversion efficiency of 45.5% (see Table S1), the total exergy associated with the electricity produced from the syngas is obtained. Because the gasification of MSW requires electricity input (the electricity required by the plasma torch), the exergy required by the plasma torch is subtracted from the electricity produced to obtain the net electricity output. The exergy efficiency, improvement potential and exergy defect of each WtE options is evaluated using Equations 5-7.

3. Parameters used in the Study

Table S1. Some parameters used in exergy analysis of WtE technologies

Parameter	Value	Reference
Waste generation		
Annual population growth	2.40%	City Population (2023)
Waste generation rate	0.53 kg/capita/day	Somorin et al. (2017)
Base year (2022) population	1,328,100	City Population (2023)
Landfill		
Methane generation rate	0.071/year	Amulah (2023)
Methane potential	170 m^3/tonne	Alexander et al. (2005)
Electricity conversion efficiency	33%	Nubi et al. (2022)
Gas collection efficiency	75%	Nubi et al. (2022)
Anaerobic digestion		
Density of methane	0.717 kg/m^3	Huang and Fooladi (2021)
Electricity conversion efficiency	26%	Ayodele et al. (2018)
Percentage of actual methane	85%	Cudjoe et al. (2020)
Incineration		
Electricity conversion efficiency	22%	da Silva et al. (2020)
Latent heat of vaporization	2,260 kJ/kg	Datt (2011)
Reference temperature	298.15 K	
Incineration temperature	1,123.15 K	Ramos and Rouboa (2022)
Plasma gasification		
Electricity consumption for plasma torch	180 kWh/tonne	Jadhao et al. (2017)
Reference temperature	298.15 K	
Gasification temperature	1,273.15 K	Jadhao et al. (2017)
Electricity conversion efficiency	45.5%	Ameri et al. (2007)

Table S2. Standard exergy of elements/compounds

		Ex_q^0 (kJ/mol)
CH_4	Methane	831.65
H_2	Hydrogen	236.12
O_2	Oxygen	3.92
N_2	Nitrogen	0.67
CO	Carbon monoxide	275.10
CO_2	Carbon dioxide	19.87
C	Carbon	410.27
S	Sulphur	609.3
H_2O	Water	9.5
NO	Nitric oxide	88.9
SO_2	Sulphur dioxide	33.4

Table S3. Specific heat capacity of elements/compounds

$c_p = A + BT^2 + CT^3 + DT^4 + ET^5$ (J/mol K)					
	A	B	C	D	E
H_2	25.399	2.0178×10^{-2}	-3.8549×10^{-5}	3.1880×10^{-8}	-8.7585×10^{-12}
O_2	29.526	-8.8999×10^{-3}	3.8083×10^{-5}	-3.2629×10^{-8}	8.8607×10^{-12}
N_2	29.342	-3.5395×10^{-3}	1.0076×10^{-5}	-4.3116×10^{-9}	2.5935×10^{-13}
CO	29.556	-6.5807×10^{-3}	2.0130×10^{-5}	-1.2227×10^{-8}	2.2617×10^{-12}
CO_2	27.437	4.2315×10^{-2}	-1.9555×10^{-5}	3.9968×10^{-9}	-2.9872×10^{-13}
CH_4	34.942	-3.9957×10^{-2}	1.9184×10^{-4}	-1.530×10^{-7}	3.9321×10^{-11}
H_2O(g)	33.933	-8.4186×10^{-3}	2.9906×10^{-5}	-1.7825×10^{-8}	3.6934×10^{-12}
H_2O(l)	92.053	-3.9953×10^{-2}	-2.1103×10^{-4}	5.3469×10^{-7}	
C	-0.832	3.4846×10^{-2}	-1.3233×10^{-5}		

Table S4. Heat of formation and Gibbs energy of elements/compounds

		Heat of formation H_f^0(kJ/mol)	Gibbs Energy G_f^0(kJ/mol)
CH_4	Methane	-74.5	-50.5
H_2	Hydrogen	0	0
O_2	Oxygen	0	0
N_2	Nitrogen	0	0
CO	Carbon monoxide	-110.5	-137.2
CO_2	Carbon dioxide	-393.5	-394.4
H_2O(l)	Water(l)	-285.8	-237.1
H_2O(g)	Water	-241.8	-228.6
C	Carbon	0	0

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