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Mean Oxidation Number of Organic Carbons for Quantifying Biomethane in Organophosphorous Compounds

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Abstract

Anaerobic digestion is a complex biochemical process in which organic matters are mineralized and stabilized into biogas and digestate by microorganisms in the absence of oxygen. Buswell's equation is an ideal model to represent anaerobic digestion for counting theoretical quantity of biogas and digestate in organic matters. Although the degradability and recovery of phosphorous element in digestate have been studied, the impact of phosphorous element on quantity of biomethane and theoretical biomethane potential in organophosphorous compounds are rarely explored. The quantity of biomethane is dependent on the elemental composition of organic matters, and the mean oxidation number of organic carbons is used as a counting parameter in Buswell's equation. Biowastes which contain organophosphorous compounds are chosen to demonstrate this notion. This article has two purposes. First, the mathematical relationships among empirical formula of organic matter, mean oxidation number of organic carbons, quantity of biomethane, and theoretical biomethane potential are explored. Second, the impact of quantity of phosphorous element on quantity of biomethane, theoretical biomethane potential, and the ratio of biomethane to carbon dioxide are studied.

Keywords: Buswell's equation, mean oxidation number of organic carbons, elemental composition, empirical formula, quantity of biomethane, theoretical biochemical methane potential, ratio of biomethane to carbon dioxide, biowaste, organophosphorous compound, $C_xH_yO_zX_wN_vS_uP_t$

1. Introduction

Anaerobic digestion is a sustainable technology used in waste treatment, bioenergy production, biofertilizer preparation, and waste volume reduction (Fang, 2010; Torales, 2013; Pullen, 2015; Horan, Yaser & Wid, 2019; Holden, Wolfe, Ogejo & Cummins, 2021). In this complex biochemical process, organic matters are mineralized and stabilized into biogas and digestate by microorganisms in the absence of oxygen. Anaerobic digestion is represented by the established Buswell's equation (Symons & Buswell, 1933; Boyle, 1977). The stoichiometric Buswell's equation (BEq) is used for counting quantity of biomethane in organic matters. An extended BEq (Yuen & Lau, 2023a) for $C_xH_yO_zX_wN_vS_uP_t$ is shown:

$$C_xH_yO_zX_wN_vS_uP_t + \frac{4x-y-2z+w+3v+2u+11t}{4} H_2O \rightarrow \frac{4x+y-2z-w-3v-2u+5t}{8} CH_4 + \frac{4x-y+2z+w+3v+2u-5t}{8} CO_2 + wHX + vNH_3$$

$$+ uH_2S + tH_3PO_4$$

Organophosphorous compounds (OPC) are present in natural environment (Fuentes, Bolan, Naidu & Mora, 2006; Xie, Wang, Castro-Jiménez, Kallenborn, Liao, Mi, Lohmann, Vila-Costa & Dachs, 2022; Jupp, Beijer, Narain, Schipper & Slootweg, 2021). In comparison to carbohydrates, proteins, and lipids, biomolecules which contain phosphorous element, such as DNA, phospholipid, NADH, and ATP have rarely been researched in anaerobic digestion. Many synthetic OPC are widely applied in the fields of agriculture, industry, defense, and medicine (Singh & Walker, 2006; Marklund, Andersson & Haglund, 2003; Demkowicz, Rachon, Daśkoa & Kozaka, 2016). They are released as agricultural, industrial, and domestic wastes. Although the degradability and recovery of phosphorous in digestate have been studied (Golroudbary, Wali & Kraslawski, 2019; Witek-Krowiak, Gorazda, Szopa, Trzaska, Moustakas & Chojnacka, 2022), the impact of phosphorous element on the quantity of biomethane (nCH_4) and theoretical biomethane potential (TBMP) in OPC have seldom been explored.

The parameter of nCH_4 is dependent on the elemental composition of organic matters and its value is strongly affected by which elements to measure, and which elements to include in the BEq calculation (Yuen & Lau, 2023a). The mathematical relationships among the mean oxidation number of organic carbons (ONc) and BEq's parameters have been established (Yuen & Lau, 2023b). In this article, ONc is used as a BEq counting parameter and empirical formulas of organophosphorous biowastes are chosen to demonstrate this notion. This article has two purposes. First, the mathematical relationships among empirical formula of organic matters, ONc, nCH_4, and TBMP are explored. Second, the impact of quantity of phosphorous element on nCH_4, TBMP, and the ratio of nCH_4 to nCO_2 are studied.

2. The Non-carbon-atom Method for ONc

Based on the structural formula of organic compounds, ONc can be determined by the fragmentation method (Yuen & Lau, 2022a; 2022b) or the carbon-atom method (Yuen & Lau, 2023c). Regarding the molecular formula method, ONc can be counted by its molecular formula through the assumed individual oxidation number of non-carbon-atom (ON_{inc}). The non-carbon-atom method is introduced to integrate the mathematical relationships among ONc, ON_{inc}, and atomic coefficients of molecular formulas by two working procedures: (i) use the molecular formula method to count ONc from either empirical formula or molecular formula, and (ii) assign all ON_{inc} according to their designated products in BEq.

2.1 For Neutral Organic Matters

$$\Sigma ON_i = 0$$

ON_i = individual oxidation number of atom

$$\Sigma ON_i = \Sigma ON_{ic} + \Sigma ON_{inc}$$

ON_{ic} = individual oxidation number of carbon atom

ON_{inc} = individual oxidation number of non-carbon-atom

$$\Sigma ON_{ic} = -\Sigma ON_{inc}$$

$$ONc = \frac{\Sigma ON_{ic}}{nc}$$

$$ONc = \frac{-\Sigma ON_{inc}}{nc}$$

ONc = mean oxidation number of organic carbons

nc = number of organic carbon atoms in organic matters

2.2 For Organic Matters in the General Molecular Formula or Empirical Formula of $C_xH_yO_zX_wN_vS_uP_t$

$C_xH_yO_zX_wN_vS_uP_t$	C	H	O	X	N	S	P
Individual oxidation number of non-carbon-atom (ON_{inc})	-	ON_H	ON_O	ON_X	ON_N	ON_S	ON_P
Atomic coefficients (AC)	x	y	z	w	v	u	t

$$ONc = \frac{-\Sigma ON_{inc}}{nc}$$

$$\Sigma ON_{inc} = [(ON_H\ y)+(ON_O\ z)+(ON_X\ w)+(ON_N\ v)+(ON_S\ u)+(ON_P\ t)]$$

$$nc = x$$

The mathematical equation of ONc is established as shown:

$$ONc = \frac{-[(ON_H\ y)+(ON_O\ z)+(ON_X\ w)+(ON_N\ v)+(ON_S\ u)+(ON_P\ t)]}{x}$$

3. Counting ONc from Empirical Formula

Organic matters are represented by the general chemical formula $C_xH_yO_zX_wN_vS_uP_t$, which is mainly composed of seven types of elements: C for carbon; H for hydrogen; O for oxygen; X for halogens; N for nitrogen; S for sulfur, and P for phosphorous. Atomic coefficients are used to represent the atomic composition with the notations of x, y, z, w, v, u, and t respectively.

In addition, BEq's stochiometric coefficients are represented by nH_2O, nCH_4, nCO_2, nHX, nNH_3, nH_2S, and nH_3PO_4. BEq are exhibited as follows:

$$C_xH_yO_zX_wN_vS_uP_t + nH_2O\ H_2O \rightarrow nCH_4\ CH_4 + nCO_2\ CO_2 + nHX\ HX + nNH_3\ NH_3 + nH_2S\ H_2S + nH_3PO_4\ H_3PO_4$$

Stoichiometric coefficients (SC) of the BEq can be determined by atomic coefficients (AC) of an empirical formula.

$C_xH_yO_zX_wN_vS_uP_t + \frac{4x-y-2z+w+3v+2u+11t}{4} H_2O \rightarrow \frac{4x+y-2z-w-3v-2u+5t}{8} CH_4 + \frac{4x-y+2z+w+3v+2u-5t}{8} CO_2 + wHX + vNH_3$

$+ uH_2S + tH_3PO_4$

According to the designated products of BEq, all ON_{inc} can be assigned as $ON_H = +1$; $ON_O = -2$; $ON_X = -1$; $ON_N = -3$; $ON_S = -2$; $ON_P = +5$, then ONc can be counted by the following mathematical equation:

$$ONc = \frac{-[(ON_H\,y)+(ON_O\,z)+(ON_X\,w)+(ON_N\,v)+(ON_S\,u)+(ON_P\,t)]}{x}$$

$$ONc = \frac{-y+2z+w+3v+2u-5t}{x}$$

Given an empirical formula of a biowaste sample (Yuen & Lau, 2023a), the procedure for calculation of ONc is shown in Example 1.

Example 1. Determine ONc of a given feedlot manure sample, $C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$

Solve: (i) Let $C_xH_yO_zX_wN_vS_uP_t = C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$

(ii) Set up a counting table

$C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$	C	H	O	Cl	N	S	P
ON_{inc}	-	+1	−2	−1	−3	−2	+5
AC	3.779	5.308	1.936	0.033	0.069	0.009	0

(iii) Use the mathematical equation

$$ONc = \frac{-[(ON_H\,y)+(ON_O\,z)+(ON_X\,w)+(ON_N\,v)+(ON_S\,u)+(ON_P\,t)]}{x}$$

$$ONc = \frac{-y+2z+w+3v+2u-5t}{x}$$

$$ONc = \frac{-1(5.308)+2(1.936)+1(0.033)+3(0.069)+2(0.009)-5(0)}{3.773} = -0.312$$

4. From Counting ONc to Determining nCH_4 and TBMP

Based on the mathematical representations of AC, ONc, and SC, the mathematical derivations from ONc to nCH_4 and TBMP are shown in Table 1.

Table 1. Mathematical representations of ONc, nCH_4, and TBMP

ONc	→	nCH_4	→	TBMP
$ONc = \frac{-y+2z+w+3v+2u-5t}{x}$ $xONc = -y+2z+w+3v+2u-5t$		$nCH_4 = \frac{4x+y-2z-w-3v-2u+5t}{8}$ $nCH_4 = \frac{4x-xONc}{8}$ $nCH_4 = \frac{x(4-ONc)}{8}$		$TBMP = \frac{22400\,nCH_4}{\mu C_xH_yO_zX_wN_vS_uP_t}$ $TBMP = \frac{22400\,x(4-ONc)}{8\mu C_xH_yO_zX_wN_vS_uP_t}$

For any empirical formula of organic matter, the triangular relationships among ONc, nCH_4, and TBMP can be established, and they are exhibited in Figure 1. The calculation from ONc to nCH_4 and TBMP is demonstrated in Example 2.

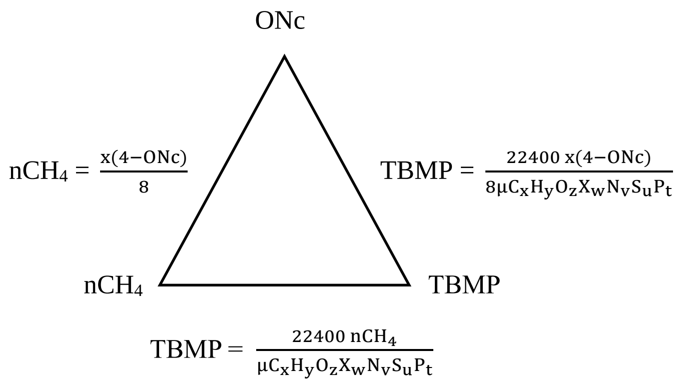

Figure 1. Triangular relationships among ONc, nCH_4, and TBMP

Example 2. Determine nCH_4 and TBMP of a given feedlot manure sample, $C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$

Solve: (i) by using mathematical equation for nCH_4

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

ONc ($C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$) = −0.312 (with reference to Example 1)

x = 3.779

$$nCH_4\,(\text{mol}) = \frac{(3.779)(4-(-0.312))}{8} = 2.037$$

(ii) by using mathematical equation for TBMP

$$TBMP = \frac{22400\,x(4-ONc)}{8\mu}$$

$\mu C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$ (g/mol) = 84.130

x = 3.779

$$TBMP\,(\text{mL/g at STP}) = \frac{22400\,(3.779)(4-(-0.312))}{8(84.130)} = 542.311$$

5. Working Procedures for Organophosphorous Matters from Mass% to nCH_4 and TBMP

Figure 2 shows the development of mass% to TBMP. When an elemental composition is identified, its ONc and empirical formula mass can be determined. Consequently, the nCH_4 and TBMP can be counted. Their mathematical representations are summarized in Table 2.

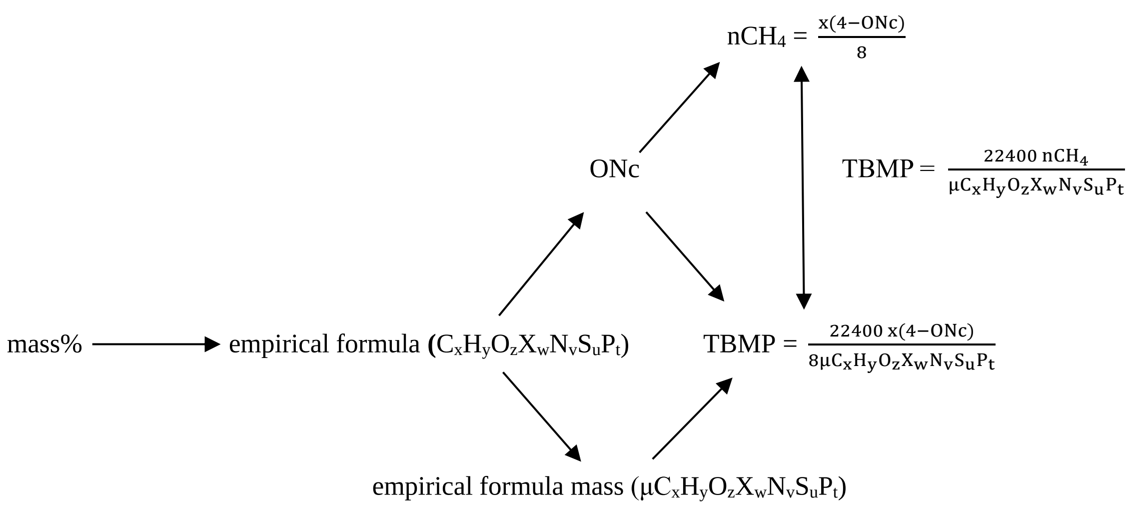

Figure 2. Relationships among mass%, empirical formula, empirical formula mass, ONc, nCH_4, and TBMP

Table 2. Mathematical representations of SC, AC, and ONc in BEq

Stochiometric coefficient (SC)	Atomic coefficient (AC)	ONc and AC
nH_2O	$nH_2O = \frac{4x-y-2z+w+3v+2u+11t}{4}$	$nH_2O = \frac{x(4+ONc)+16t-4z}{4}$
nCH_4	$nCH_4 = \frac{4x+y-2z-w-3v-2u+5t}{8}$	$nCH_4 = \frac{x(4-ONc)}{8}$
nCO_2	$nCO_2 = \frac{4x-y+2z+w+3v+2u-5t}{8}$	$nCO_2 = \frac{x(4+ONc)}{8}$
nHX	$nHX = w$	
nNH_3	$nNH_3 = v$	
nH_2S	$nH_2S = u$	
nH_3PO_4	$nH_3PO_4 = t$	

The classic BEq is represented by AC and the newly developed ONc-BEq model is represented by ONc and AC. They are shown as follows:

$$C_xH_yO_zX_wN_vS_uP_t + \frac{4x-y-2z+w+3v+2u+11t}{4} H_2O \rightarrow \frac{4x+y-2z-w-3v-2u+5t}{8} CH_4 + \frac{4x-y+2z+w+3v+2u-5t}{8} CO_2 + wHX + vNH_3 + uH_2S + tH_3PO_4$$

$$C_xH_yO_zX_wN_vS_uP_t + \frac{x(4+ONc)+16t-4z}{4} H_2O \rightarrow \frac{x(4-ONc)}{8} CH_4 + \frac{x(4+ONc)}{8} CO_2 + wHX + vNH_3 + uH_2S + tH_3PO_4$$

6. ONc-BEq Model for Empirical Formula of Biowastes

The ONc-BEq model can be used to study organic matters, which are mainly composed of C/H/O/X/N/S/P elements. The data of the ultimate analyses are retrieved from literature.

6.1 Data Collection

The C/H/O/N/S contents of most organic matters are studied by elemental analysis. Among them, biomatters which include mass% of phosphorous element were not often reported. The biowaste samples, which contain phosphorous element are chosen to exemplify. The selected ultimate analysis of biowastes which include the six elements of C/H/O/N/S/P are retrieved from literature (Zaher, Khachatryan, Ewing, Johnson, Chen & Stockle, 2010). They are listed in Table 3.

The mathematical relationship for ultimate analysis is shown:

$$100\% = ash\% + \Sigma\ Element\%$$

For $C_xH_yO_zN_vS_uP_t$ organic or bioorganic matters:

$$\Sigma\ Element\% = (C\%+H\%+O\%+N\%+S\%+P\%)$$

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

Table 3. Ultimate analysis of biowastes, $C_xH_yO_zN_vS_uP_t$

Biowaste	Mass%							
	Total%	Ash%	C%	H%	O%(*)	N%	S%	P%
Milk Cow Manure	100	8.42	44.70	5.90	37.96	2.24	0.30	0.48
MSW Food Waste	100	11.00	45.40	5.94	35.84	0.89	0.53	0.40
Horse Manure	100	17.78	46.90	4.20	28.20	1.20	1.50	0.22
Beef Cow Manure	100	14.90	45.40	5.40	30.97	2.56	0.29	0.48
Biosolids Generation	100	28.10	40.40	6.20	21.40	0.80	0.80	2.30
Poultry Manure	100	13.02	39.57	5.11	35.20	2.93	0.77	3.40
Meat Processing	100	1.85	50.50	7.70	25.50	13.80	0.50	0.15
Swine	100	20.27	45.70	6.45	21.30	3.45	0.38	2.45

Remark: * O% are recalculated by the mathematical equation,

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

6.2 Elemental Composition: $C_xH_yO_zN_vS_uP_t$

The mathematical equations and atomic masses for converting mass% of elements to empirical formula are shown:

$$\text{mole (of element)} = \frac{\text{mass of element}}{\text{atomic mass}}$$

$$nC : nH : nO : nN : nS : nP = \frac{C\%}{\mu C} : \frac{H\%}{\mu H} : \frac{O\%}{\mu O} : \frac{N\%}{\mu N} : \frac{S\%}{\mu S} : \frac{P\%}{\mu P} = x : y : z : v : u : t$$

Atomic mass (g/mol)	μC	μH	μO	μN	μS	μP
	12.011	1.008	15.999	14.007	32.065	30.974

Let the mass of a waste be 100.000 g, then the elemental ratios in biowastes are counted. The empirical formulas and empirical formula masses are summarized in Table 4.

Table 4. Empirical formula and empirical formula mass: biowastes, $C_xH_yO_zN_vS_uP_t$

Biowaste	$C_xH_yO_zN_vS_uP_t$	$\mu C_xH_yO_zN_vS_uP_t$
Milk Cow Manure	$C_{3.722}H_{5.853}O_{2.373}N_{0.160}S_{0.009}P_{0.015}$	91.580
MSW Food Waste	$C_{3.780}H_{5.893}O_{2.240}N_{0.064}S_{0.017}P_{0.013}$	89.000
Horse Manure	$C_{3.905}H_{4.167}O_{1.763}N_{0.086}S_{0.047}P_{0.007}$	82.220
Beef Cow Manure	$C_{3.780}H_{5.357}O_{1.936}N_{0.183}S_{0.009}P_{0.015}$	85.100
Biosolids Generation	$C_{3.364}H_{6.151}O_{1.338}N_{0.057}S_{0.025}P_{0.074}$	71.900
Poultry Manure	$C_{3.294}H_{5.069}O_{2.200}N_{0.209}S_{0.024}P_{0.110}$	86.980
Meat Processing	$C_{4.204}H_{7.639}O_{1.594}N_{0.985}S_{0.016}P_{0.005}$	98.150
Swine	$C_{3.805}H_{6.399}O_{1.331}N_{0.246}S_{0.012}P_{0.079}$	79.730

6.3 Calculation of ONc, nCH_4, and TBMP: $C_xH_yO_zN_vS_uP_t$

With reference to Examples 1 and 2, ONc, nCH_4, and TBMP (shown in Table 5) can be calculated by the following mathematical equations.

$ONc = \frac{-y+2z+w+3v+2u-5t}{x}$	$nCH_4 = \frac{x(4-ONc)}{8}$	$TBMP = \frac{22400\,x(4-ONc)}{8\mu C_xH_yO_zX_wN_vS_uP_t}$

Table 5. Resulted ONc, nCH_4, and TBMP for $C_xH_yO_zN_vS_uP_t$

Biowaste	nC = x	$\mu C_xH_yO_zN_vS_uP_t$	ONc	nCH_4	TBMP
Milk Cow Manure	3.722	91.580	-0.185	1.947	476.142
MSW Food Waste	3.780	89.000	-0.332	2.047	515.104
Horse Manure	3.905	82.220	-0.084	1.993	543.020
Beef Cow Manure	3.780	85.100	-0.264	2.015	530.264
Biosolids Generation	3.364	71.900	-1.078	2.135	665.146
Poultry Manure	3.294	86.980	-0.165	1.715	441.677
Meat Processing	4.204	98.150	-0.354	2.288	522.243
Swine	3.805	79.730	-0.885	2.324	652.797

7. Effect of the Content of Phosphorous Elements on nCH_4, TBMP, and $\frac{nCH_4}{nCO_2}$

Ultimate analyses for biomasses which contain the phosphorous element were rarely measured and the content of phosphorous element was often neglected when counting nCH_4 and TBMP.

Compare $C_xH_yO_zN_vS_uP_t$ to $C_xH_yO_zN_vS_u$. The working scheme is shown below:

$C_xH_yO_zN_vS_uP_t \rightarrow ONc \rightarrow nCH_4$ and TBMP

$C_xH_yO_zN_vS_u \rightarrow ONc \rightarrow nCH_4$ and TBMP

7.1 Calculation of ONc and nCH_4: Comparing $C_xH_yO_zN_vS_uP_t$ to $C_xH_yO_zN_vS_u$

The resulted ONc and nCH_4 for $C_xH_yO_zN_vS_uP_t$ and $C_xH_yO_zN_vS_u$ are summarized in Table 6. By using $C_xH_yO_zN_vS_uP_t$ as a reference, when the phosphorous elements are not included in calculation, the result will be $C_xH_yO_zN_vS_u$. The atomic coefficient of x demonstrates that there is no difference between $C_xH_yO_zN_vS_uP_t$ and $C_xH_yO_zN_vS_u$, and the atomic coefficient t of phosphorous is zero.

Table 6. Resulted ONc and nCH_4 for $C_xH_yO_zN_vS_uP_t$ and $C_xH_yO_zN_vS_u$

Biowaste	nC = x	$C_xH_yO_zN_vS_uP_t$		$C_xH_yO_zN_vS_u$	
		ONc	nCH_4	ONc	nCH_4
Milk Cow Manure	3.722	-0.185	1.947	-0.164	1.937
MSW Food Waste	3.780	-0.332	2.047	-0.315	2.039
Horse Manure	3.905	-0.084	1.993	-0.074	1.989
Beef Cow Manure	3.780	-0.264	2.015	-0.243	2.005
Biosolids Generation	3.364	-1.078	2.135	-0.968	2.089
Poultry Manure	3.294	-0.165	1.715	0.002	1.646
Meat Processing	4.204	-0.354	2.288	-0.348	2.285
Swine	3.805	-0.885	2.324	-0.782	2.274

When the phosphorous element is not included in calculation, x is the same and t equals zero. An increase of ONc in $C_xH_yO_zN_vS_u$ causes a decrease of $nCH_4 = \frac{x(4-ONc)}{8}$. ONc in $C_xH_yO_zN_vS_uP_t$ is smaller (more negative; much reduced) than ONc in $C_xH_yO_zN_vS_u$. Consequently, nCH_4 in $C_xH_yO_zN_vS_uP_t$ is greater than nCH_4 in $C_xH_yO_zN_vS_u$.

7.2 Counting TBMP: Comparing $C_xH_yO_zN_vS_uP_t$ to $C_xH_yO_zN_vS_u$

The resulted TBMP for $C_xH_yO_zN_vS_uP_t$ and $C_xH_yO_zN_vS_u$ are summarized in Table 7. When x does not change, its TBMP is proportional to the ratio $\frac{(4-ONc)}{\mu_{\text{empirical formula}}}$.

Table 7. Resulted TBMP for $C_xH_yO_zN_vS_uP_t$ and $C_xH_yO_zN_vS_u$

Biowaste	x	$C_xH_yO_zN_vS_uP_t$			$C_xH_yO_zN_vS_u$		
		ONc	$\mu C_xH_yO_zN_vS_uP_t$	TBMP	ONc	$\mu C_xH_yO_zN_vS_u$	TBMP
Milk Cow Manure	3.722	-0.185	91.580	476.142	-0.164	91.100	476.269
MSW Food Waste	3.780	-0.332	89.000	515.104	-0.315	88.600	515.389
Horse Manure	3.905	-0.084	82.220	543.020	-0.074	82.000	543.264
Beef Cow Manure	3.780	-0.264	85.100	530.264	-0.243	84.620	530.708
Biosolids Generation	3.364	-1.078	71.900	665.146	-0.968	69.600	672.190
Poultry Manure	3.294	-0.165	86.980	441.677	0.002	83.580	441.257
Meat Processing	4.204	-0.354	98.150	522.243	-0.348	98.000	522.350
Swine	3.805	-0.885	79.730	652.797	-0.782	77.280	659.163

When the phosphorous element is not included in calculation, x is the same and t equals 0. Decreases of (4−ONc) and $\mu C_xH_yO_zN_vS_u$ cause TBMP = $\frac{22400\,x(4-ONc)}{8\mu C_xH_yO_zX_wN_vS_uP_t}$ $(\frac{decrease}{decrease})$ to either increase or decrease. TBMP is proportional to (4−ONc) or nCH_4 and inversely proportional to its empirical mass. Comparing the values of TBMP between $C_xH_yO_zN_vS_uP_t$ and $C_xH_yO_zN_vS_u$, the resulting TBMP in $C_xH_yO_zN_vS_u$ either increase or decrease.

7.3 Counting the ratio of nCH_4 to nCO_2: Comparing $C_xH_yO_zN_vS_uP_t$ to $C_xH_yO_zN_vS_u$

The counting of nCH_4 is critical in BEq. The sum of nCH_4 and nCO_2 is equal to x, whereas $\frac{nCH_4}{nCO_2}$ is equal to $\frac{4-ONc}{4+ONc}$ (Yuen & Lau, 2023b). When ONc of biowaste is determined, the parameters of nCH_4, nCO_2, and $\frac{nCH_4}{nCO_2}$ can be counted accordingly. The resulted $\frac{nCH_4}{nCO_2}$ for $C_xH_yO_zN_vS_uP_t$ and $C_xH_yO_zN_vS_u$ are summarized in Table 8.

$$nCH_4 = \frac{x(4-ONc)}{8};\ nCO_2 = \frac{x(4+ONc)}{8}$$

$$x = nCH_4 + nCO_2$$

$$\frac{nCH_4}{nCO_2} = \frac{4-ONc}{4+ONc}$$

Table 8. Resulted nCH_4, nCO_2, and $\frac{nCH_4}{nCO_2}$ for $C_xH_yO_zN_vS_uP_t$ and $C_xH_yO_zN_vS_u$

Biowaste	x	$C_xH_yO_zN_vS_uP_t$				$C_xH_yO_zN_vS_u$			
		ONc	nCH_4	nCO_2	$\frac{nCH_4}{nCO_2}$	ONc	nCH_4	nCO_2	$\frac{nCH_4}{nCO_2}$
Milk Cow Manure	3.722	-0.185	1.947	1.775	1.097	-0.164	1.937	1.785	1.085
MSW Food Waste	3.780	-0.332	2.047	1.733	1.181	-0.315	2.039	1.741	1.171
Horse Manure	3.905	-0.084	1.993	1.912	1.042	-0.074	1.989	1.916	1.038
Beef Cow Manure	3.780	-0.264	2.015	1.765	1.142	-0.243	2.005	1.775	1.129
Biosolids Generation	3.364	-1.078	2.135	1.229	1.737	-0.968	2.089	1.275	1.638
Poultry Manure	3.294	-0.165	1.715	1.579	1.086	0.002	1.646	1.648	0.999
Meat Processing	4.204	-0.354	2.288	1.916	1.194	-0.348	2.285	1.919	1.191
Swine	3.805	-0.885	2.324	1.481	1.569	-0.782	2.274	1.531	1.486

When the phosphorous element is not included in calculation, x is the same and t equals 0. An increase of ONc in $C_xH_yO_zN_vS_u$ causes (4−ONc) to decrease, then it affects nCH_4 to decrease and nCO_2 to increase. The value of $\frac{nCH_4}{nCO_2}$ $(\frac{decrease}{increase})$ decreases. ONc in $C_xH_yO_zN_vS_uP_t$ is more negative and much reduced than ONc in $C_xH_yO_zN_vS_u$. Consequently, the nCH_4 and $\frac{nCH_4}{nCO_2}$ in $C_xH_yO_zN_vS_uP_t$ will be greater than the nCH_4 and $\frac{nCH_4}{nCO_2}$ in $C_xH_yO_zN_vS_u$.

8. The Impact of Phosphorous, Sulfur, and Nitrogen Contents on ONc

In the study of quantity of phosphorous element in biowastes, data has been processed and attained. The quantity of phosphorous element has significant impact on ONc, empirical formula, empirical formula mass, nCH_4, TBMP, and $\frac{nCH_4}{nCO_2}$.

Calculation of ONc for $C_xH_yO_zN_vS_uP_t$, $C_xH_yO_zN_vS_u$, $C_xH_yO_zN_v$, and $C_xH_yO_z$ are summarized in Table 9. The impact of phosphorous, sulfur, and nitrogen contents on ONc are compared and shown in the following.

Table 9. Resulted ONc for $C_xH_yO_zN_vS_uP_t$, $C_xH_yO_zN_vS_u$, $C_xH_yO_zS_uP_t$, and $C_xH_yO_zN_vS_uP_t$

Biowaste	$C_xH_yO_zN_vS_uP_t$	ONc			
		$C_xH_yO_zN_vS_uP_t$	$C_xH_yO_zN_vS_u$	$C_xH_yO_zN_v$	$C_xH_yO_z$
Milk Cow Manure	$C_{3.722}H_{5.853}O_{2.373}N_{0.160}S_{0.009}P_{0.015}$	-0.185	-0.164	-0.169	-0.298
MSW Food Waste	$C_{3.780}H_{5.893}O_{2.240}N_{0.064}S_{0.017}P_{0.013}$	-0.332	-0.315	-0.323	-0.374
Horse Manure	$C_{3.905}H_{4.167}O_{1.763}N_{0.086}S_{0.047}P_{0.007}$	-0.084	-0.074	-0.098	-0.164
Beef Cow Manure	$C_{3.780}H_{5.357}O_{1.936}N_{0.183}S_{0.009}P_{0.015}$	-0.264	-0.243	-0.248	-0.393
Biosolids Generation	$C_{3.364}H_{6.151}O_{1.338}N_{0.057}S_{0.025}P_{0.074}$	-1.078	-0.968	-0.982	-1.033
Poultry Manure	$C_{3.294}H_{5.069}O_{2.200}N_{0.209}S_{0.024}P_{0.110}$	-0.165	0.002	-0.013	-0.203
Meat Processing	$C_{4.204}H_{7.639}O_{1.594}N_{0.985}S_{0.016}P_{0.005}$	-0.354	-0.348	-0.356	-1.059
Swine	$C_{3.805}H_{6.399}O_{1.331}N_{0.246}S_{0.012}P_{0.079}$	-0.885	-0.782	-0.788	-0.982

8.1 Comparing Phosphorous-Content: $C_xH_yO_zN_vS_uP_t$ and $C_xH_yO_zN_vS_u$

$C_xH_yO_zN_vS_uP_t \rightarrow C_xH_yO_zN_vS_u$

ONc: increases from ONc of $C_xH_yO_zN_vS_uP_t$ to ONc of $C_xH_yO_zN_vS_u$

Redox property: changes from reduced form of $C_xH_yO_zN_vS_uP_t$ to oxidized form of $C_xH_yO_zN_vS_u$

Since $ON_P = +5$, when the phosphorous-content in chemical formula decreases, its ONc increases and appears in a lower reduced form or higher oxidized form.

8.2 Comparing Sulfur-content: $C_xH_yO_zN_vS_u$ and $C_xH_yO_zN_v$

$C_xH_yO_zN_vS_u \rightarrow C_xH_yO_zN_v$

ONc: decreases from ONc of $C_xH_yO_zN_vS_u$ to ONc of $C_xH_yO_zN_v$

Redox property: changes from oxidized form of $C_xH_yO_zN_vS_u$ to reduced form of $C_xH_yO_zN_v$

Since $ON_S = -2$, when the sulfur-content in chemical formula decreases, its ONc decreases and appears in a higher reduced form.

8.3 Comparing Nitrogen-content: $C_xH_yO_zN_v$ and $C_xH_yO_z$

$C_xH_yO_zN_v \rightarrow C_xH_yO_z$

ONc: decreases from ONc of $C_xH_yO_zN_v$ to ONc of $C_xH_yO_z$

Redox property: changes from oxidized form of $C_xH_yO_zN_v$ to reduced form of $C_xH_yO_z$

Since $ON_N = -3$, when the nitrogen-content in chemical formula decreases, its ONc decreases and appears in a higher reduced form.

In summary, the positive $ON_P = +5$ makes ONc more negative whereas the negative $ON_S = -3$ or $ON_N = -3$ makes ONc more positive. Positive ON_{inc} causes more negative ONc and a higher reduced form whereas negative ON_{inc} causes more positive ONc and a higher oxidized form.

9. Conclusion

This article shows that ONc acts as a BEq counting parameter. Based on the empirical formula of any organic matter, its ONc can be determined by the non-carbon-atom method. The newly developed ONc-BEq model has effectively established the mathematical relationships among the parameters of an empirical formula, empirical formula mass, ONc, nCH_4, and TBMP. Furthermore, ONc of any given empirical formula of organic matter can be used to quantify nCH_4

($nCH_4 = \frac{x(4-ONc)}{8}$) and TBMP ($TBMP = \frac{22400\,x(4-ONc)}{8\mu_{empirical\ formula}}$). In addition, by using organic matters as examples, they demonstrate that positive ON_{inc} causes more negative ONc and a higher reduced form whereas negative ON_{inc} causes more positive ONc and a higher oxidized form according to their empirical formulas. In the case of OPC which contains the designated product H_3PO_4 (ON_P = +5) in BEq, when the quantity of phosphorous element increases, its ONc will become more negative and possess higher reducing property. Consequently, nCH_4 and ratio of biomethane to carbon dioxide ($\frac{nCH_4}{nCO_2}$) will be increased.

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Authors contributions

Dr. Pong Kau Yuen was responsible for designing the study and drafting the manuscript. Dr. Cheng Man Diana Lau was responsible for revising the manuscript. All authors read and approved the final manuscript.

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