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Calculations Reconsidered: From Mass Percentages of Elements to Empirical Formula and From Empirical Formula to Theoretical Biomethane Potential

Pong Kau Yuen[1], Cheng Man Diana Lau[1], Kuok In Gabriel Yuen[2]

[1]Macau Chemical Society, Macao, Macao

[2]Clear Horizons Early College High School, Houston, Texas, USA

Correspondence: Pong Kau Yuen, Macau Chemical Society, Macao, Macao. ORCID number: 0000-0002-3045-2484

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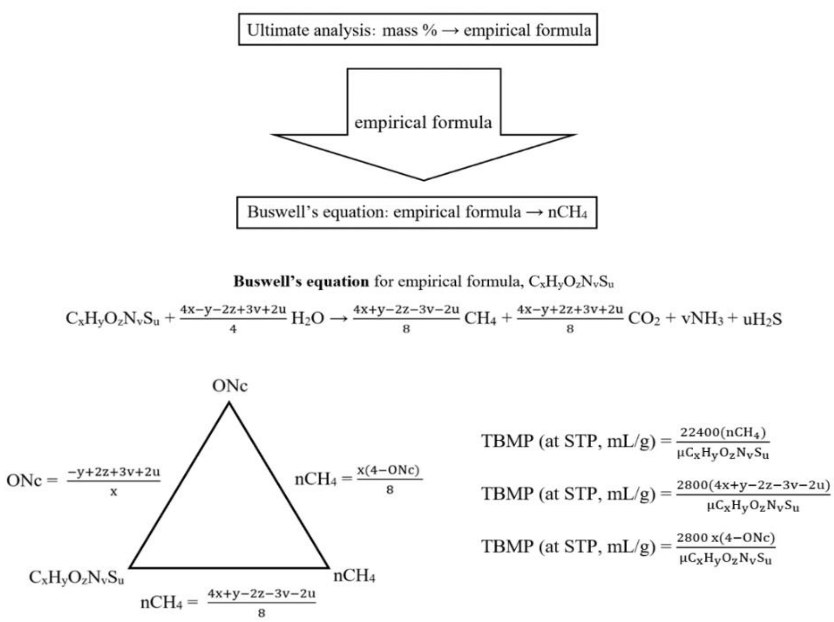
Abstract

Anaerobic digestion is an organic carbon-based process and sustainable technology. In this process, empirical formulas and theoretical biomethane potentials of organic matters are two important parameters. Mass percentages of elements can be found by ultimate analysis, and then empirical formula can be calculated by the known mass percentages of elements. Other data, such as quantity amount of biomethane and theoretical biomethane potential can also be attained by calculations. Although empirical formulas are important for quantifying theoretical biomethane potentials, they are not always available in published papers. In some cases, the theoretical biomethane potential cannot be verified. This article has two purposes. First, it identifies the valid empirical formulas of organic matters. Second, it examines the correctness of a series of calculations: from mass percentages of elements to empirical formulas and from empirical formulas to theoretical biomethane potential. The mean oxidation number of organic carbons is used as an assessor that validates the empirical formulas and their corresponding mass percentages of elements. The relative percentage of theoretical biomethane potential is designed as an indicator that measures the discrepancy between the published theoretical biomethane potential and the recalculated theoretical biomethane potential.

Keywords: Buswell's Equation, ultimate analysis, mass percentages of elements, empirical formula, theoretical biomethane potential, mean oxidation number of organic carbons

Graphical Abstract



1. Introduction

Anaerobic digestion (AD) is an organic carbon-based process and sustainable technology (Wu et al., 2022) for waste management and non-fossil energy generation, in which biomethane potential (BMP) is a measure of organic matter (OM) biodegradability (Owen, et al., 1979). The BMP test has been developed as a standard protocol in the laboratory (Holliger, et al., 2016; Koch, et al., 2020; Holliger, et al., 2021). Volatile solid (VS) is generally treated as a measurement of the organic fraction of total solid (TS) (American Public Health Association, 1999; Hamilton & Zhang, 2016), and it is considered a biodegradable organic fraction. The experimental biomethane potential (EBMP) is defined as the ratio of maximum amount of produced volumetric methane (VCH_4) to mass of added VS. The equation of EBMP is shown in the following (Owen, et al., 1979):

$$\text{EBMP (at STP, mL/g)} = \frac{V_{CH4}}{\text{mass of added VS}}$$

The empirical formula of $C_xH_yO_z$ (Angelidaki & Sanders, 2004) solves the theoretical biomethane potential (TBMP), and the counting equation is shown in the following:

$$\text{TBMP (at STP, L/g)} = \frac{22.4\left(\frac{x}{2}+\frac{y}{8}-\frac{z}{4}\right)}{12x+y+16z}$$

Based on the empirical formula of $C_xH_yO_zN_vS_v$, the mathematical equation for TBMP (Yuen & Lau, 2023) is shown in the following:

$$\text{TBMP (at STP, mL/g)} = \frac{22400(nCH_4)}{\mu C_xH_yO_zN_vS_u}$$

The biodegradability index (BDI) evaluates the biodegradable effectiveness of OM. It is defined by the ratio percentage of EBMP to TBMP (Nielfa et al., 2015).

$$\text{BDI (\%)} = \frac{\text{EBMP}}{\text{TBMP}} \times 100\%$$

Any empirical formula of OM can be determined by its mass percentages of elements (mass%). The atomic coefficients (AC) and mean oxidation number of organic carbons (ONc) of an empirical formula are critical for counting quantitative amount of biomethane (nCH_4) and TBMP (Yuen & Lau, 2024a). The general balanced Buswell's equation (BEq) (Buswell & Mueller, 1952; Boyle, 1977) for $C_xH_yO_zN_vS_u$ is shown in the following:

$$C_xH_yO_zN_vS_u + \frac{4x-y-2z+3v+2u}{4} H_2O \rightarrow \frac{4x+y-2z-3v-2u}{8} CH_4 + \frac{4x-y+2z+3v+2u}{8} CO_2 + vNH_3 + uH_2S$$

The nCH_4 can be determined by the mathematical equation of $nCH_4 = \frac{4x+y-2z-3v-2u}{8}$. The ONc is a redox parameter of OM. The relationship between ONc and nCH_4 is established as $nCH_4 = \frac{x(4-ONc)}{8}$ (Yuen & Lau, 2024b).

Measurements and calculations are two major sections that make up the BMP test. In ultimate analysis (UA), mass% is the critical experimental data. Although empirical formulas are important to quantify nCH_4 and TBMP, they are not accessible in some literatures. Furthermore, in some cases, the published TBMP cannot be verified.

This article serves two purposes. First, it identifies the valid mass% and empirical formulas of OM. Second, it examines the correctness of a series of calculations: from mass% to empirical formulas and from empirical formulas to TBMP. The ONc is used as an assessor that validates the empirical formulas and their corresponding mass%. The relative percentage of TBMP is designed as an indicator that measures the discrepancy between the published TBMP and the recalculated TBMP.

The empirical formula of an OM is at the core of counting nCH_4 and TBMP in the study of BEq. When an accurate TBMP parameter is available, the degradability of OM can be properly evaluated and the BDI can be correctly counted. The significance of this study is that by simple calculation, it is possible to evaluate: (1) the validity of mass% and empirical formulas, and (2) the correctness of empirical formulas and TBMP.

2. Methods and Materials

2.1 Empirical Formula of Organic Matter (OM)

The elemental composition of OM is represented by an empirical formula in the general form of $C_aH_bO_cN_dS_e$. C, H, O, N, and S represent carbon, hydrogen, oxygen, nitrogen and sulphur elements respectively; a, b, c, d, and e are atomic coefficients (AC). In chemistry, AC (a, b, c, d, and e) are shown in the smallest integer ratio. Due to the presence of complex mixtures of OM, such as biomass and biowaste, the AC (x, y, z, v, and u) of $C_xH_yO_zN_vS_u$ are represented by non-integer ratio. $CH_{y/x}O_{z/x}N_{v/x}S_{u/x}$ (AC of carbon atom =1), $C_{x/v}H_{y/v}O_{z/v}NS_{u/v}$ (AC of nitrogen atom =1), and $C_{x/u}H_{y/u}O_{z/u}N_{v/u}S$ (AC of sulfur atom =1) are also used. Table 1 shows five forms of empirical formulas and their corresponding empirical formula masses.

Table 1. Representations of empirical formulas and their empirical formula masses

Empirical formula	Empirical formula mass (μ)
$C_aH_bO_cN_dS_e$	$\mu = a\mu C + b\mu H + c\mu O + d\mu N + e\mu S$
$C_xH_yO_zN_vS_u$	$\mu = x\mu C + y\mu H + z\mu O + v\mu N + u\mu S$
$CH_{y/x}O_{z/x}N_{v/x}S_{u/x}$	$\mu = \frac{x\mu C + y\mu H + z\mu O + v\mu N + u\mu S}{x}$
$C_{x/v}H_{y/v}O_{z/v}NS_{u/v}$	$\mu = \frac{x\mu C + y\mu H + z\mu O + v\mu N + u\mu S}{v}$
$C_{x/u}H_{y/u}O_{z/u}N_{v/u}S$	$\mu = \frac{x\mu C + y\mu H + z\mu O + v\mu N + u\mu S}{u}$

2.2 Ultimate Analysis (UA)

Regarding biomass or biowaste, the AC (x, y, z, v, and u) of the empirical formula, $C_xH_yO_zN_vS_u$, are represented by non-integer ratio. The C/H/N/S contents of dried OM are analyzed by UA. Mathematical relationships of the elemental analysis are shown in the following:

$$100\% = \Sigma \text{ Elemental Analysis\% } (\Sigma EA\%) + ash\%$$

$$\Sigma EA\% = C\% + H\% + O\% + N\% + S\%$$

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

2.3 ONc of Empirical Formulas

For any given empirical formula of OM, its ONc can be determined (Yuen & Lau, 2024b). Regarding the empirical formula $C_xH_yO_zN_vS_u$ of OM, its individual oxidation numbers of hydrogen, oxygen, nitrogen, and sulfur atoms (H, O, N, and S) are assumed to be +1, −2, −3, and −2 respectively. For empirical formula $C_xH_yO_zN_vS_u$, the mathematical equation is shown as ONc = $\frac{-y+2z+3v+2u}{x}$.

2.4 ONc: An Assessor of Empirical Formula and Mass %

ONc is used as a redox metric for OM (Yuen & Lau, 2023; 2024b). The ONc of the highest reduced CH_4 (the minimum oxidation number) and the highest oxidized CO_2 (the maximum oxidation number) are −4 and +4, respectively. The allowed ONc for empirical formulas of OM must lie between −4 and +4. The empirical formula is determined by the mass%, therefore, it shows that ONc can be used as an assessor to validate both the calculated empirical formulas and the experimental mass%.

2.5 Buswell's Equation (BEq)

When the empirical formula of an OM is identified, the corresponding stoichiometric BEq can be determined (Yuen & Lau, 2024c). Based on the empirical formula of $C_xH_yO_zN_vS_u$, the quantitative amount of nCH_4 can be found by the following mathematical equation: $nCH_4 = \frac{4x+y-2z-3v-2u}{8}$ or $nCH_4 = \frac{x(4-ONc)}{8}$ (Yuen & Lau, 2024a; 2024b).

2.6 Relationships between Empirical Formula, ONc, and nCH_4

Figure 1 demonstrates the triangular relationships between empirical formula, ONc and nCH_4. Based on the given AC of an empirical formula, ONc and nCH_4 can be determined.

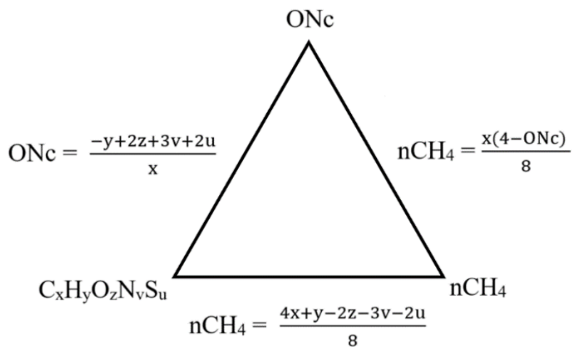


Figure 1. Triangular relationships between empirical formula, ONc, and nCH_4

2.7 Theoretical Biomethane Potential (TBMP)

Based on the empirical formula of $C_xH_yO_zN_vS_u$, the mathematical equations for counting TBMP are shown in the following:

$$\text{TBMP (at STP, mL/g)} = \frac{22400(nCH_4)}{\mu C_xH_yO_zN_vS_u}$$

$$\text{TBMP (at STP, mL/g)} = \frac{22400(4x+y-2z-3v-2u)}{8\mu C_xH_yO_zN_vS_u} = \frac{2800(4x+y-2z-3v-2u)}{\mu C_xH_yO_zN_vS_u}$$

$$\text{TBMP (at STP, mL/g)} = \frac{22400\,x(4-ONc)}{8\mu C_xH_yO_zN_vS_u} = \frac{2800\,x(4-ONc)}{\mu C_xH_yO_zN_vS_u}$$

2.8 Collecting Data from Literature

After recalculations of selected published mass%, the empirical formulas of OM and TBMP can be found. In cases where empirical formulas are available, they can be used to recalculate the corresponding TBMP.

3. Determining Empirical Formula Using Ultimate Analysis (UA)

3.1 Working Procedures

The working procedures for determining the empirical formula of OM are provided in this section. Table 2 shows the steps of the UA from working procedures to counting parameters (Yuen & Lau, 2023).

Table 2. Ultimate analysis: working procedures and parameters

Working procedure	**Measured and/or calculated parameters**	**Calculated parameters**
Ultimate analysis	Mass%, ash%	O% = 100% − ash% − (C% + H% + N% + S%) ΣEA% = C% + H% + O% + N% + S%
Counting AC	EA%, μ_{atom}	C%, H%, O%, N%, S% μ_C (g/mol) = 12.011 μ_H (g/mol) = 1.008 μ_O (g/mol) = 15.999 μ_N (g/mol) = 14.007 μ_S (g/mol) = 32.065 AC: x, y, z, v, and u $x = \frac{C\%}{\mu_C}; y = \frac{H\%}{\mu_H}; z = \frac{O\%}{\mu_O}; v = \frac{N\%}{\mu_N}; u = \frac{S\%}{\mu_S}$ $x = \frac{C\%}{12.011}; y = \frac{H\%}{1.008}; z = \frac{O\%}{15.999}; v = \frac{N\%}{14.007}; u = \frac{S\%}{32.065}$
Determining empirical formula	AC	$C_xH_yO_zN_vS_u$
Counting empirical formula mass	AC, μ_{atom}	$\mu C_xH_yO_zN_vS_u = x\mu_C + y\mu_H + z\mu_O + v\mu_N + u\mu_S$ $\mu C_xH_yO_zN_vS_u = x(12.011) + y(1.008) + z(15.999) + v(14.007) + u(32.065)$ $\mu C_xH_yO_zN_vS_u$ = ΣEA%

When the TS of an OM is assumed to be 100 grams and VS to be 1 mole, the empirical formula mass ($\mu C_xH_yO_zN_vS_u$) of VS is equal to the sum of individual mass percentages of elements (ΣEA%).

Example 1. Find the empirical formula and its corresponding empirical formula mass from the collected data (Yu et al., 2023).

Biowaste	Ultimate analysis				
	C%	H%	O%	N%	S%
Chicken manure	37.5	4.2	26.6	3.7	0.6

Step 1. Calculate ΣEA%

ΣEA% = C% + H% + O% + N% + S%

= 37.5% + 4.2% + 26.6% + 3.7% + 0.6% = 72.6%

Step 2. Count AC

AC: $x = \frac{C\%}{\mu_C}; y = \frac{H\%}{\mu_H}; z = \frac{O\%}{\mu_O}; v = \frac{N\%}{\mu_N}; u = \frac{S\%}{\mu_S}$

$x = \frac{37.5}{12.011}; y = \frac{4.2}{1.008}; z = \frac{26.6}{15.999}; v = \frac{3.7}{14.007}; u = \frac{0.6}{32.065}$

x = 3.122; y = 4.167; z = 1.663; v = 0.264; u = 0.019

Step 3. Find the empirical formula

The resulted empirical formula: $C_xH_yO_zN_vS_u = C_{3.122}H_{4.167}O_{1.663}N_{0.264}S_{0.019}$

Step 4. Determine the empirical formula mass

Empirical formula mass: $\mu C_xH_yO_zN_vS_u = x\mu_C + y\mu_H + z\mu_O + v\mu_N + u\mu_S$

$\mu C_{3.122}H_{4.167}O_{1.663}N_{0.264}S_{0.019} = (3.122)(12.011) + (4.167)(1.008) + (1.663)(15.999) + (0.264)(14.007) + (0.019)(32.065)$

The resulted empirical formula mass: $\mu C_{3.122}H_{4.167}O_{1.663}N_{0.264}S_{0.019}$ = 72.60 g/mol

The resulted empirical formula mass equals the value of ΣEA%.

Example 2. Given an empirical formula $\mu C_{3.122}H_{4.167}O_{1.663}N_{0.264}S_{0.019}$, find its ONc, nCH_4, and TBMP.

Step 1. Count ONc

For empirical formula $C_xH_yO_zN_vS_u$, ONc = $\frac{-y+2z+3v+2u}{x}$

For $C_{3.122}H_{4.167}O_{1.663}N_{0.264}S_{0.019}$,

$$\text{ONc} = \frac{-y+2z+3v+2u}{x}$$

$$= \frac{-(4.167)+2(1.663)+3(0.264)+2(0.019)}{3.122}$$

$$= -0.004$$

Step 2. Calculate nCH_4

$$nCH_4 = \frac{x(4-\text{ONc})}{8}$$

$$nCH_4 = \frac{(3.122)(4-(-0.004))}{8}$$

$$= 1.563 \text{ (mol)}$$

Step 3. Determine TBMP

$$nCH_4 = 1.563 \text{ (mol)}$$

$$\mu C_{3.122}H_{4.167}O_{1.663}N_{0.264}S_{0.019} = (3.122)(12.011) + (4.167)(1.008) + (1.663)(15.999) + (0.264)(14.007) + (0.019)(32.065)$$

$$= 72.60 \text{ (g/mol)}$$

$$\text{TBMP (at STP, mL/g)} = \frac{22400(nCH_4)}{\mu C_xH_yO_zN_vS_u}$$

$$= \frac{(22400)(1.563)}{72.60}$$

$$= 482.25 \text{ (mL/g)}$$

3.2 Using ONc to Validate Empirical Formula and Mass%

With reference to step 1 in Example 2, the ONc of empirical formula $C_{3.122}H_{4.167}O_{1.663}N_{0.264}S_{0.019}$ is equal to −0.004. Since it lies between −4 and +4, the empirical formula is valid. Furthermore, a set of data of the chicken manure: C% = 37.5, H% = 4.2, O% = 26.6, N% = 3.7, and S% = 0.6% from Example 1 is found to be the empirical formula $C_{3.122}H_{4.167}O_{1.663}N_{0.264}S_{0.019}$. Since the mentioned empirical formula $C_{3.122}H_{4.167}O_{1.663}N_{0.264}S_{0.019}$ is valid, the mass% of the set is also valid.

4. Recalculation: Determining Empirical Formula and Counting TBMP

In most publications, only mass% and calculated TBMP are available; specifically, only a few publications have mass%, empirical formula, and TBMP present concurrently. Even in those that show empirical formulas, they are presented in different ways. Due to this reason, the comparison among empirical formulas is difficult.

The following examples show a series of recalculations: (1) from mass% to empirical formula, and (2) from empirical formula to TBMP. The validity of mass% is evaluated by the ONc of its empirical formula. When ONc of any empirical formula lies between −4 and +4, the empirical formula and corresponding mass% are valid. The discrepancy between recalculated TBMP and published TBMP is measured by the relative percentage of TBMP (%).

For publications in which only mass% and calculated TBMP are available, the relative percentage of $\text{TBMP}_{\text{pub-UA}}$% is calculated by the following mathematical equation. $TBMP_{UA}$ represents the recalculated TBMP from mass%, and $TBMP_{pub\text{-}UA}$ represents the published TBMP.

$$TBMP_{pub\text{-}UA}\,\% = \frac{(TBMP_{UA} - TBMP_{pub-UA})}{TBMP_{UA}} \times 100\%$$

For publications in which mass%, empirical formula, and TBMP are available, both the $TBMP_{pub\text{-}UA}$% and $TBMP_{pub\text{-}EF}$% can be calculated. In the mathematical equation of $TBMP_{pub\text{-}EF}$%, $TBMP_{UA}$ represents the recalculated TBMP from mass% and $TBMP_{pub\text{-}EF}$ represents the recalculated TBMP from the published empirical formula.

$$TBMP_{pub\text{-}UA}\,\% = \frac{(TBMP_{UA} - TBMP_{pub-UA})}{TBMP_{UA}} \times 100\%$$

$$TBMP_{pub\text{-}EF}\,\% = \frac{(TBMP_{UA} - TBMP_{pub-EF})}{TBMP_{UA}} \times 100\%$$

Example 3. Based on the collected data of mass%, recalculate TBMP and determine empirical formulas of biowaste $C_xH_yO_zN_v$ (Nielfa et al., 2015).

Step 1. Collect data from literature

The collected data are summarized in Table 3a.

Table 3a. Collected published data of mass% and TBMP

Biowaste	C%	H%	O%	N%	$TBMP_{pub\text{-}UA}$
Biological sludge	5.4	9.1	36.4	0.6	333.9
OFMSW	20.3	7.8	31.0	0.4	494.3
Co-digestion 1	17.3	8.0	32.1	0.4	465.8
Co-digestion 2	14.4	8.3	33.2	0.5	435.6
Co-digestion 3	11.4	8.6	34.3	0.5	403.7
Co-digestion 4	8.4	8.8	35.3	0.6	369.8

Step 2. Recalculate $TBMP_{UA}$ and determine empirical formulas

After recalculation, data of empirical formulas, μ, nCH_4, and $TBMP_{UA}$ are summarized in Table 3b.

Table 3b. Recalculated data from mass%

Biowaste	Empirical formula	μ	nCH_4	$TBMP_{UA}$
Biological sludge	$C_{0.450}H_{9.028}O_{2.275}N_{0.043}$	51.51	0.77	334.13
OFMSW	$C_{1.690}H_{7.738}O_{1.938}N_{0.029}$	59.51	1.32	495.78
Co-digestion 1	$C_{1.440}H_{7.937}O_{2.006}N_{0.029}$	57.81	1.20	464.92
Co-digestion 2	$C_{1.119}H_{8.234}O_{2.075}N_{0.036}$	56.41	1.10	435.40
Co-digestion 3	$C_{0.949}H_{8.532}O_{2.144}N_{0.036}$	54.81	0.99	405.25
Co-digestion 4	$C_{0.699}H_{8.730}O_{2.206}N_{0.043}$	53.11	0.87	368.29

Step 3. Examine the validity of mass% and the discrepancy of TBMP

The calculated empirical formulas, ONc, $TBMP_{UA}$, $TBMP_{pub\text{-}UA}$, and $TBMP_{pub\text{-}UA}$% are listed in Table 3c. All $TBMP_{pub\text{-}UA}$% lie within ±0.4%. Results from the published calculation and recalculation show that the TBMP are accurate. However, the resulted ONc of empirical formulas for biological sludge, Co-digestion 3, and Co-digestion 4 are beyond the range (ONc < −4). These experimental mass% are not valid.

Table 3c. Recalculated data from empirical formulas

Biowaste	Empirical formula	ONc	$TBMP_{UA}$	$TBMP_{pub\text{-}UA}$	$TBMP_{pub\text{-}UA}$ %
Biological sludge	$C_{0.450}H_{9.028}O_{2.275}N_{0.043}$	-9.672*	334.13	333.9	0.07
OFMSW	$C_{1.690}H_{7.738}O_{1.938}N_{0.029}$	-2.234	495.78	494.3	0.30
Co-digestion 1	$C_{1.440}H_{7.937}O_{2.006}N_{0.029}$	-2.664	464.92	465.8	-0.19
Co-digestion 2	$C_{1.119}H_{8.234}O_{2.075}N_{0.036}$	-3.316	435.40	435.6	-0.05
Co-digestion 3	$C_{0.949}H_{8.532}O_{2.144}N_{0.036}$	-4.358*	405.25	403.7	0.38
Co-digestion 4	$C_{0.699}H_{8.730}O_{2.206}N_{0.043}$	-5.989*	368.29	369.8	-0.41

Example 4. Based on the collected data of mass% and published empirical formula, recalculate TBMP and determine empirical formulas of biowaste $C_xH_yO_zN_v$. (Prem & Shanmugam, 2021).

Step 1. Collect data

The collected data are summarized in Table 4a.

Table 4a. Collected published data of mass%, empirical formulas, and TBMP

Biowaste	C%	H%	O%	N%	Empirical formula	$TBMP_{pub\text{-}UA}$ (L/g)	$TBMP_{pub\text{-}UA}$ (mL/g)
Banana plantain	39.00	6.81	44.53	1.21	$C_{40}H_{79}O_{32}N$	0.44	440
Beetroot	44.10	8.50	30.51	1.60	$C_{27}H_{74}O_{17}N$	0.59	590
Broad Beans	43.82	8.32	40.59	1.55	$C_{22}H_{59}O_{17}N$	0.53	530
Bottle Gourd	38.42	8.41	38.95	2.00	$C_{33}H_{77}O_{23}N$	0.51	510
Cabbage	35.58	7.42	41.00	1.72	$C_{24}H_{60}O_{21}N$	0.45	450

Step 2. Recalculate $TBMP_{UA}$ from mass% and determine empirical formulas

Resulted data are summarized in Table 4b.

Table 4b. Resulted data from mass% to $TBMP_{UA}$

Biowaste	Empirical formula	μ	nCH_4	$TBMP_{UA}$
Banana plantain	$C_{3.247}H_{6.756}O_{2.783}N_{0.086}$	91.55	1.74	425.68
Beetroot	$C_{3.672}H_{8.433}O_{1.907}N_{0.114}$	84.71	2.37	626.78
Broad Beans	$C_{3.648}H_{8.254}O_{2.537}N_{0.111}$	94.28	2.18	517.98
Bottle Gourd	$C_{3.099}H_{8.343}O_{2.435}N_{0.143}$	87.78	1.98	505.29
Cabbage	$C_{2.962}H_{7.361}O_{2.563}N_{0.123}$	85.72	1.71	448.04

Step 3. Recalculate $TBMP_{pub\text{-}EF}$ from published empirical formulas

Resulted data are summarized in Table 4c. The ONc of biowastes lies between −1.370 and −0.300, therefore, the published empirical formulas are valid.

Table 4c. Resulted data from published empirical formulas

Biowaste	Published empirical formula	ONc	μ	nCH_4	$TBMP_{pub\text{-}EF}$
Banana plantain	$C_{40}H_{79}O_{32}N$	-0.300	1086.05	21.50	443.44
Beetroot	$C_{27}H_{74}O_{17}N$	-1.370	684.88	18.13	592.81
Broad Beans	$C_{22}H_{59}O_{17}N$	-1.000	609.70	13.75	505.16
Bottle Gourd	$C_{33}H_{77}O_{23}N$	-0.848	855.96	20.00	523.39
Cabbage	$C_{24}H_{60}O_{21}N$	-0.625	698.73	13.88	444.81

Step 4. Compare published and recalculated empirical formulas

Table 4d demonstrates the published and recalculated empirical formulas of biowastes. The recalculated empirical formula-1 and empirical formula-2 are presented in the forms of $C_xH_yO_zN_v$ and $C_{x/v}H_{y/v}O_{z/v}N$, respectively. The recalculated empirical formulas (non-integer AC) from published mass% are more accurate than the published empirical formula (integer AC).

Table 4d. Comparison of published and recalculated empirical formulas

Biowaste	Published empirical formula	Recalculated empirical formula-1	Recalculated empirical formula-2
Banana plantain	$C_{40}H_{79}O_{32}N$	$C_{3.247}H_{6.756}O_{2.783}N_{0.086}$	$C_{37.756}H_{78.558}O_{32.360}N$
Beetroot	$C_{27}H_{74}O_{17}N$	$C_{3.672}H_{8.433}O_{1.907}N_{0.114}$	$C_{32.211}H_{73.974}O_{16.728}N$
Broad Beans	$C_{22}H_{59}O_{17}N$	$C_{3.648}H_{8.254}O_{2.537}N_{0.111}$	$C_{32.865}H_{74.360}O_{22.856}N$
Bottle Gourd	$C_{33}H_{77}O_{23}N$	$C_{3.099}H_{8.343}O_{2.435}N_{0.143}$	$C_{21.671}H_{58.343}O_{17.028}N$
Cabbage	$C_{24}H_{60}O_{21}N$	$C_{2.962}H_{7.361}O_{2.563}N_{0.123}$	$C_{24.081}H_{59.846}O_{20.837}N$

Step 5. Examine validity of mass% and discrepancy of TBMP

The calculated ONc and TBMP% are listed in Table 4e. Since the ONc of biowastes lies between −1.165 and −0.286, the recalculated empirical formulas are valid. Published $TBMP_{pub\text{-}UA}$ deviates from $TBMP_{UA}$ by −4.17% to +5.42%, and $TBMP_{pub\text{-}EF}$ deviates from $TBMP_{UA}$ by −3.36% to +5.87%.

Table 4e. Recalculated data from empirical formulas to ONc, μ, nCH_4, TBMP, and TBMP%

Biowaste	Empirical formula	ONc	$TBMP_{UA}$	$TBMP_{pub\text{-}EF}$	$TBMP_{pub\text{-}UA}$	$TBMP_{pub\text{-}EF}$ %	$TBMP_{pub\text{-}UA}$ %
Banana plantain	$C_{3.247}H_{6.756}O_{2.783}N_{0.086}$	-0.286	425.68	443.44	440	-4.17	-3.36
Beetroot	$C_{3.672}H_{8.433}O_{1.907}N_{0.114}$	-1.165	626.78	592.81	590	5.42	5.87
Broad Beans	$C_{3.648}H_{8.254}O_{2.537}N_{0.111}$	-0.781	517.98	505.16	530	2.47	-2.32
Bottle Gourd	$C_{3.099}H_{8.343}O_{2.435}N_{0.143}$	-0.952	505.29	523.39	510	-3.58	-0.93
Cabbage	$C_{2.962}H_{7.361}O_{2.563}N_{0.123}$	-0.630	448.04	444.81	450	0.72	-0.44

Example 5. Based on the collected data of mass%, recalculate TBMP and determine empirical formulas (Yasim & Buyong, 2023).

Step 1. Collect data

Collected data are summarized in Table 5a.

Table 5a. Collected published data of mass% and TBMP

Biowaste	C%	H%	O%	N%	S%	$TBMP_{pub\text{-}UA}$
CFW	46.29	8.16	33.66	7.35	0.54	487.20
UCFW	33.04	1.80	49.86	5.30	0.00	117.39
VW	43.62	6.45	31.56	5.21	0.16	401.17
FW	41.07	6.10	41.16	2.68	0.00	362.50
GW	40.79	5.31	39.32	1.59	0.00	336.65
PW	51.00	6.25	39.93	1.82	0.00	496.84
TW	76.30	3.63	17.86	0.21	0.00	743.10

Step 2. Recalculate $TBMP_{UA}$ and determine empirical formulas

Resulted data of empirical formulas, μ, nCH_4, and TBMP are summarized in Table 5b.

Table 5b. Recalculated data from mass%

Biowaste	Empirical formula	μ	nCH_4	$TBMP_{UA}$
CFW	$C_{3.845}H_{8.095}O_{2.104}N_{0.525}S_{0.017}$	96.00	2.21	516.12
UCFW	$C_{2.751}H_{1.786}O_{3.116}N_{0.378}$	90.00	0.68	168.65
VW	$C_{3.632}H_{6.399}O_{1.973}N_{0.372}S_{0.005}$	87.00	1.98	510.26
FW	$C_{3.419}H_{12.248}O_{2.573}N_{0.191}$	91.01	1.75	431.02
GW	$C_{3.396}H_{6.052}O_{2.458}N_{0.114}$	87.01	1.70	437.53
PW	$C_{4.246}H_{6.200}O_{2.496}N_{0.130}$	99.00	2.23	503.53
TW	$C_{6.353}H_{3.601}O_{1.116}N_{0.015}$	98.00	3.34	763.82

Step 3. Examine validity of mass% and discrepancy of TBMP

The calculated ONc and TBMP% are listed in Table 5c. The ONc of biowastes lie between −0.591 and +2.029, therefore, their mass% and empirical formulas are valid. $TBMP_{pub\text{-}UA}$ deviates from $TBMP_{UA}$ by +1.33% to +30.39%.

Table 5c. Recalculated data from empirical formula to ONc, μ, nCH_4, and $TBMP_{UA}$

Biowaste	Empirical formula	ONc	$TBMP_{UA}$	$TBMP_{pub\text{-}UA}$	$TBMP_{pub\text{-}UA}\%$
CFW	$C_{3.845}H_{8.095}O_{2.104}N_{0.525}S_{0.017}$	-0.591	516.12	487.20	5.60
UCFW	$C_{2.751}H_{1.786}O_{3.116}N_{0.378}$	+2.029	168.65	117.39	30.39
VW	$C_{3.632}H_{6.399}O_{1.973}N_{0.372}S_{0.005}$	-0.366	510.26	401.17	21.38
FW	$C_{3.419}H_{12.248}O_{2.573}N_{0.191}$	-0.097	431.02	362.50	15.90
GW	$C_{3.396}H_{6.052}O_{2.458}N_{0.114}$	-0.004	437.53	336.65	23.06
PW	$C_{4.246}H_{6.200}O_{2.496}N_{0.130}$	-0.193	503.53	496.84	1.33
TW	$C_{6.353}H_{3.601}O_{1.116}N_{0.015}$	-0.208	763.82	743.10	2.71

5. Importance of Empirical Formula

In the study of AD, the empirical formula is the key concept to show the biodegradable nature of OM. The BEq's parameters, nCH_4 and TBMP, can be determined by empirical formulas. Table 6 shows the resulted ONc, μ, nCH_4, and TBMP in four different forms of empirical formulas regarding the same OM. In these empirical formulas, μ and nCH_4 have different values, and ONc, $\frac{nCH_4}{\mu}$, and TBMP have same values.

Table 6. Representations of empirical formulas: resulted ONc, μ, nCH_4, and TBMP

Empirical formula	ONc	Empirical formula mass (μ)	nCH_4	TBMP
$C_xH_yO_zN_vS_u$	$ONc = \frac{-y+2z+3v+2u}{x}$	$\mu = x\mu C + y\mu H + z\mu O + v\mu N + u\mu S$	$= \frac{x(4-ONc)}{8}$	$TBMP = \frac{2800\,x(4-ONc)}{\mu C_xH_yO_zN_vS_u}$
$CH_{y/x}O_{z/x}N_{v/x}S_{u/x}$		$\mu_1 = \frac{x\mu C + y\mu H + z\mu O + v\mu N + u\mu S}{x}$	$= \frac{1(4-ONc)}{8}$	
$C_{x/v}H_{y/v}O_{z/v}NS_{u/v}$		$\mu_2 = \frac{x\mu C + y\mu H + z\mu O + v\mu N + u\mu S}{v}$	$= \frac{(\frac{x}{v})(4-ONc)}{8}$	
$C_{x/u}H_{y/u}O_{z/u}N_{v/u}S$		$\mu_3 = \frac{x\mu C + y\mu H + z\mu O + v\mu N + u\mu S}{u}$	$= \frac{(\frac{x}{u})(4-ONc)}{8}$	

With reference to Table 4d and step 4 in Example 4, the empirical formulas that contain non-integer AC will give more accurate nCH_4 and TBMP results than those that contain integer AC. Therefore, the empirical formulas that contain non-integer AC ($C_xH_yO_zN_vS_u$) are recommended to be the standardized empirical formulas of OM.

6. Conclusion

Empirical formula is at the core of a series of AD calculations: from mass% to empirical formula, from empirical formula to nCH_4 and TBMP. Although the empirical formulas of OM are critical parameters for showing their biodegradable nature, they are not always accessible in literature and, in some cases, the published TBMP cannot be verified. By redoing the series of AD calculations, this article arrives at the following conclusions:

(1) The ONc can be used as an assessor that validates any empirical formula and its corresponding mass%. When an empirical formula of an OM is identified and valid, its corresponding mass% can be validated.

(2) When the series of AD calculations from mass% to empirical formula is done correctly, the value of the resulting non-integer AC of empirical formulas will be more accurate than that of the integer AC of empirical formulas.

(3) The relative percentage of TBMP is designed as an indicator that measures the discrepancy between the published TBMP and the recalculated TBMP.

(4) When non-integer AC of empirical formulas are used to calculate nCH_4 and TBMP, the values will be more accurate.

(5) When an empirical formula is identified, the BEq parameters nCH_4 and TBMP can be determined by simple mathematical equations.

List of abbreviations

AC	Atomic coefficients
AD	Anaerobic digestion
BDI	Biodegradability index
BMP	Biomethane potential
ΣEA%	Sum of individual mass percentages of elements
EBMP	Experimental biomethane potential
EF	Empirical formula
Mass%	Mass percentages of elements
OM	Organic matter
ONc	Mean oxidation number of organic carbons
TBMP	Theoretical biomethane potential
$TBMP_{pub\text{-}EF}$	Calculated TBMP from the published EF
$TBMP_{Pub\text{-}UA}$	Collected TBMP from the published mass%
$TBMP_{UA}$	Calculated TBMP from the published mass%
TS	Total solid
UA	Ultimate analysis
VS	Volatile solid

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Authors contributions

Dr. Pong Kau Yuen is responsible for designing the study, drafting, and revising the manuscript. Dr. Cheng Man Diana Lau is responsible for revising the manuscript. Kuok In Gabriel Yuen is responsible for data processing and figures drawing. All authors read and approved the final manuscript.

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