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Ionic Buswell's Equation for Biohydrogen

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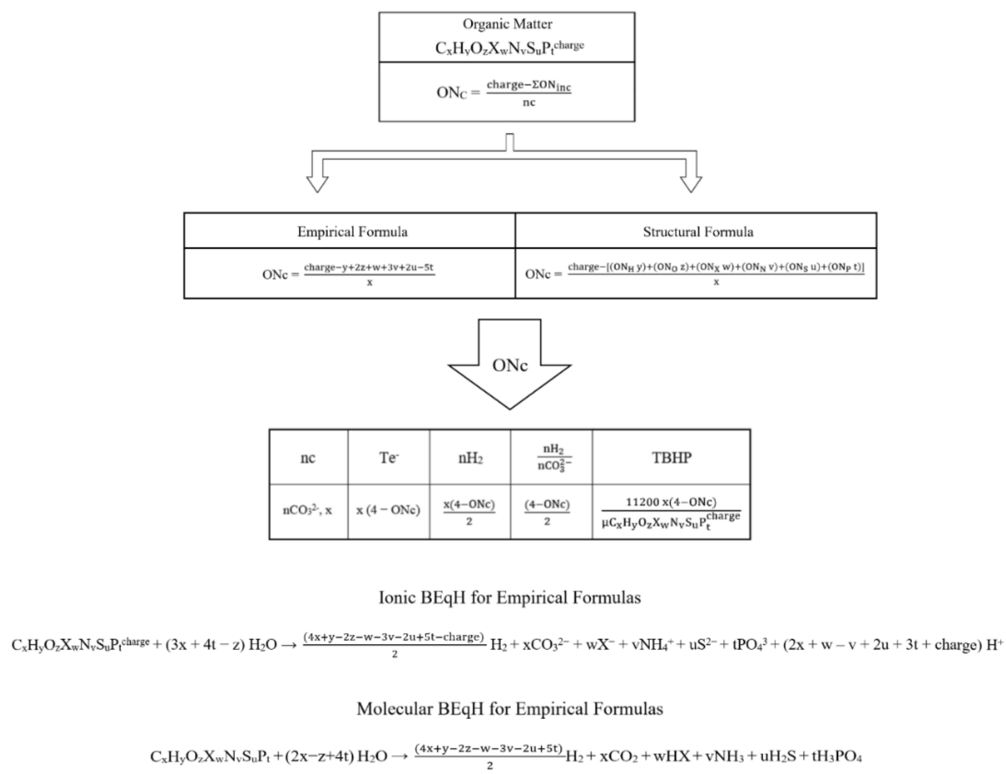
Abstract

Molecular hydrogen (H_2) can be generated by thermochemical, electrochemical, photochemical, or biochemical methods. Biohydrogen, specifically, can be produced by biochemical methods such as dark fermentation and two-stage anaerobic digestion, which may be represented by Buswell's equation. Although the molecular Buswell's equation for biohydrogen has been explored, the study of ionic Buswell's equation for biohydrogen has rarely been considered. This article shows that an ionic Buswell's equation for biohydrogen can be balanced and deduced by the proton method when an empirical formula of organic matter is given. The relationships between the mean oxidation number of organic carbons, number of transferred electrons, and quantity of biohydrogen are established. Furthermore, using the mean oxidation number of organic carbons as a metric, the number of transferred electrons, quantity of biohydrogen, ratio of quantity of biohydrogen to quantity of organic carbons, and theoretical biohydrogen potential can be determined through the derived mathematical equations by any given empirical or structural formula.

Graphical Abstract



Keywords: biohydrogen, ionic Buswell's equation, proton method, mean oxidation number of organic carbons, theoretical biochemical hydrogen potential, $C_xH_yO_zX_wN_vS_uP_t^{charge}$

1. Introduction

Molecular hydrogen (H_2) can be generated by thermochemical, electrochemical, photochemical, or biochemical methods, and it is significant in the fields of non-fossil energy, transportation, laboratory, and industry. Biohydrogen can be produced by biochemical methods such as dark fermentation (Moussa et al., 2022; Dzulkarnain et al., 2022; Sarangi & Nanda, 2020) and two-stage anaerobic digestion (Algapani et al., 2019; O-Thong et al, 2018) using biomass, biowaste, food waste, and wastewater as feedstocks. Anaerobic digestion is chemically represented by Buswell's equation (BEq) (Buswell & Boruff, 1932; Buswell & Mueller, 1952; Boyle, 1977). The stoichiometric Buswell's equation is useful in counting biomethane, though the use of Buswell's equation in counting biohydrogen has not been well studied. Based on an elemental composition of neutral organic matter, the general balanced molecular Buswell's equation for biohydrogen (BEqH) (Yuen & Lau, 2024a) is shown in the following:

$$C_xH_yO_zX_wN_vS_uP_t+(2x-z+4t)H_2O \rightarrow \frac{(4x+y-2z-w-3v-2u+5t)}{2}H_2+xCO_2+wHX+vNH_3+uH_2S+tH_3PO_4$$

Although the molecular BEqH for neutral organic matter has been studied (Yuen & Lau, 2024a; Pererva et al., 2020), the discussion of ionic BEqH for charged organic matter has not been considered. In this article, the ionic BEqH is balanced and deduced using the proton method (Yuen & Lau, 2022a). When an empirical formula of neutral or ionic organic matter is given, the corresponding ionic BEqH can be attained. Based on the stoichiometric BEqH, the relationships between the mean oxidation number of organic carbons (ONc), number of transferred electrons (Te^-), and quantity of biohydrogen (nH_2) are established. Using ONc as a metric (Yuen & Lau, 2024b), the Te^-, nH_2, and theoretical biohydrogen potential (TBHP) can be counted by any given empirical formula or structural formula through the derived mathematical equations.

2. Determination of Mean Oxidation Number of Organic Carbons

2.1 Mean Oxidation Number of Organic Carbons (ONc)

The ONc of neutral and charged organic matters can be assigned by the non-carbon atom method (Yuen & Lau, 2024c).

When charge ≠ 0, $ONc = \frac{charge-\Sigma ON_{inc}}{nc}$.

When charge = 0, $ONc = \frac{-\Sigma ON_{inc}}{nc}$.

For organic matters: $C_xH_yO_zX_wN_vS_uP_t^{charge}$

C, H, O, X, N, S, P = carbon, hydrogen, oxygen, halogen, nitrogen, sulfur, and phosphorus elements

x, y, z, w, v, u, t = atomic coefficients (AC) for C, H, O, X, N, S, P

charge = electrical charge of organic matter

nc = x = number of organic carbons

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

2.2 Empirical Formula

The empirical formula of an organic matter shows the matter's elemental composition. Chemical formulas of biomasses, biowastes, or unknown structures of pure and mixed organic matters are considered empirical formulas. Additionally, all ON_{inc} in empirical formulas are assumed to be $ON_H = +1$, $ON_O = -2$, $ON_X = -1$, $ON_N = -3$, $ON_S = -2$, $ON_P = +5$. For any given empirical formula, the ONc of an organic matter can be counted either by the molecular formula method (Yuen & Lau, 2022b) or the non-carbon atom method (Yuen & Lau, 2024c). The mathematical equation for calculating ONc of organic matter, $C_xH_yO_zX_wN_vS_uP_t^{charge}$, is established.

$\Sigma ON_{inc} = (y-2z-w-3v-2u+5t)$

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

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

2.3 Structural Formula

A structural formula identifies all covalent bonds in a skeleton of all atoms. Based on the structural formula of an organic matter, the individual oxidation number of non-carbon atoms (ON_{inc}) and mean oxidation number of organic carbons

(ONc) can be assigned by the fragmentation method (Yuen & Lau, 2022b), carbon-atom method (Yuen & Lau, 2023), or non-carbon atom method (Yuen & Lau, 2024c). For the general structural formula of an organic matter, $C_xH_yO_zX_wN_vS_uP_t^{charge}$, the mathematical equation for calculating ONc is established.

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

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

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

3. The Proton Method: Procedures for Balancing and Deducing Ionic BEqH

The proton method is a half reaction-based approach in which H^+, O, H_2O, and e^- are balancing tools (Yuen & Lau; 2022a). For any empirical formula of organic matter, the ON_{inc} are assumed to be $ON_H = +1$, $ON_O = -2$, $ON_X = -1$, $ON_N = -3$, $ON_S = -2$, and $ON_P = +5$. The corresponding ionic products are designated as CO_3^{2-}, X^-, NH_4^+, S^{2-}, and PO_4^{3-}.

Example 1. Given a charged empirical formula $C_2H_3O_2^-$ to balance the ionic BEqH.

Unbalanced ionic BEqH: $C_2H_3O_2^- + H_2O \rightarrow H_2 + CO_3^{2-} + H^+$

Step 1. Divide into two half reactions

$C_2H_3O_2^- \rightarrow CO_3^{2-}$

$H^+ \rightarrow H_2$

Step 2. Balance all atoms (from C→O→H) and charges (by e^-) in two half reactions

$C_2H_3O_2^- \rightarrow CO_3^{2-}$

$C_2H_3O_2^- \rightarrow 2CO_3^{2-}$

$C_2H_3O_2^- + 4O \rightarrow 2CO_3^{2-} + 3H^+$

$C_2H_3O_2^- + 4O + 8H^+ \rightarrow 2CO_3^{2-} + 3H^+ + 8H^+$

$C_2H_3O_2^- + 4H_2O \rightarrow 2CO_3^{2-} + 11H^+$

$C_2H_3O_2^- + 4H_2O \rightarrow 2CO_3^{2-} + 11H^+ + 8e^-$

$H^+ \rightarrow H_2$

$2H^+ \rightarrow H_2$

$2H^+ + 2e^- \rightarrow H_2$

Step 3. Make electrons of two half reactions equivalent (LCM = 8)

$(C_2H_3O_2^- + 4H_2O \rightarrow 2CO_3^{2-} + 11H^+ + 8e^-) \times 1$

$(2H^+ + 2e^- \rightarrow H_2) \times 4$

Step 4. Combine two half reactions and simplify the overall reaction

$C_2H_3O_2^- + 4H_2O \rightarrow 4H_2 + 2CO_3^{2-} + 3H^+$

Example 2. Given an empirical formula of organic ion $C_xH_yO_zX_wN_vS_uP_t^{charge}$ to deduce the ionic BEqH.

Unbalanced ionic BEqH: $C_xH_yO_zX_wN_vS_uP_t^{charge} + H_2O \rightarrow H_2 + CO_3^{2-} + X^- + NH_4^+ + S^{2-} + PO_4^{3-} + H^+$

Step 1. Divide into two half reactions

$C_xH_yO_zX_wN_vS_uP_t^{charge} \rightarrow CO_3^{2-} + X^- + NH_4^+ + S^{2-} + PO_4^{3-}$

$H^+ \rightarrow H_2$

Step 2. Balance all atoms (from C→XNSP→O→H) and charges in two half reactions

$C_xH_yO_zX_wN_vS_uP_t^{charge} \rightarrow xCO_3^{2-} + wX^- + vNH_4^+ + uS^{2-} + tPO_4^{3-}$

$C_xH_yO_zX_wN_vS_uP_t^{charge} + (3x+4t-z)O \rightarrow xCO_3^{2-} + wX^- + vNH_4^+ + uS^{2-} + tPO_4^{3-} + (y-4v)H^+$

$C_xH_yO_zX_wN_vS_uP_t^{charge} + (3x+4t-z)O + 2(3x+4t-z)H^+ \rightarrow xCO_3^{2-} + wX^- + vNH_4^+ + uS^{2-} + tPO_4^{3-} + (y-4v)H^+ + 2(3x+4t-z)H^+$

$C_xH_yO_zX_wN_vS_uP_t^{charge} + (3x+4t-z)H_2O \rightarrow xCO_3^{2-} + wX^- + vNH_4^+ + uS^{2-} + tPO_4^{3-} + (6x+y-2z-4v+8t)H^+$

$C_xH_yO_zX_wN_vS_uP_t^{charge}$ +(3x+4t−z)H_2O→ xCO_3^{2-}+wX^-+vNH_4^++uS^{2-}+tPO_4^{3-}+(6x+y−2z+4v+8t)H^+ +(4x+y−2z−w−3v−2u+5t−charge)e^-

$H^+ \rightarrow H_2$

$2H^+ \rightarrow H_2$

$2H^+ + 2e^- \rightarrow H_2$

Step 3. Make electrons of two half reactions equivalent {LCM = 2(4x+y−2z−w−3v−2u+5t−charge)}

($C_xH_yO_zX_wN_vS_uP_t^{charge}$ +(3x+4t−z)H_2O→xCO_3^{2-}+wX^-+vNH_4^++uS^{2-}+tPO_4^{3-}+(6x+y−2z−4v+8t)H^++ (4x+y−2z−w−3v−2u+5t−charge)e^-) × 2

($2H^+ + 2e^- \rightarrow H_2$) × (4x+y−2z−w−3v−2u+5t−charge)

Step 4. Combine two half reactions and simplify the overall reaction

2($C_xH_yO_zX_wN_vS_uP_t^{charge}$ +2(3x+4t−z)H_2O→(4x+y−2z−w−3v−2u+5t−charge)H_2+2xCO_3^{2-}+2wX^-+2vNH_4^+ +2uS^{2-}+2tPO_4^{3-}+2(2x+w−v+2u+3t+charge)H^+

$$C_xH_yO_zX_wN_vS_uP_t^{charge}+(3x+4t-z)H_2O \rightarrow \frac{(4x+y-2z-w-3v-2u+5t-charge)}{2}H_2+xCO_3^{2-}+wX^-+vNH_4^++uS^{2-}+tPO_4^{3-}+(2x+w-v+2u+3t+charge)H^+$$

As demonstrated in Example 3, a stoichiometric ionic BEqH can be identified by any given empirical formula of organic matter.

Example 3. Given an empirical formula of $C_{10}H_{12}O_7N_5P^{2-}$, identify the ionic BEqH.

Step 1. Identify AC and charge of an empirical formula

∵ $C_xH_yO_zX_wN_vS_uP_t^{charge} = C_{10}H_{12}O_7N_5P^{2-}$

∴ x = 10, y = 12, z = 7, w = 0, v = 5, u = 0, t = 1, and charge = −2

Step 2. Count stoichiometric coefficients (SC) of ionic BEqH

Based on the general BEqH: $C_xH_yO_zX_wN_vS_uP_t^{charge}+(3x+4t-z)H_2O \rightarrow \frac{(4x+y-2z-w-3v-2u+5t-charge)}{2}H_2+xCO_3^{2-}+wX^-+vNH_4^++uS^{2-}+tPO_4^{3-}+(2x+w-v+2u+3t+charge)H^+$

nH_2O = (3x+4t−z) = [3(10) + 4(1) − (7)] = 27

$$nH_2 = \frac{(4x+y-2z-w-3v-2u+5t-charge)}{2} = \frac{[4(10)+(12)-2(7)-(0)-3(5)-2(0)+5(1)-(-2)]}{2} = 15$$

nCO_3^{2-} = x = 10

nX^- = w = 0

nNH_4^+ = v = 5

nS^{2-} = u = 0

nPO_4^{3-} = t = 1

nH^+ = (2x+w−v+2u+3t+charge) = [(2(10) + (0) − (5) + 2(0) + 3(1) + (−2)] = 16

Step 3. Attain ionic BEqH

$C_{10}H_{12}O_7N_5P^{2-} + 27H_2O \rightarrow 15H_2 + 10CO_3^{2-} + 5NH_4^+ + PO_4^{3-} + 16H^+$

4. Counting Number of Transferred Electrons (Te^-) for Empirical Formulas

4.1 Te^- (Oxidation) and Te^- (Reduction)

BEqH is a biochemical redox reaction in the absence of O_2, all non-carbon and non-hydrogen atoms are non-redox atoms (Yuen & Lau, 2024a). Using the electron model (IUPAC, 2019), the redox terms of $C_2H_3O_2^- + 4H_2O \rightarrow 4H_2 + 2CO_3^{2-} + 3H^+$ are demonstrated. The carbon atoms (from $C_2H_3O_2^-$) lose electrons to form CO_2 and the protons (from $C_2H_3O_2^-$ and/or H_2O) gain electrons to form H_2. Carbon atoms are defined as reducing agents and protons are defined as oxidizing agents.

Considering the half oxidation reaction of $C_xH_yO_zX_wN_vS_uP_t^{charge}$ +(3x+4t−z)H_2O→xCO_3^{2-}+wX^-+vNH_4^++uS^2+tPO_4^3+ (6x+y−2z+4v+8t)H^++(4x+y−2z−w−3v−2u+5t−charge)e^-, organic carbon atoms act as reducing agents and lose the number of (4x+y−2z−w−3v−2u+5t−charge) electrons.

$$Te^- \text{ (oxidation)} = 4x+y-2z-w-3v-2u+5t-\text{charge}$$

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

$$xONc = \text{charge}-y+2z+w+3v+2u-5t$$

$$4x-xONc = 4x-(\text{charge}-y+2z+w+3v+2u-5t)$$

$$\therefore x(4-ONc) = 4x+y-2z-w-3v-2u+5t-\text{charge}$$

$$Te^- \text{ (oxidation)} = x(4-ONc)$$

Protons (H^+) function as oxidizing agents. Considering the half reaction of $2H^+ + 2e^- \rightarrow H_2$, when Te^- (oxidation) equals 2, it represents a gain of 2 electrons to form 1 mole of molecular hydrogen.

$$Te^- \text{ (reduction)} = 2\ nH_2$$

$$nH_2 = \frac{(4x+y-2z-w-3v-2u+5t-\text{charge})}{2} = \frac{x(4-ONc)}{2}$$

$$Te^- \text{ (reduction)} = 4x+y-2z-w-3v-2u+5t-\text{charge} = x(4-ONc)$$

$$Te^- \text{ (oxidation)} = Te^- \text{ (reduction)}$$

4.2 Counting Te^- in BEqH

Example 4. Given an empirical formula $C_2H_3O_2^-$

$C_xH_yO_z^{charge} = C_2H_3O_2^-$

x = 2, y =3, z = 2, and charge = −1

$Te^- = 4x+y-2z-\text{charge}$

$= 4(2) + (3) - 2(2) - (-1)$

$= 8$

In BEqH, carbon atoms (from $C_2H_3O_2^-$) lose 8 electrons and protons (from $C_2H_3O_2^-$ and H_2O) gain 8 electrons.

Example 5. Given an empirical formula $C_{10}H_{16}O_{13}N_5P_3$

$C_xH_yO_zX_wN_vS_uP_t^{charge} = C_{10}H_{16}O_{13}N_5P_3$

x = 10, y = 16, z = 13, w = 0, v = 5, u = 0, t = 3, and charge = 0

$Te^- = 4x+y-2z-w-3v-2u+5t-\text{charge}$

$= 4(10) + (16) - 2(13) - (0) - 3(5) - 2(0) + 5(3) - (0)$

$= 30$

In BEqH, carbon atoms (from $C_{10}H_{16}O_{13}N_5P_3$) lose 30 electrons and protons (from $C_{10}H_{16}O_{13}N_5P_3$ and H_2O) gain 30 electrons.

4.3 Relationships between Empirical Formula, Te^-, and ONc

With a given empirical formula, the corresponding AC and charge can be identified. Consequently, the ONc and Te^- in BEqH can be counted. Figure 1 demonstrates the triangular relationships between empirical formula, Te^-, and ONc.

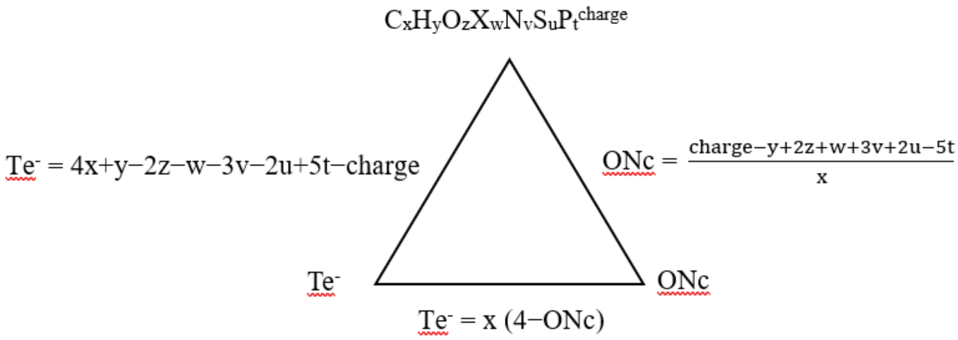


Figure 1. Triangular relationships between empirical formula, Te^-, and ONc

4.4 Relationships between ONc, Te^-, and nH_2

According to the mathematical equation of $Te^- = nc\ \Delta ONc$ (Yuen & Lau, 2022a; 2024d), the relationship between ONc and Te^- is derived.

$$Te^- = nc\ \Delta ONc$$

$$Te^- = nc\ [(ONc(CO_3^{2-}) - ONc(C_xH_yO_zX_wN_vS_uP_t^{charge})]$$

$$Te^- = nc\ (4 - ONc)$$

$$Te^- = x\ (4 - ONc)$$

The relationship between nH_2 and Te^- is represented as $Te^- = 2\ nH_2$ and $nH_2 = \frac{Te^-}{2}$. Through bridging the relationships of $Te^- = x\ (4 - ONc)$ and $Te^- = 2\ nH_2$, the relationship between ONc and Te^- is further demonstrated as $nH_2 = \frac{x(4-ONc)}{2}$ and $ONc = 4 - \frac{2nH_2}{x}$. The triangular relationships between Te^-, ONc, and nH_2 are shown in Figure 2.

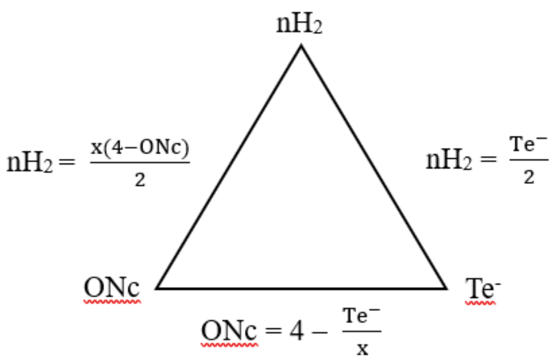


Figure 2. Triangular relationships between Te^-, ONc, and nH_2

5. Quantifying BEqH's Parameters for Empirical Formulas: ONc, Te^-, $\frac{nH_2}{nCO_3^{2-}}$, nH_2, and TBHP

$$C_xH_yO_zX_wN_vS_uP_t^{charge}+(3x+4t-z)H_2O \rightarrow \frac{(4x+y-2z-w-3v-2u+5t-charge)}{2}H_2+xCO_3^{2-}+wX^-+vNH_4^++uS^{2-}+tPO_4^{3-}+(2x+w-v+2u+3t+charge)H^+$$

$$C_xH_yO_zX_wN_vS_uP_t^{charge}+(3x+4t-z)H_2O \rightarrow \frac{x(4-ONc)}{2}H_2+xCO_3^{2-}+wX^-+vNH_4^++uS^{2-}+tPO_4^{3-}+(2x+w-v+2u+3t+charge)H^+$$

Based on a given empirical formula of an organic matter, the mathematical equations for counting BEqH parameters are shown in Table 1.

Table 1. Mathematical relationships between ONc, AC, and SC in BEqH

Stochiometric coefficient (SC)	Stochiometric coefficient (SC) and atomic coefficient (AC)	Mathematical equation
nH_2O	$nH_2O = (3x+4t-z)$	
nH_2	$nH_2 = \frac{(4x+y-2z-w-3v-2u+5t-charge)}{2}$	$nH_2 = \frac{x(4-ONc)}{2}$
nCO_3^{2-}	$nCO_3^{2-} = x$	$nCO_3^{2-} = nc = x$
nX^-	$nX^- = w$	
nNH_4^+	$nNH_4^+ = v$	
nS^{2-}	$nS^{2-} = u$	
nPO_4^{3-}	$nPO_4^{3-} = t$	
nH^+	$nH^+ = (2x+w-v+2u+3t+charge)$	
		$\frac{nH_2}{nCO_3^{2-}} = \frac{nH_2}{nc} = \frac{(4x+y-2z-w-3v-2u+5t-charge)}{2}$ $\frac{nH_2}{nCO_3^{2-}} = \frac{nH_2}{nc} = \frac{(4-ONc)}{2}$
		$ONc = \frac{charge-y+2z+w+3v+2u-5t}{x}$ $ONc = 4 - \frac{Te^-}{x}$ $ONc = 4 - \frac{2\,nH_2}{x}$
		$Te^- = 4x+y-2z-w-3v-2u+5t-charge$ $Te^- = x\,(4 - ONc)$ $Te^- = 2\,nH_2$
		$TBHP = \frac{22400(nH_2)}{\mu C_xH_yO_zX_wN_vS_uP_t^{charge}}$ $TBHP = \frac{11200\,x(4-ONc)}{\mu C_xH_yO_zX_wN_vS_uP_t^{charge}}$

Example 6. For a given empirical formula $C_{10}H_{12}O_7N_5P^{2-}$, count the ONc, Te^-, nH_2, and TBHP.

Step 1. Identify AC and charge of $C_{10}H_{12}O_7N_5P^{2-}$

$C_xH_yO_zN_vP_t^{charge} = C_{10}H_{12}O_7N_5P^{2-}$

x = 10, y = 12, z = 7, v = 5, t = 1, and charge = −2

Step 2. Determine ONc of $C_{10}H_{12}O_7N_5P^{2-}$

$$ON_C = \frac{charge-\Sigma ON_{inc}}{nc}$$

$\Sigma ON_{inc} = (y-2z-3v+5t)$

$$ONc = \frac{charge-y+2z+3v-5t}{x} = \frac{(-2)-(12)+2(7)+3(5)-5(1)}{10} = \frac{10}{10} = +1$$

Step 3. Count Te^-

$Te^- = x\,(4 - ONc)$

$Te^- = (10)\,[4 - (+1)] = 30$

Step 4. Count $\frac{nH_2}{nCO_3^{2-}}$

$$\frac{nH_2}{nCO_3^{2-}} = \frac{(4-ONc)}{2} = \frac{[4-(+1)]}{2} = \frac{3}{2}$$

Step 5. Calculate nH_2

$$nH_2\ (\text{mole}) = \frac{x(4-ONc)}{2} = \frac{10[4-(+1)]}{2} = 15$$

Step 6. Calculate TBHP

$\mu C_{10}H_{12}O_7N_5P^{2-}$ (g/mol) = 10(12.011) + 12(1.008) + 7(15.999) + 5(14.007) + 1(30.974)

= 120.11 + 12.096 +7 0.035 + 111.993 + 30.974 = 345.208

$$\text{TBHP (mL/g at STP)} = \frac{22400(nH_2)}{\mu C_{10}H_{12}O_7N_5P^{2-}} = \frac{22400(15)}{345.208} = 973.326$$

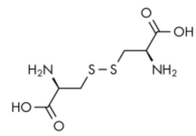
With reference to Example 6, the calculated BEqH's parameters of the selected empirical formulas of organic matters are summarized in Table 2.

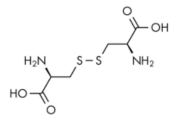
Table 2. Empirical formulas: resulted ONc and BEqH's parameters

Empirical formula	Formula mass (μ)	ONc	x	Te^-	$\frac{nH_2}{nCO_3^{2-}}$	nH_2	TBHP
$C_{10}H_{12}O_7N_5P^{2-}$	345.208	+1	10	30	1.5	15	973.326
CO_3^{2-}	60.008	+4	1	0	0	0	0.000
CO_2	44.009	+4	1	0	0	0	0.000
CH_4	16.043	−4	1	8	4	4	5584.990
CHO_2^-	45.017	+2	1	2	1	1	497.590
CH_2O_2	46.025	+2	1	2	1	1	486.692
C_2H_6O	46.069	–2	2	12	3	6	2917.363
$C_2H_5O_2^+$	61.060	0	2	8	2	4	1467.409
$C_2H_4O_2$	60.052	0	2	8	2	4	1492.040
$C_2H_3O_2^-$	59.044	0	2	8	2	4	1517.512
$C_5H_7O_2N$	113.116	0	5	20	2	10	1980.268
$C_8H_{14}O_4N$	188.203	–0.375	8	35	2.188	17.5	2082.857
$C_{118}H_{170}O_{57}N_{17}P$	2769.694	–0.085	118	482.03	2.043	241.015	1949.217

6. Quantifying BEqH's Parameters for Structural Formulas: AC, ON_{inc}, charge, ONc, Te^-, $\frac{nH_2}{nCO_3^{2-}}$, nH_2, and TBHP

When the known structure of molecule/molecular ion is given, its ON_{inc} and molecular/ionic formula can be identified.

The ONc of a structural formula is calculated by $ONc = \frac{\text{charge} - [(ON_H\,y) + (ON_O\,z) + (ON_X\,w) + (ON_N\,v) + (ON_S\,u) + (ON_P\,t)]}{x}$ but not by ONc = $\frac{\text{charge}-y+2z+w+3v+2u-5t}{x}$. For example, the structural formula of Cystine is  and the chemical formula is $C_6H_{12}O_4N_2S_2$, in which two ON_N are −3 and two ON_S are −1. Its calculated ONc equals $+\frac{2}{3}$ using ONc = $\frac{\text{charge}-[(ON_H\ y)+(ON_O\ z)+(ON_N\ v)+(ON_S\ u)]}{x} = \frac{0-[(+1)12+(-2)4+(-3)(2)+(-1)2]}{6} = +\frac{2}{3}$. If the ONc of Cystine is calculated by ONc = $\frac{\text{charge}-y+2z+w+3v+2u-5t}{x} = \frac{0-12+2(4)+3(2)+2(2)}{6}$ = +1, the incorrect value of +1 is delivered.

Example 7. For a given structural formula  (Cystine, $C_6H_{12}O_4N_2S_2$), count the ONc, Te^-, nH_2, and TBMP.

Step 1. Identify ON_{inc}, AC, and charge of $C_6H_{12}O_4N_2S_2$

ON_H = +1, ON_O = −2, ON_N = −3, ON_S = −1, and charge = 0

x = 6, y = 12, z = 4, v = 2, and u = 2

Step 2. Determine ONc of $C_6H_{12}O_4N_2S_2$

$$ON_C = \frac{\text{charge}-\Sigma ON_{inc}}{nc}$$

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

$$ONc = \frac{\text{charge}-[(ON_H\ y)+(ON_O\ z)+(ON_N\ v)+(ON_S\ u)]}{x} = \frac{0-[(+1)12+(-2)4+(-3)(2)+(-1)2]}{6} = +\frac{2}{3}$$

Step 3. Count Te^-

$$Te^- = x\ (4 - ONc)$$

$$Te^- = (6)\ [4 - (+\tfrac{2}{3})] = 20$$

Step 4. Count $\frac{nH_2}{nCO_3^{2-}}$

$$\frac{nH_2}{nCO_3^{2-}} = \frac{(4-ONc)}{2} = \frac{[4-\left(+\frac{2}{3}\right)]}{2} = \frac{5}{3}$$

Step 5. Calculate nH_2

$$nH_2\ (\text{mole}) = \frac{x(4-ONc)}{2} = \frac{6[4-\left(+\frac{2}{3}\right)]}{2} = 10$$

Step 6. Calculate TBHP

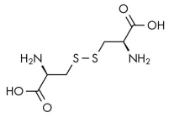
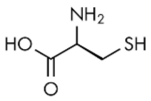
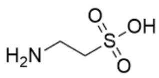
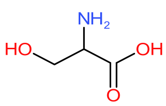
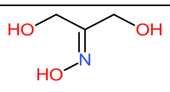
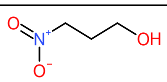
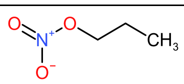
$\mu C_6H_{12}O_4N_2S_2$ (g/mol) = 6(12.011) + 12(1.008) + 4(15.999) + 2(14.007) + 2(32.065)

= 72.066 + 12.096 + 63.996 + 28.014 + 6.413 = 240.302

$$\text{TBHP (mL/g at STP)} = \frac{11200\ x(4-ONc)}{\mu C_6H_{12}O_4N_2S_2} = \frac{11200\ (6)[4-\left(+\frac{2}{3}\right)]}{240.302} = 932.160$$

In comparison to the value above, the published TBHP (mL/g) for Cystine is 850.626 (Pererva et al., 2020). In the cases of counting ONc with structural formulas, the use of empirical formulas in the same calculation may cause miscalculations. With reference to Example 7, the calculated BEqH's parameters of the selected structural formulas of organic matters (Yuen & Lau, 2024e) are summarized in Table 3.

Table 3. Structural formulas: resulted ONc and BEqH's parameters

Structural formula (ON_{inc})	Molecular or ionic formula	Formula mass (μ)	ONc	x	Te^-	$\frac{nH_2}{nCO_3^{2-}}$	nH_2	TBHP
 ($ON_N = -3$; $ON_S = -1$)	$C_6H_{12}O_4N_2S_2$	240.302	+0.667	6	20	1.667	10	932.160
 ($ON_N = -3$; $ON_S = -2$)	$C_3H_7O_2NS$	121.159	+0.667	3	10	1.667	5	924.405
 ($ON_N = -3$; $ON_S = +4$)	$C_2H_7O_3NS$	125.147	−1	2	10	2.5	5	894.948
$HO\text{-}CH_2\text{-}CH_2\text{-}OH$ ($ON_O = -2$)	$C_2H_6O_2$	62.068	−1	2	10	2.5	5	1804.473
$H_3C\text{-}O\text{-}O\text{-}CH_3$ ($ON_O = -1$)	$C_2H_6O_2$	62.068	−2	2	12	3	6	2165.367
$HS\text{-}CH_2\text{-}CH_2\text{-}SH$ ($ON_S = -2$)	$C_2H_6S_2$	94.200	−1	2	10	2.5	5	1188.960
$H_3C\text{-}S\text{-}S\text{-}CH_3$ ($ON_S = -1$)	$C_2H_6S_2$	94.200	−2	2	12	3	6	1426.752
 ($ON_N = -3$)	$C_3H_7O_3N$	105.093	+0.667	3	10	1.667	5	1065.723
 ($ON_N = +1$)	$C_3H_7O_3N$	105.093	0	3	12	2	6	1278.867
 ($ON_N = +3$)	$C_3H_7O_3N$	105.093	−1.333	3	16	2.667	8	1705.156
 ($ON_N = +5$)	$C_3H_7O_3N$	105.093	−2	3	18	3	9	1918.301

The value of $\frac{nH_2}{nCO_3^{2-}}$ is only related to ONc. The values of Te^- and nH_2 are related to ONc and nc. The TBHP is related to ONc, nc, and μ of organic matter. When comparing the same set of isomers, the more positive the values of ON_{inc} are, the more negative the value of ONc and the greater the values of Te^-, $\frac{nH_2}{nCO_3^{2-}}$, nH_2, and TBHP are.

7. Importance of Stoichiometric Ionic BEqH in Aqueous Solutions

For any given organic matter, the stoichiometric redox half reactions and overall reactions can be attained using the proton method. In the cases of dark fermentation or anaerobic digestion, biohydrogen and biomethane can be generated by the corresponding stoichiometric Buswell's equation. Up to date, there is no study on anaerobic biorefinery chemicals using the concept of Buswell's equation.

Ionic BEqH acts like a connector between a stoichiometric equation and an aqueous solution, in which water molecules and ionic species are important in biochemical processes (Brouckaert et al., 2021). There is little information in biohydrogen production under the framework of stoichiometry in aqueous solutions, it better explores BEqH:

- to demonstrate the gas phase-aqueous solution-solid phase multiphases interactions;
- to use modelling organic molecule or molecular ion, $C_xH_yO_zX_wN_vS_uP_t^{charge}$, to study the intermediates or products under the influences of various ions;
- to know how characteristics of digestates, types of cations, or types of anions impact the biohydrogen process;
- to understand the relationship between carbon-balanced and charged-balanced of biohydrogen production;
- to integrate hydrogen production and biorefinery chemicals.

8. Conclusion

Based on the H-atom method for molecular redox reactions (Yuen & Lau, 2022c), the proton method is developed for both molecular and ionic redox reactions (Yuen & Lau, 2022a). This article expands the ionic BEqH for neutral and charged organic matters, where the molecular BEqH for neutral organic matters has already been established (Yuen & Lau, 2024a). Additionally, the article establishes mathematical equations for counting ONc in empirical and structural formulas of organic matters; the mathematical relationships between the chemical formulas, ONc, Te^-, and nH_2, thus, can be determined. In this study of fermentation and anaerobic digestion, the general ionic BEqH is deduced, with which the stoichiometric BEqH can be attained by any given empirical formula of organic matter. Using ONc as a counting metric, Te^-, nH_2, $\frac{nH_2}{nCO_3^{2-}}$, and TBHP can be quantified by any given empirical or structural formula of organic matter.

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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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Data sharing statement

No additional data are available.

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References

Algapani, D. E., Qiao, W., Ricci, M., Bianchi, D., Wandera, S. M., Adani, F., & Dong, R. (2019). Bio-hydrogen and bio-methane production from food waste in a two-stage anaerobic digestion process with digestate recirculation. *Renewable Energy, 130*, 1108-1115. https://doi.org/10.1016/j.renene.2018.08.079

Boyle, W. C. (1977). Energy Recovery from Sanitary Landfills. In: Microbial Energy Conversion. Edited by H. G. Schlegel & J. Barnea, 119-138. https://doi.org/10.1016/B978-0-08-021791-8.50019-6

Brouckaert, C., Brouckaert, B. M., & Ekama, G. A. (2021). Integration of complete elemental mass-balanced stoichiometry and aqueous-phase chemistry for bioprocess modelling of liquid and solid waste treatment systems – Part 5: Ionic speciation. *Water SA, 48*(1), 32-39. https://doi.org/10.17159/wsa/2022.v48.i1.3738

Buswell, A. M., & Boruff, C. S. (1932). The Relation between the Chemical Composition of Organic Matter and the Quality and Quantity of Gas Produced during Sludge Digestion. *Sewage Works Journal, 4*(3), 454-460. https://www.jstor.org/stable/25028162

Buswell, A. M., Mueller, H. F. (1952). The mechanism of methane fermentation. *Ind. Eng. Chem., 44*(3), 550-552. https://doi.org/10.1021/ja01185a034

Dzulkarnain, E. L. N, Audu, J. O., Dagang, W. R. Z. W., & Abdul-Wahab, M. F. (2022). Microbiomers of biohydrogen production from dark fermentation of industrial wastes: current trends, advanced tools and future outlook. *Bioresources and Bioprocessing, 9*(1), 16. https://doi.org/10.1186/s40643-022-00504-8

IUPAC (2019). Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. https://doi.org/10.1351/goldbook.

Moussa, R. N., Moussa, N., & Dionisi, D. (2022). Hydrogen production from biomass and organic waste using dark fermentation: An Analysis of Literature Data on the Effect of Operating Parameters on process performance. *Processes, 10*, 156. http://doi.org/10.3390/pr10010156

O-Thong, S., Mamimin, C., & Prasertsan, P. (2018). Biohythane production from organic wastes by two-stage anaerobic fermentation technology. In book: *Advances in Biofuels and Bioenergy.* https://doi.org/10.5772/intechopen.74392

Pererva, Y., Miler, C. D., & Sims, R. C. (2020). Sulfur, phosphorous and metals in the stoichiometric estimation of biomethane and biohydrogen yields. *Processes, 8*, 714. https://doi.org/10.3390/pr8060714

Sarangi, P. K., & Nanda, S. (2020). Biohydrogen production through dark fermentation. *Chemical Engineering Technology, 43*(4), 601-612. https://doi.org/10.1002/ceat.201900452

Yuen, P. K. & Lau, C. M. D. (2022a). From balancing redox reactions to determining change of oxidation number. *Journal of College Science Teaching, 51*(3), 22-26. https://doi.org/10.1080/0047231x.2022.12290556

Yuen, P. K., & Lau, C. M. D. (2022b). Fragmentation method for assigning oxidation numbers in organic and bioorganic compounds. *Biochemistry and Molecular Biology Education, 50* (1), 29-43. https://doi.org/10.1002/bmb.21582

Yuen, P. K., & Lau, C. M. D. (2022c). H-atom and O-atom Methods: from Balancing Redox Reactions to Determining the Number of Transferred Electrons. *Chemistry Teacher International, 4*(3), 207-220. https://doi.org/10.1515/cti-2021-0028

Yuen, P. K., & Lau, C. M. D. (2023). Using the Carbon-Atom Method to Determine Mean Oxidation Number of Organic Carbons. *International Journal of Chemistry, 15*(2), 13-25. https://doi.org/10.5539/ijc.v15n2p13

Yuen, P. K., & Lau, C. M. D. (2024a). Buswell's equation for quantifying biohydrogen. *International Journal of Chemistry, 16*(1), 78-87. https://doi.org/10.5539/ijc.v16n1p78

Yuen, P. K., & Lau, C. M. D. (2024b). Using Mean Oxidation Number of Organic Carbons to Quantify Buswell's Equation.

International journal of chemistry, 16(1), 41-56. https://doi.org/10.5539/ijc.v16n1p41

Yuen, P. K., & Lau, C. M. D. (2024c). Mean oxidation number of organic carbons for quantifying biomethane in organophosphorous compounds. *International Journal of Chemistry, 16*(1), 11-21. https://doi.org/10.5539/ijc.v16n1p11

Yuen, P. K., & Lau, C. M. D. (2024d). Counting and Demonstrating Electron Transfer in Buswell's Equation. *International Journal of Chemistry, 16* (2), 42-61. https://doi.org/10.5539/ijc.v16n2p42

Yuen, P. K., & Lau, C. M. D. (2024e). Using Mean Oxidation Number of Organic Carbons to Count Theoretical Chemical Oxygen Demand. *International Journal of Chemistry, 16*(1), 88-101. https://doi.org/10.5539/ijc.v16n1p88