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Using Buswell's Equation to Count Quantity of Biomethane in Organochlorine Compounds

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Abstract

Anaerobic digestion is a sustainable technology used in waste treatment and bioenergy production. It is chemically represented by the Buswell's equation which is a significant model for counting theoretical quantity of biomethane. Although pure organic degradable substances or mixtures have been well studied by using Buswell's equation, organochlorine compounds have not yet been explored. This article has three purposes. First, a new general Buswell's equation for organochlorine compounds is deducted. Second, the impact of chlorine element in agricultural wastes on quantity of biomethane is studied. Third, the mathematical relationships among quantity of biomethane, theoretical biochemical methane potential, and biodegradability index are explored.

Keywords: Buswell's equation, stoichiometric coefficient, empirical formula, elemental composition, quantity of biomethane, theoretical biochemical methane potential, biodegradability index, organochlorine compound, $C_xH_yO_zCl_wN_vS_u$

1. Introduction

Anaerobic digestion is a sustainable technology used in waste treatment and bioenergy production (Fang, 2010; Torales, 2013; Pullen, 2015; Horan, Yaser & Wid, 2019; Holden, Wolfe, Ogejo & Cummins, 2021). During the complex biochemical stages, organic biodegradable matters are broken down into biogas and digestate in the absence of oxygen. Buswell established an overall chemical equation to represent anaerobic digestion (Symons & Buswell, 1933). It is a model which integrates chemistry, biochemistry, and mathematics in the biosystem. The stoichiometric Buswell's equation (BEq) plays a paramount role in counting quantity of biomethane either in pure or mixed organic matters. An example of the balanced BEq is shown:

$$C_xH_yO_z + (x - \frac{y}{4} - \frac{z}{2})\ H_2O \rightarrow (\frac{x}{2} + \frac{y}{8} - \frac{z}{4})\ CH_4 + (\frac{x}{2} - \frac{y}{8} + \frac{z}{4})\ CO_2$$

The modified BEq which includes nitrogen and sulfur elements (Boyle, 1977) is demonstrated as:

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

The extended BEq which includes phosphorous element (Yuen & Lau, 2023a) has been deducted:

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

Organohalogen compounds have been identified as naturally and abiotically occurring materials (Gribble, 2009) which exist in vegetations, animals, humans, soils (Fleming, 1995; Oberg, 2003), and crude oils (Badamshin, Nosov, Presniakov, Voloshin, Nevyadovskiy & Dokichev, 2021). Many artificial organohalogen compounds, especially organochlorine compounds, are important industrial, agricultural, and pharmaceutical chemicals. They are used as solvents, synthetic polymer, drugs, and pesticides (Abelson, 1994). Organohalogen compounds are widely present in the natural environment, and they are also released as domestic, agricultural, and industrial wastes. However, the BEq which contains halogen element has not been revealed.

The BEq is a significant model for understanding anaerobic digestion and counting quantity of biomethane which consequently helps count the theoretical biochemical methane potential (Angelidaki & Sanders, 2004; Buswell & Boruff, 1932; Neave & Buswell, 1930). Theoretical biochemical methane potential (TBMP) considers all organic matters are biodegradable (Buswell & Mueller, 1952). Experimental biochemical methane potential (EBMP) is defined as a measure of sample biodegradability (Owen & Chynweth, 1993), and batch bioassay technique is designed to measure EBMP (Raposo, De la Rubia, Fernández-Cegrí, Borja, 2012; Raposo, Fernández-Cegrí, de la Rubia, Borja, Béline, Cavinato, Demirer, Fernández, Fdz-Polanco, Frigon, Ganesh, Kaparaju, Koubova, Méndez, Menin, Peene, Scherer, Torrijos, Uellendahl, & de Wilde, 2011; Angelidaki, Alves, Bolzonella, Borzacconi, Campos, Guwy, Kalyuzhnyi, Jenicek & van Lier, 2009; Owen, Stuckey, Healy Jr., Young & McCarty, 1979). The biodegradability index (BDI) is applied to evaluate the effectiveness of anaerobic digestion. It is defined as the ratio between EBMP and TBMP (Nielfa, Cano & Fdz-Polanco, 2015).

Quantity of biomethane (nCH_4) is a parameter which depends on the elemental composition of organic matters. When this quantity must be measured, its accuracy is strongly affected by two decisions: (1) which elements to measure, and (2) which elements to include in calculation. Although halogens are important elements and organohalogen compounds play a vital role in the chemical world, the BEq which includes halogen elements has not yet been reported. This article has three purposes. First, the general BEq of organohalogen compounds is deducted. Second, the impact of quantity of chlorine element on nCH_4 is studied. Third, the mathematical relationships among nCH_4, TBMP, and BDI are explored.

2. Deducting General Buswell's Equation of Organohalogen Compounds

The H-atom method has been used to study organic combustion reactions (Yuen & Lau, 2021; 2022a; 2023b) and redox reactions (Yuen & Lau, 2022b). It is applied here to deduct the new general BEq of $C_xH_yO_zX_wN_vS_u$.

Example 1. Deducting the general Buswell's equation of $C_xH_yO_zX_wN_vS_u$

Unbalanced BEq: $C_xH_yO_zX_wN_vS_u + H_2O \rightarrow CH_4 + CO_2 + HX + NH_3 + H_2S$

Step 1. Divide an overall reaction into two half reactions

$$C_xH_yO_zX_wN_vS_u \rightarrow CH_4 + HX + NH_3 + H_2S$$

$$C_xH_yO_zX_wN_vS_u \rightarrow CO_2 + HX + NH_3 + H_2S$$

Step 2. Balance two half reactions

$$C_xH_yO_zX_wN_vS_u \rightarrow CH_4 + HX + NH_3 + H_2S$$

$$C_xH_yO_zX_wN_vS_u \rightarrow xCH_4 + wHX + vNH_3 + uH_2S$$

$$C_xH_yO_zX_wN_vS_u + (4x+w+3v+2u-y)H \rightarrow xCH_4 + wHX + vNH_3 + uH_2S + zO$$

$$C_xH_yO_zX_wN_vS_u + (4x+w+3v+2u-y)H + 2zH \rightarrow xCH_4 + wHX + vNH_3 + uH_2S + zO + 2zH$$

$$C_xH_yO_zX_wN_vS_u + (4x-y+2z+w+3v+2u)H \rightarrow xCH_4 + wHX + vNH_3 + uH_2S + zH_2O$$

$$C_xH_yO_zX_wN_vS_u \rightarrow CO_2 + HX + NH_3 + H_2S$$

$$C_xH_yO_zX_wN_vS_u \rightarrow xCO_2 + wHX + vNH_3 + uH_2S$$

$$C_xH_yO_zX_wN_vS_u + (2x-z)O \rightarrow xCO_2 + wHX + vNH_3 + uH_2S + (y-w-3v-2u)H$$

$$C_xH_yO_zX_wN_vS_u + (2x-z)O + 2(2x-z)H \rightarrow xCO_2 + wHX + vNH_3 + uH_2S + (y-w-3v-2u)H + 2(2x-z)H$$

$$C_xH_yO_zX_wN_vS_u + (2x-z)H_2O \rightarrow xCO_2 + wHX + vNH_3 + uH_2S + (4x+y-2z-w-3v-2u)H$$

Step 3. Equalize the number of H-atom of two half reactions

LCM of the H-atom = $(4x-y+2z+w+3v+2u)\ (4x+y-2z-w-3v-2u)$

$$[C_xH_yO_zX_wN_vS_u + (4x-y+2z+w+3v+2u)H \rightarrow xCH_4 + wHX + vNH_3 + uH_2S + zH_2O] \times (4x+y-2z-w-3v-2u)$$

$$[C_xH_yO_zX_wN_vS_u + (2x-z)H_2O \rightarrow xCO_2 + wHX + vNH_3 + uH_2S + (4x+y-2z-w-3v-2u)H] \times (4x-y+2z+w+3v+2u)$$

Step 4. Regenerate an overall BEq reaction by combining two half reactions

$$(8x)C_xH_yO_zX_wN_vS_u + (8x^2-2xy-4xz+2xw+6xv+4xu)H_2O \rightarrow (4x^2+xy-2xz-xw-3xv-2xv)CH_4 +$$
$$(4x^2-xy+2xz+xw+3xv+2xu)CO_2 + 8xwHX + 8xvNH_3 + 8xuH_2S$$

Step 5. Attain the deducted BEq

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

By using the same strategy, the new BEq of $C_xH_yO_zX_wN_vS_uP_t$ can also be attained. The known developed BEqs are summarized in Table 1. Stoichiometric coefficients of the BEq can be determined by the elemental composition either of molecular formula or empirical formula.

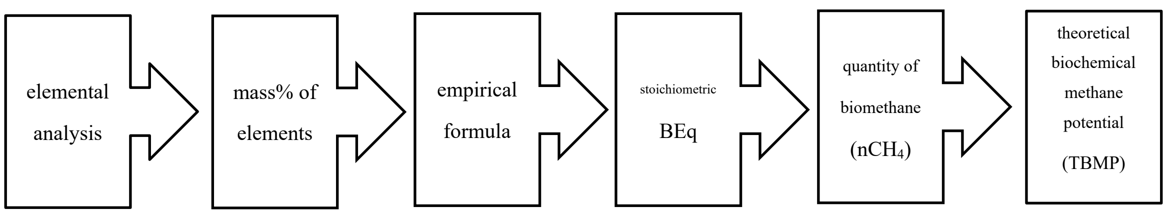
Table 1. General Buswell's equation of organic biodegradable matters

Developed Buswell's equation in general form	Source
$C_xH_yO_z + \frac{4x-y-2z}{4} H_2O \rightarrow \frac{4x+y-2z}{8} CH_4 + \frac{4x-y+2z}{8} CO_2$	Symons & Buswell, 1933
$C_xH_yO_zN_vS_u + \frac{4x-y-2z+3z+2u}{4} H_2O \rightarrow \frac{4x+y-2z-3v-2u}{8} CH_4 + \frac{4x-y+2z+3v+2u}{8} CO_2 + vNH_3 + uH_2S$	Boyle, 1977
$C_xH_yO_zN_vS_uP_t + \frac{4x-y-2z+3v+2u+11t}{4} H_2O \rightarrow \frac{4x+y-2z-3v-2u+5t}{8} CH_4 + \frac{4x-y+2z+3v+2u-5t}{8} CO_2 + vNH_3 + uH_2S + tH_3PO_4$	Yuen & Lau, 2023a
$C_xH_yO_zX_wN_vS_u + \frac{4x-y-2z+w+3v+2u}{4} H_2O \rightarrow \frac{4x+y-2z-w-3v-2u}{8} CH_4 + \frac{4x-y+2z+w+3v+2u}{8} CO_2 + wHX + vNH_3 + uH_2S$	This article
$C_xH_yO_zX_wN_vS_uP_t + \frac{4x-y-2z+w+3v+2u+11t}{4} H_2O \rightarrow \frac{4x+y-2z-w-3v-2u+5t}{8} CH_4 + \frac{4x-y+2z+w+3v+2u-5t}{8} CO_2 + wHX + vNH_3 + uH_2S + tH_3PO_4$	This article

Although ultimate analyses for biomasses or biowastes which contain the chlorine element were measured in literature, the content of chlorine element is neglected when counting nCH_4 and TBMP. The newly developed BEq which includes halogen element provides a solution to count critical parameters accurately.

3. Organochlorine Compound $C_xH_yO_zCl_wN_vS_u$

Only a few agricultural and domestic wastes which include mass% of chlorine element were reported (Maj, 2022; Maj, Kalisz, Szymajda, Łaska & Gołombek, 2021; Haugen, Halvorsen & Eikeland, 2015). In the following section, two agricultural wastes, both of which contain organochlorine matters, $C_xH_yO_zCl_wN_vS_u$, are selected for study. Based on elemental analysis, the empirical formula of an organic matter can be determined. Then stoichiometric BEq can be used for counting nCH_4 and TBMP. The working procedure is shown in scheme 1.



Scheme 1. The working procedure: from elemental analysis to theoretical biochemical methane potential

3.1 From Mass% of Elements to Empirical Formula

3.1.1 Ultimate Analysis of Agricultural Wastes

For most organic matters, their C/H/N/S contents are analyzed by elemental analysis. The dried chicken litter and feedlot manure samples, both of which contain chlorine element (Achinas & Euverink, 2016) are chosen to exemplify the calculation. The mass% of elements of samples are demonstrated in Table 2.

The mathematical relationship for ultimate analysis is shown:

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

For $\underline{C_xH_yO_zCl_wN_vS_u}$ matters:

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

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

Table 2. Mass% of elements (C/H/O/Cl/N/S) of chicken litter and feedlot manure

Sample	Ash%*	Mass% of elements					
	ash	C	H	O	Cl	N	S
Chicken litter	15.49	45.32	5.85	27.38	0.35	5.16	0.45
Feedlot manure	15.87	45.39	5.35	30.98	1.16	0.96	0.29

Remark: * Ash% is calculated by the mathematical equation, ash% = 100% – Σ Element%

3.1.2 Empirical Formula

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

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

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

Atomic mass (g/mol)	μC	μH	μO	μCl	μN	μS
	12.011	1.008	15.999	35.453	14.007	32.065

Let the mass of a waste be 100.000 g, then the elemental ratios in chicken litter and feedlot manure are counted. Through calculation of each sample, the elemental composition of its empirical formula, and its empirical mass can be determined. The elemental ratios of chicken litter and feedlot manure are shown in Table 3. The empirical formulas and empirical masses of chicken litter and feedlot manure are summarized in Table 4.

Table 3. The elemental ratios of chicken litter and feedlot manure

mole / sample	nC = x	nH = y	nO = z	nCl = w	nN = v	nS = u
Chicken litter	3.773	5.804	1.711	0.010	0.368	0.014
Feedlot manure	3.779	5.308	1.936	0.033	0.069	0.009

Table 4. The empirical formulas and empirical masses of chicken litter and feedlot manure

Sample	empirical formula, $C_xH_yO_zCl_wN_vS_u$	empirical mass, $\mu C_xH_yO_zCl_wN_vS_u$
Chicken litter	$C_{3.773}H_{5.804}O_{1.711}X_{0.010}N_{0.368}S_{0.014}$	84.510
Feedlot manure	$C_{3.779}H_{5.308}O_{1.936}X_{0.033}N_{0.069}S_{0.009}$	84.130

3.2 From Empirical Formula to Stoichiometric BEq

3.2.1 Stoichiometric Coefficients of BEq

$$C_xH_yO_zCl_wN_vS_u + nH_2O\ H_2O \rightarrow nCH_4\ CH_4 + nCO_2\ CO_2 + nHCl\ HCl + nNH_3\ NH_3 + nH_2S\ H_2S$$

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

With reference to Table 2, all stoichiometric coefficients (nH_2O, nCH_4, nCO_2, nHCl, nNH_3 and nH_2S) of the Buswell's equation (shown in Table 5) can be determined by the empirical formulas' elemental composition (x, y, z, w, v, and u).

Table 5. Stoichiometric coefficients of the BEq for chicken litter and feedlot manure

Sample	nH_2O	nCH_4	nCO_2	nHCl	nNH_3	nH_2S
Chicken litter	1.752	2.042	1.732	0.010	0.368	0.014
Feedlot manure	1.549	2.037	1.742	0.033	0.069	0.009

Empirical formula and BEq for chicken litter are demonstrated:

$C_xH_yO_zCl_wN_uS_v = C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014}$

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

$$C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014} + 1.752H_2O \rightarrow 2.042CH_4 + 1.732CO_2 + 0.010HCl + 0.368NH_3 + 0.014H_2S$$

Empirical formula and BEq for feedlot manure are shown:

$C_xH_yO_zCl_wN_uS_v = C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$

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

$$C_{3.779}H_{5.308}O_{1.936}X_{0.033}N_{0.069}S_{0.009} + 1.549H_2O \rightarrow 2.037CH_4 + 1.742CO_2 + 0.033HCl + 0.069NH_3 + 0.009H_2S$$

3.2.2 Counting Quantity of Biomethane and Biogas (nbiomethane and nbiogas)

The nbiomethane (nCH_4) and nbiogas can be determined by using either its elemental composition or stoichiometric coefficients of BEq.

$$nC = x = nCH_4 + nCO_2$$

$$\text{mole of biomethane} = \text{nbiomethane} = nCH_4 = \frac{4x+y-2z-w-3v-2u}{8}$$

$$\text{mole of biogas} = \text{nbiogas} = nCH_4 + nCO_2 + nHCl + nNH_3 + nH_2S = x + w + v + u$$

For chicken litter:

$$C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014} + 1.752H_2O \rightarrow 2.042CH_4 + 1.732CO_2 + 0.010HCl + 0.368NH_3 + 0.014H_2S$$

$$\text{nbiogas} = x + w + v + u$$
$$= 3.773 + 0.010 + 0.368 + 0.014$$
$$= 4.165$$

$$\text{nbiomethane} = \frac{4x+y-2z-w-3v-2u}{8}$$
$$= \frac{4(3.773)+(5.804)-2(1.711)-(0.010)-3(0.368)-2(0.014)}{8}$$
$$= 2.042$$

For feedlot manure:

$$C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009} + 1.549H_2O \rightarrow 2.037CH_4 + 1.742CO_2 + 0.033HCl + 0.069NH_3 + 0.009H_2S$$

$$\text{nbiogas} = x + w + v + u$$
$$= 3.779 + 0.033 + 0.069 + 0.009$$
$$= 3.971$$

$$\text{nbiomethane} = \frac{4x+y-2z-w-3v-2u}{8}$$
$$= \frac{4(3.779)+(5.308)-2(1.936)-(0.033)-3(0.069)-2(0.009)}{8}$$
$$= 2.037$$

3.2.3 Counting Percentage Parameters of $\frac{\text{nbiomethane}}{\text{nbiogas}}\%$ and $\frac{nCH_4}{nCH_4+nCO_2}\%$

The percentage parameters of anaerobic digestion can be determined by the following mathematical expressions:

$\frac{\text{nbiomethane}}{\text{nbiogas}}\%$ and $\frac{nCH_4}{nCH_4+nCO_2}\%$ (or $\frac{nCH_4}{x}\%$)

With reference to Table 5, their calculated results are summarized in Table 6. The sum of nCH_4 and nCO_2 (equal to nC or x) represents the carbon-containing nbiogas which do not include non-carbon gas ingredients. The value of nbiogas is greater than the sum of nCH_4 and nCO_2.

Table 6. Percentage of nCH_4 in biogas for chicken litter and feedlot manure

Sample	nC = x	nCH_4	nCO_2	nbiogas	$\frac{\text{nbiomethane}}{\text{nbiogas}}\%$	$\frac{nCH_4}{nCH_4+nCO_2}\% = \frac{nCH_4}{x}\%$
Chicken litter	3.773	2.042	1.732	4.165	49.03%	54.12%
Feedlot manure	3.779	2.037	1.742	3.971	51.30%	53.90%

3.3 From either Elemental Composition or Stoichiometric Coefficients to Volume of Biogas

Based either on the elemental composition (x, y, z, w, v, and u) or the stoichiometric coefficients (nH_2O, nCH_4, nCO_2, nHCl, nNH_3 and nH_2S), all individual gas volumes and their summation can be counted and are shown in Table 7.

$$VCH_4 = \text{TBMP (mL/g at STP)} = \frac{22400(nCH_4)}{\mu C_xH_yO_zCl_wN_vS_u}$$

$$\text{Vgas, (mL/g at STP)} = \frac{22400(\text{ngas})}{\mu C_xH_yO_zCl_wN_vS_u}$$

$$\text{Vbiogas} = \Sigma\text{Vgas} = VCH_4 + VCO_2 + VHCl + VNH_3 + VH_2S$$

$$\text{Vbiogas} = \Sigma\text{Vgas} = Vx + Vw + Vv + Vu$$

Table 7. Individual gas volumes and biogas volumes for chicken litter and feedlot manure

Sample	VCH_4	VCO_2	VHCl	VNH_3	VH_2S	Vbiogas
Chicken litter	541.11	458.95	2.65	97.54	3.71	1103.96
Feedlot manure	542.29	463.88	8.79	18.37	2.40	1035.73

4. Quantity of Chlorine Element Impacting Empirical Formula and Empirical Mass of Organochlorine Matters

When nCH_4 is calculated, the accuracy is significantly affected by two factors: (1) which elements to measure, and (2) which elements to include for calculation. Take $\underline{C_xH_yO_zCl_wN_vS_u}$ waste as an example, when the BEq model is used to count nCH_4, two problems will emerge. First, quantity of chlorine is not measured. Second, in some cases where quantity of chlorine is measured, it is not included in the calculation. These two problems are studied by using chicken litter and feedlot manure as examples.

4.1 Problem 1: "Quantity of Chlorine Element is not Measured."

4.1.1 Mass%: Change in Quantity of Oxygen Element

The mathematical equation for ultimate analysis is shown:

$$100\% = \text{ash}\% + \Sigma\ \text{Element}\%$$

For $\underline{C_xH_yO_zN_vS_u}$ matters:

$$\Sigma\ \text{Element}\% = (C\%+H\%+O\%+N\%+S\%)$$

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

For $\underline{C_xH_yO_zCl_wN_vS_u}$ matters:

$$\Sigma\ \text{Element}\% = (C\%+H\%+O\%+Cl\%+N\%+S\%)$$

$$O\% = 100\% - \text{ash}\% - (C\%+H\%+Cl\%+N\%+S\%)$$

The two cases, one measuring C/H/N/S elements only and the other measuring C/H/N/S/Cl elements, generate different mass% of oxygen element. The mass% of oxygen when measuring C/H/N/S elements only is equal to the sum of mass% of oxygen and mass% of chlorine when measuring C/H/N/S/Cl elements. Mass% of elements in $C_xH_yO_zCl_wN_vS_u$ (Table 8a) and mass% of elements in $C_xH_yO_zN_vS_u$ (Table 8b) are compared.

Table 8a. Mass% of elements in $C_xH_yO_zCl_wN_vS_u$

Sample	Mass% of elements: $C_xH_yO_zCl_wN_vS_u$						
	Ash	C	H	**O**	**Cl**	N	S
Chicken litter	15.49	45.32	5.85	**27.38**	**0.35**	5.16	0.45
Feedlot manure	15.87	45.39	5.35	**30.98**	**1.16**	0.96	0.29

When the chlorine element is present but not measured, the mass% of Cl is counted as a part of the mass% of O. $C_xH_yO_zCl_wN_vS_u$ becomes $C_xH_yO_zN_vS_u$.

Table 8b. Mass% of elements in $C_xH_yO_zN_vS_u$

Sample	Mass% of elements: $C_xH_yO_zN_vS_u$						
	Ash	C	H	**O**	~~**Cl**~~	N	S
Chicken litter	15.49	45.32	5.85	**27.73**	~~**0.35**~~ **(0)**	5.16	0.45
Feedlot manure	15.87	45.39	5.35	**32.14**	~~**1.16**~~ **(0)**	0.96	0.29

4.1.2 Elemental Composition: Difference in Oxygen Element

The elemental composition of samples in the empirical formulas are calculated and shown in Table 9a and 9b. When chlorine element is not measured, the elemental composition of oxygen element (z) of $C_xH_yO_zN_vS_u$ becomes greater.

Table 9a. Elemental composition in $C_xH_yO_zCl_wN_vS_u$

mole / sample	nC = x	nH = y	**nO = z**	**nCl = w**	nN = v	nS = u
Chicken litter	3.773	5.804	**1.711**	**0.010**	0.368	0.014
Feedlot manure	3.779	5.308	**1.936**	**0.033**	0.069	0.009

Table 9b. Elemental composition in $C_xH_yO_zN_vS_u$

mole / sample	nC = x	nH = y	**nO = z**	~~**nCl = w**~~	nN = v	nS = u
Chicken litter	3.773	5.804	**1.733**	~~**0.010**~~ **(0)**	0.368	0.014
Feedlot Manure	3.779	5.308	**2.009**	~~**0.033**~~ **(0)**	0.069	0.009

4.1.3 Same Empirical Masses: $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$

Empirical formula and empirical mass for $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$ are summarized in Table 10a and Table 10b respectively. Although $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$ have different empirical formulas, they have the same empirical masses.

Table 10a. Empirical formula and empirical mass for $C_xH_yO_zCl_wN_vS_u$

Sample	empirical formula, $C_xH_yO_zCl_wN_vS_u$	empirical mass, $\mu C_xH_yO_zCl_wN_vS_u$
Chicken litter	$C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014}$	84.510
Feedlot manure	$C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$	84.130

Table 10b. Empirical formula and empirical mass for $C_xH_yO_zN_vS_u$

Sample	empirical formula, $C_xH_yO_zN_vS_u$	empirical mass, $\mu C_xH_yO_zN_vS_u$
Chicken litter	$C_{3.773}H_{5.804}O_{1.733}N_{0.368}S_{0.014}$	84.510
Feedlot manure	$C_{3.779}H_{5.308}O_{2.009}N_{0.069}S_{0.009}$	84.130

4.1.4 Counting nbiomethane and nbiogas: Different Elemental Compositions Between $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$

The nbiomethane and nbiogas for $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$ are summarized in Table 11a and Table 11b respectively.

For $C_xH_yO_zCl_wN_uS_v$, $nCH_4 = \frac{4x+y-2z-w-3v-2u}{8}$, nbiogas = nx + nw + nu + nv

Table 11a. nbiomethane and nbiogas for $C_xH_yO_zCl_wN_vS_u$

$C_xH_yO_zCl_wN_uS_v$	nCH_4	nCO_2	nbiogas
Chicken litter, $C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014}$	2.042	1.732	4.165
Feedlot manure, $C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$	2.037	1.742	3.971

For $C_xH_yO_zN_uS_v$, $nCH_4 = \frac{4x+y-2z-3v-2u}{8}$, nbiogas = nx + nu + nv

Table 11b. nbiomethane and nbiogas for $C_xH_yO_zN_vS_u$

$C_xH_yO_zN_uS_v$	nCH_4	nCO_2	nbiogas
Chicken litter, $C_{3.773}H_{5.804}O_{1.733}N_{0.368}S_{0.014}$	2.037	1.736	4.155
Feedlot manure, $C_{3.779}H_{5.308}O_{2.009}N_{0.069}S_{0.009}$	2.023	1.756	3.857

When the quantity of chlorine element is not measured, nCH_4 becomes smaller whereas nCO_2 becomes greater.

4.1.5 Counting VCH_4 and Vbiogas: Difference Between $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$

$$VCH_4 = TBMP = \frac{22400(nCH_4)}{\mu C_xH_yO_zCl_wN_vS_u}$$

The VCH_4 and Vbiogas for $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$ are summarized in Table 12a and Table 12b respectively.

For $C_xH_yO_zCl_wN_uS_v$:

$$VCH_4 = \frac{22400(4x+y-2z-w-3v-2u)}{8\mu C_xH_yO_zCl_wN_vS_u}$$

$$Vbiogas = VCH_4 + VCO_2 + VHCl + VNH_3 + VH_2S$$

Table 12a. VCH_4 and Vbiogas for $C_xH_yO_zCl_wN_vS_u$

$C_xH_yO_zCl_wN_uS_v$	VCH_4	VCO_2	Vbiogas
Chicken litter, $C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014}$	541.11	458.95	1103.96
Feedlot manure, $C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$	542.29	463.88	1035.73

For $C_xH_yO_zN_uS_v$:

$$VCH_4 = \frac{22400(4x+y-2z-3v-2u)}{8\mu C_xH_yO_zN_vS_u}$$

$$Vbiogas = VCH_4 + VCO_2 + VNH_3 + VH_2S$$

Table 12b. VCH_4 and Vbiogas for $C_xH_yO_zN_vS_u$

$C_xH_yO_zN_uS_v$	VCH_4	VCO_2	Vbiogas
Chicken litter, $C_{3.773}H_{5.804}O_{1.733}N_{0.368}S_{0.014}$	539.99	460.07	1101.31
Feedlot manure, $C_{3.779}H_{5.308}O_{2.009}N_{0.069}S_{0.009}$	538.53	467.64	1026.94

TBMP (VCH_4) is directly proportional to nCH_4 and inversely proportional to empirical mass. When the quantity of chlorine element is not measured, VCH_4 becomes smaller whereas VCO_2 becomes greater.

4.2 Problem 2: "Quantity of Chlorine Element is Measured but not Included in Calculation."

In general practices, when the contents of elements are small compared to other elemental fractions, they will not be included in calculation. Here the quantity of chlorine element is selected as an example.

4.2.1 Mass%: No Difference in Oxygen Element

The mass% for $C_xH_yO_zCl_wN_vS_u$ and for $C_xH_yO_zN_vS_u$ are summarized in Table 13a and Table 13b respectively.

Table 13a. Mass% for $C_xH_yO_zCl_wN_vS_u$

Sample	Mass%: $C_xH_yO_zCl_wN_vS_u$					
	Ash	C	H	**O**	**Cl**	N	S
Chicken litter	15.49	45.32	5.85	**27.38**	**0.35**	5.16	0.45
Feedlot manure	15.87	45.39	5.35	**30.98**	**1.16**	0.96	0.29

When quantity of chlorine element is not included in calculation, its mass% of Cl is zero. $C_xH_yO_zCl_wN_vS_u$ becomes $C_xH_yO_zN_vS_u$.

Table 13b. Mass% for $C_xH_yO_zN_vS_u$

Sample	Mass%: $C_xH_yO_zN_vS_u$						
	Ash	C	H	**O**	~~**Cl**~~	N	S
Chicken litter	15.49	45.32	5.85	**27.38**	~~**0.35**~~ **(0)**	5.16	0.45
Feedlot manure	15.87	45.39	5.35	**30.98**	~~**1.16**~~ **(0)**	0.96	0.29

4.2.2 Elemental Ratios: No Difference in Oxygen Element

When the chlorine element is not included in calculation, there is no difference in the elemental composition of oxygen element (z). The elemental ratios for $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$ are summarized in Table 14a and Table 14b respectively.

Table 14a. The elemental ratio for $C_xH_yO_zCl_wN_vS_u$

mole / sample	nC = x	nH = y	**nO = z**	**nCl = w**	nN = v	nS = u
Chicken litter	3.773	5.804	**1.711**	**0.010**	0.368	0.014
Feedlot manure	3.779	5.308	**1.936**	**0.033**	0.069	0.009

Table 14b. The elemental ratio for $C_xH_yO_zN_vS_u$

mole / sample	nC = x	nH = y	**nO = z**	~~**nCl = w**~~	nN = v	nS = u
Chicken litter	3.773	5.804	**1.711**	~~**0.010**~~ **(0)**	0.368	0.014
Feedlot Manure	3.779	5.308	**1.936**	~~**0.033**~~ **(0)**	0.069	0.009

4.2.3 Empirical Formulas: Difference Between $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$

The empirical mass with chlorine element is heavier than that without chlorine element. The empirical formulas for $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$ are summarized in Table 15a and Table 15b respectively.

Table 15a. The empirical mass for $C_xH_yO_zCl_wN_vS_u$

Sample	empirical formula, $C_xH_yO_zCl_wN_vS_u$	empirical mass, $\mu C_xH_yO_zCl_wN_vS_u$
Chicken litter	$C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014}$	84.510
Feedlot manure	$C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$	84.130

Table 15b. The empirical mass for $C_xH_yO_zN_vS_u$

Sample	empirical formula, $C_xH_yO_zN_vS_u$	empirical mass, $\mu C_xH_yO_zN_vS_u$
Chicken litter	$C_{3.773}H_{5.804}O_{1.711}N_{0.368}S_{0.014}$	84.160
Feedlot manure	$C_{3.779}H_{5.308}O_{1.936}N_{0.069}S_{0.009}$	82.970

4.2.4 Counting nbiomethane and nbiogas: Difference Between $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$

The nbiomethane and nbiogas for $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$ are summarized in Table 16a and Table 16b respectively.

For $C_xH_yO_zCl_wN_uS_v$, $nCH_4 = \frac{4x+y-2z-w-3v-2u}{8}$, nbiogas = nx + nw + nu + nv

Table 16a. The nbiomethane and nbiogas for $C_xH_yO_zCl_wN_vS_u$

$C_xH_yO_zCl_wN_uS_v$	nCH_4	nCO_2	nbiogas
Chicken litter, $C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014}$	2.042	1.732	4.165
Feedlot manure, $C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$	2.037	1.742	3.971

For $C_xH_yO_zN_uS_v$, $nCH_4 = \frac{4x+y-2z-3v-2u}{8}$, nbiogas = nx + nu + nv

Table 16b. The nbiomethane and nbiogas for $C_xH_yO_zN_vS_u$

$C_xH_yO_zN_uS_v$	nCH_4	nCO_2	nbiogas
Chicken litter, $C_{3.773}H_{5.804}O_{1.711}N_{0.368}S_{0.014}$	2.043	1.730	4.155
Feedlot manure, $C_{3.779}H_{5.308}O_{1.936}N_{0.069}S_{0.009}$	2.041	1.738	3.857

When the chlorine element is not included in calculation, nCH_4 becomes greater whereas both nCO_2 and nbiogas become smaller.

4.2.5 Counting Vbiomethane and Vbiogas: Difference Between $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$

$$VCH_4 = TBMP = \frac{22400(nCH_4)}{\mu C_xH_yO_zCl_wN_vS_u}$$

The Vbiomethane and Vbiogas for $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$ are summarized in Table 17a and Table 17b respectively.

For $C_xH_yO_zCl_wN_uS_v$, $VCH_4 = \frac{22400(4x+y-2z-w-3v-2u)}{8\mu C_xH_yO_zCl_wN_vS_u}$, $Vbiogas = VCH_4 + VCO_2 + VHCl + VNH_3 + VH_2S$

Table 17a. The Vbiomethane and Vbiogas for $C_xH_yO_zCl_wN_vS_u$

$C_xH_yO_zCl_wN_uS_v$	VCH_4	VCO_2	Vbiogas
Chicken litter, $C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014}$	541.11	458.95	1103.96
Feedlot manure, $C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$	542.29	463.88	1035.73

For $C_xH_yO_zN_uS_v$, $VCH_4 = \frac{22400(4x+y-2z-3v-2u)}{8\mu C_xH_yO_zN_vS_u}$, $Vbiogas = VCH_4 + VCO_2 + VNH_3 + VH_2S$

Table 17b. The Vbiomethane and Vbiogas for $C_xH_yO_zN_vS_u$

$C_xH_yO_zN_uS_v$	VCH_4	VCO_2	Vbiogas
Chicken litter, $C_{3.773}H_{5.804}O_{1.711}N_{0.368}S_{0.014}$	543.70	460.52	1105.89
Feedlot manure, $C_{3.779}H_{5.308}O_{1.936}N_{0.069}S_{0.009}$	550.99	469.25	1041.30

TBMP is relevant to both nCH_4 and empirical mass. When the chlorine element is not included, nCH_4 becomes greater whereas empirical formula mass becomes smaller. Both VCH_4 and VCO_2 become greater also.

5. Counting Biodegradability Index of Anaerobic Digestion

The mathematical representation of biodegradability index (BDI) (Asha, Keerthi, Muthukrishnaraj & Balasubramanian, 2014; Bhatnagar, Ryan, Murphy & Enright, 2020) is demonstrated:

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

$$= \frac{\text{Experimental } VCH_4}{\text{Theoretical } VCH_4} \times 100\%$$

BDI is a parameter for evaluating the effectiveness of anaerobic digestion. Improving the efficiency of biochemical treatment is conducted in bioengineering. BDI is dependent on experimental VCH_4 (EBMP) and theoretical VCH_4 (TBMP). Although EBMP has been developed as a standard protocol (Holliger, Alves, Andrade, etc. 2016; Koch, Hafner, Weinrich, Astals, Holliger, 2020; Holliger, Astals, de Laclos, Hafner, Koch, Weinrich, 2021), TBMP is relatively less studied. If TBMP is erroneous, BDI will be adversely affected.

6. Relationships among Empirical Formula, Empirical Mass, nCH_4, and TBMP

Scheme 2 shows the established relationships among parameters of empirical formula, empirical mass, nCH_4, TBMP, and BDI. When the mass% of elements are measured, their elemental composition and empirical mass can be determined. Consequently, nCH_4, and then TBMP can be counted. Their mathematical representations are summarized in Table 18.

Scheme 2. Relationships among empirical formula, empirical mass, nCH_4, TBMP, and BDI in $C_xH_yO_zCl_wN_vS_u$

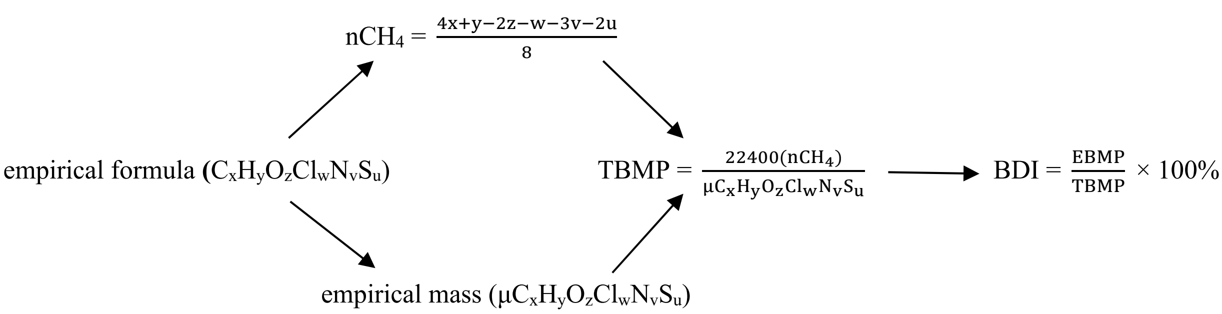


Table 18. Mathematical representations based on elemental composition and stoichiometric coefficients

Property	Representation	Attained parameter
empirical formula	$C_xH_yO_zCl_wN_vS_u$	elemental composition; empirical mass
balanced BEq	$nCH_4 = \frac{4x+y-2z-w-3v-2u}{8}$	stoichiometric coefficients; nCH_4
empirical mass	$\mu C_xH_yO_zCl_wN_vS_u$	mass% of elements; $\Sigma\mu_{atom}$
TBMP	$TBMP = \frac{22400(nCH_4)}{\mu C_xH_yO_zCl_wN_vS_u}$ $TBMP = \frac{22400(4x+y-2z-w-3v-2u)}{8\mu C_xH_yO_zCl_wN_vS_u}$	ratio of $\frac{nCH_4}{\mu C_xH_yO_zCl_wN_vS_u}$ ratio of $\frac{(4x+y-2z-w-3v-2u)}{\mu C_xH_yO_zCl_wN_vS_u}$
BDI	$BDI = \frac{EBMP}{TBMP} \times 100\%$	ratio of $\frac{EBMP}{TBMP}$

7. Effect of Quantity of Chlorine Elements on nCH_4, TBMP and BDI

From the study about quantity of chlorine element in wastes, data has been attained and processed. The quantity of chlorine element has critical impact on elemental composition, empirical formula, empirical mass, and stochiometric coefficients. Consequently, it affects the values of nCH_4, TBMP, and BDI.

7.1 Standard Case

Using the BEq of $C_xH_yO_zCl_wN_vS_u$ as a standard, all quantities of C/H/O/Cl/N/S elements are measured and included in calculation, the relevant parameters are shown in the following:

$C_xH_yO_zCl_wN_vS_u \rightarrow nCH_4 \rightarrow TBMP \rightarrow BDI$

$\quad \llcorner \rightarrow \mu C_xH_yO_zCl_wN_vS_u$

$$nCH_4 = \frac{4x+y-2z-w-3v-2u}{8}$$

The relevant and calculated data of standard case is summarized in Table 19.

Table 19. Standard case: Relationships among empirical formula, empirical mass, nCH_4, and TBMP

Standard	Empirical formula, $C_xH_yO_zCl_wN_vS_u$	nCH_4	Empirical mass, $\mu C_xH_yO_zCl_wN_vS_u$	$\frac{nCH_4}{\mu C_xH_yO_zCl_wN_vS_u}$	TBMP
Chicken litter	$C_{3.773}H_{5.804}O_{1.711}Cl_{0.010}N_{0.368}S_{0.014}$	2.042	84.510	2.416×10^{-2}	541.11
Feedlot manure	$C_{3.779}H_{5.308}O_{1.936}Cl_{0.033}N_{0.069}S_{0.009}$	2.037	84.130	2.421×10^{-2}	542.29

7.2 Case 1

When chlorine element is present but not measured, $C_xH_yO_zCl_wN_vS_u$ becomes $C_xH_yO_{z'}N_vS_u$. The following scheme demonstrates the case 1 flow of BEq parameters:

$C_xH_yO_zCl_wN_vS_u \rightarrow C_xH_yO_{z'}N_vS_u \rightarrow nCH_4 \rightarrow TBMP \rightarrow BDI$

$\quad \llcorner \rightarrow \mu C_xH_yO_{z'}N_vS_u$

$C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_{z'}N_vS_u$: elemental composition of z' in $C_xH_yO_{z'}N_vS_u$ becomes greater.

$\mu C_xH_yO_zCl_wN_vS_u = \mu C_xH_yO_{z'}N_vS_u$: empirical mass is the same.

z' (becomes greater) → $nCH_4 = \frac{4x+y-2z'-3v-2u}{8}$ (2z' > 2z and w = 0; becomes smaller) → $TBMP = \frac{22400(nCH_4)}{\mu C_xH_yO_{z'}N_vS_u}$ ($\frac{\text{becomes smaller}}{\text{same}}$; becomes smaller) → $BDI = \frac{EBMP}{TBMP} \times 100\%$ ($\frac{\text{same}}{\text{becomes smaller}}$; becomes greater)

The relevant and calculated data of case 1 is summarized in Table 20. When chlorine element is not measured, nCH_4 will have negative error.

Table 20. Case 1: Relationships among empirical formula, empirical mass, nCH_4, and TBMP

Case 1 Cl element not measured	Empirical formula, $C_xH_yO_{z'}N_vS_u$	nCH_4 (becomes smaller)	Empirical mass, $\mu C_xH_yO_{z'}N_vS_u$ (same)	$\frac{nCH_4}{\mu C_xH_yO_{z}{'}N_vS_u}$ (becomes smaller)	TBMP (becomes smaller)
Chicken litter	$C_{3.773}H_{5.804}O_{1.733}N_{0.368}S_{0.014}$	2.037	84.510	2.410×10^{-2}	539.99
Feedlot manure	$C_{3.779}H_{5.308}O_{2.009}N_{0.069}S_{0.009}$	2.023	84.130	2.405×10^{-2}	538.53

7.3 Case 2

When chlorine element is measured but not included in calculation: $C_xH_yO_zCl_wN_vS_u$ becomes $C_xH_yO_zN_vS_u$ and $\mu C_xH_yO_zCl_wN_vS_u$ becomes $\mu C_xH_yO_zN_vS_u$. The following scheme exhibits the case 2 flow of BEq parameters by the content of chlorine element.

$C_xH_yO_zCl_wN_vS_u$ → $C_xH_yO_zN_vS_u$ → nCH_4 → TBMP → BDI
 └→ $\mu C_xH_yO_zN_vS_u$

$C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$: elemental composition of z is the same between $C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$; elemental composition of w becomes zero.

$\mu C_xH_yO_zCl_wN_vS_u > \mu C_xH_yO_zN_vS_u$: empirical mass becomes smaller when $C_xH_yO_zCl_wN_vS_u$ becomes $C_xH_yO_zN_vS_u$.

z (same) → $nCH_4 = \frac{4x+y-2z-3v-2u}{8}$ (z is the same and w = 0; becomes greater) → TBMP = $\frac{22400(nCH_4)}{\mu C_xH_yO_zN_vS_u}$ ($\frac{\text{becomes greater}}{\text{becomes smaller}}$; becomes greater) → BDI = $\frac{EBMP}{TBMP} \times 100\%$ ($\frac{\text{same}}{\text{becomes greater}}$; becomes smaller)

The relevant and calculated data of case 2 is summarized in Table 21. When chlorine element is measured but not included in the calculation of empirical formula and empirical mass, TBMP will have significant positive error.

Table 21. Case 2: Relationships among empirical formula, empirical mass, nCH_4, and TBMP

Case 2 Cl element is neither measured nor included in the calculation of empirical formula (w = 0) and empirical mass (μCl = 0)	Empirical formula, $C_xH_yO_zN_vS_u$	nCH_4 (becomes greater)	Empirical mass, $\mu C_xH_yO_zN_vS_u$ (becomes smaller)	$\frac{nCH_4}{\mu C_xH_yO_zN_vS_u}$ (becomes greater)	TBMP (becomes greater)
Chicken litter	$C_{3.773}H_{5.804}O_{1.711}N_{0.368}S_{0.014}$	2.043	84.160	2.428×10^{-2}	543.70
Feedlot manure	$C_{3.779}H_{5.308}O_{1.936}N_{0.069}S_{0.009}$	2.041	82.970	2.460×10^{-2}	550.99

7.4 Case 3

When mass% of Cl is measured but not included in the calculation of empirical formula, $C_xH_yO_zCl_wN_vS_u$ becomes $C_xH_yO_zN_vS_u$. When element of Cl is included in the calculation of empirical mass, $\mu C_xH_yO_zCl_wN_vS_u$ remains the same. Shown below is the case 3 flow scheme of BEq parameters by the content of chlorine element.

$$C_xH_yO_zCl_wN_vS_u \rightarrow C_xH_yO_zN_vS_u \rightarrow nCH_4 \rightarrow TBMP \rightarrow BDI$$

$$C_xH_yO_zCl_wN_vS_u \longrightarrow \mu C_xH_yO_zCl_wN_vS_u$$

$C_xH_yO_zCl_wN_vS_u$ and $C_xH_yO_zN_vS_u$: elemental composition of z is the same when $C_xH_yO_zCl_wN_vS_u$ becomes $C_xH_yO_zN_vS_u$; elemental composition of w becomes zero.

$\mu C_xH_yO_zCl_wN_vS_u = \mu C_xH_yO_zCl_wN_vS_u$: empirical mass is the same.

z (same) → $nCH_4 = \frac{4x+y-2z-3v-2u}{8}$ (z is the same and w = 0; becomes greater) → $TBMP = \frac{22400(nCH_4)}{\mu C_xH_yO_zCl_wN_vS_u}$

($\frac{\text{becomes greater}}{\text{same}}$; becomes greater) → $BDI = \frac{EBMP}{TBMP} \times 100\%$ ($\frac{\text{same}}{\text{becomes greater}}$; becomes smaller)

The relevant and calculated data of case 3 is summarized in Table 22. When chlorine element is only included in the calculation of empirical mass but not empirical formula, TBMP will have positive error. Case 3 produces a smaller positive error than case 2.

Table 22. Case 3: Relationships among empirical formula, empirical mass, nCH_4, and TBMP

Case 3 Cl element: (i) measured, (ii) not included in empirical formula (w = 0), and (iii) included in empirical mass ($\mu Cl \neq 0$)	Empirical formula, $C_xH_yO_zN_vS_u$	nCH_4 (becomes greater)	Empirical mass, $\mu C_xH_yO_zCl_wN_vS_u$ (same)	$\frac{nCH_4}{\mu C_xH_yO_zCl_wN_vS_u}$ (becomes greater)	TBMP (becomes greater)
Chicken litter	$C_{3.773}H_{5.804}O_{1.711}N_{0.368}S_{0.014}$	2.043	84.510	24.275×10^{-2}	541.45
Feedlot manure	$C_{3.779}H_{5.308}O_{1.936}N_{0.069}S_{0.009}$	2.041	84.130	24.599×10^{-2}	543.39

To summarize all the cases, when chlorine element is present but not measured, value of nCH_4 becomes smaller. When chlorine element is measured but not included in calculation, value of nCH_4 becomes greater.

8. Research Methodology and Limitations

The research methodology of this article is desk research. Data of chicken litter and feedlot manure are collected from secondary sources and then studied by applying chemistry knowledge and mathematical concepts to manage the biochemical challenges of anaerobic digestion. The research focuses on deducting a new BEq of $C_xH_yO_zCl_wN_vS_u$, establishing the mathematical relationships among the BEq's parameters, and studying the impact of the content of chlorine element on nCH_4, TBMP, and BDI.

The BEq is a theoretical model with the following assumptions: (i) all carbons atoms in biomasses or biowastes totally convert to CH_4 and CO_2, (ii) all nitrogen/sulfur/halogen atoms in organic matters convert to NH_3/H_2S/HX respectively, and (iii) no other side reactions occur. In practice, other volatile organic compounds may decompose from chicken litter and feedlot manure through incomplete anaerobic digestion or other organic side reactions. It is also possible that the nitrogen element is not only converted to NH_3, but also to N_2O and other nitrogen-containing gases.

The research is limited because there is a lack of firsthand experimental data about ultimate analysis of biomasses and biowastes, and EBMP. There is no plan to carry on studying chicken litter and feedlot manure samples regarding margin of error, nor conduct EBMP studies for bio-samples and biowastes. The areas of interest are to fully explore how BEq can be used, to understand mathematical relationships among empirical formula, empirical mass, nCH_4, TBMP, and BDI, and to open a dialogue between theoretical studies and experimental developments.

9. Conclusion

Organochlorine compounds are abundant in nature, and they are widely used in society. This article established the stoichiometric Buswell's equation of $C_xH_yO_zCl_wN_vS_u$. An elemental composition (x, y, z, w, v, and u) of an empirical formula can be identified by measuring mass% of elements, and then all stoichiometric coefficients (nH_2O, nCH_4, nCO_2, nHCl, nNH_3, and nH_2S) of the Buswell's equation can be determined. Furthermore, quantity of biomethane can be counted by the mathematical equation, $nCH_4 = \frac{4x+y-2z-w-3v-2u}{8}$, and the mathematical relationships among nCH_4, TBMP, and BDI can be established. Regarding organochlorine matters, when the quantity of chlorine element is not measured, or measured but not included in calculation, there will be discrepancy between the counting of quantity of biomethane, theoretical biomethane potential, and biodegradability index.

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