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ORIGINAL ARTICLE

Methane productivity evaluation of an invasive wetland plant, common reed

Giang Van Tran[1] · Yuwalee Unpaprom[2] · Rameshprabu Ramaraj[1]

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Abstract

This study aims to investigate the potential of substrate for producing biogas from common reed (*Phragmites australis*), a perennial grass, and provide the techniques to select optimal and reasonable materials with high methane production. By determining the parameters such as chemical oxygen demand (COD), volatile solids (VS), and percentage of element chemicals, carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) of raw materials henceforth through the TBMP (theoretical biochemical methane potential) via calculations give the maximum methane potential of particular available in feedstock and present by methane yield per unit of mass of feedstock (mlCH$_4$/gVS). In this study, the results were obtained from TBMP$_{ThEC}$ and TBMP$_{ThCOD}$ that were highest at 460.890 mlCH$_4$/gVS and 130.88 mlCH$_4$/gVS, respectively. The results showed that based on COD calculations, the results were consistent with the ability to create methane in the experiment and based on elemental compositions showed that the further potential to produce methane of feedstock.

Keywords Methane · Common reed · Substrate · Biogas · Gas yield

1 Introduction

Currently, depletion of fossil fuels was regarded as a top global concern. Furthermore, burning fossil energy for heating, electricity, and transportation gradually leads it to environmental degradation [1]. Hence, increasing of greenhouse gas (GHG) emissions gives rise to climate change and global warming [2]; it has caused and taken it to the proliferation of numerous studies which focused on the generation of renewable and the mitigation of emissions [3–5]. Bioenergy, clean energy, plays a part as an alternative resource not only to contribute to environmental protection but also to reduce cost-effectively [6, 7]. Biofuels are considered excellent substitute fuels for combustion and reducing climatic impact; it can be produced from various types of biomass [8]. According to Unpaprom et al. [9], biofuels are high energy because of low-carbon transportation and the long-term regenerability of fuel resources. Both gaseous fuels (biohydrogen and biogas) and liquid fuels (ethanol, methanol, biobutanol, and biodiesel) are two types of biofuel [10].

Biogas is gaseous energy. It is generated from the anaerobic digestion (AD) by the activity of several types of anaerobic bacteria cultures in the absence of oxygen condition [11]. The organic compounds are broken down into a mixture of gases with main compositions of methane (CH$_4$ with 50–70%) and carbon dioxide (CO$_2$ with 30–50%), the percentage of anthropogenic gases based on potential material [12]. Organic wastes such as agricultural crops and residues, sewage, municipal solid waste, animal residues, and industrial residues were suitable biomass for AD [13]. Biogas of lignocellulose materials, such as crops and wastes, has the potential to provide energy with environmental benefit. In which, the grass was "set up" by nature as a potential feedstock for biogas production. However, the abundant component of lignocellulose and the crystalline structure of materials are an essential factor to evaluate the accessibility and biodegradability of microorganism [14, 15]. According to Seppala [16], the matuincreases were higher; meanwhile, percentage of cell contents (proteins, lipids, sugars) were lower. Therefore, to reach high yield biogas, the lignin contents of biomass are required to be low because high lignin content inhibits the process of digestibility of material [17–19].

Common reed (*Phragmites australis*), a common perennial grass, is known as a plant that grew aggressively in aquatic and semi-aquatic surroundings [20] and contributed in the world

✉ Rameshprabu Ramaraj
rameshprabu@mju.ac.th; rrameshprabu@gmail.com

[1] School of Renewable Energy, Maejo University, Chiang Mai 50290, Thailand

[2] Program in Biotechnology, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand

except for Antarctica continent [21]. This plant spreads widely in temperate and tropical climatic regions, the stems of common reed are erect, smooth, and hollow and can grow up to 6 m in height [22], thrive in the warm season, and have an optimum range temperature of 30–35 °C. Common reed has been successfully applied and proved in bioethanol production [23], paper production [22], and wastewater treatment, which contains metals [24]. Furthermore, there are several issues, and research publication conversation about methane flux, plant biomass, and methanogenic wetland plant species. Methane dynamics varied across plant functional groupings, with patterns distinctive among forbs, clonal dominants, and tussock/clump-forming graminoids. Wetland plants were influencing net methane emissions. Methane flux exhibited a general pattern across these wetland plant species [25]. Therefore, this experimental research tries to study the methane generation that characterizes and applies wetland plant (i.e., common read) for biogas production. Also, one way is to control greenhouse effect, and another way is to utilize this massive biomass of common reed to energy. Therefore, the aim of this paper to estimate the methane production potential of common reed through the theoretical biochemical methane potential (TBMP) via elemental chemical compositions $TBMP_{(ThEC)}$ and chemical oxygen demand $TBMP_{(ThCOD)}$. Furthermore, the prediction from the calculation in this study can be applied for another biomass material.

2 Material and methods

2.1 Sample collection and preparation

Common reed (*Phragmites australis*) was collected from the field in Nong Han, San Sai District, Chiang Mai City, Thailand (at coordinate 18°54′48.0″ N–98°59′30.2″ E), near Maejo University. After collection, the common reed was air-dried for a week and then shredded by chipping disk machine (multi-purpose shredder model MJU-EB8) to reduce particle size from 5 to 10 mm, and then it was transferred to the laboratory. After that, to analyze the physical and chemical characterizations, and biological compositions, the feedstock will be transformed into powder. Therefore, the common reed was pulverized by a blender (Philip HR2116/01 600W) (Fig. 1).

2.2 Analytical methods

TS (total solid), VS (volatile solid), COD (chemical oxygen demand), and pH were measured primarily according to the standard methods [26]. Ash content was measured by AOAC official method 942.05 [27]. Carbon and nitrogen contents of the samples were determined with the help of a C–H–N–S–O analyzer using an element analyzer (2400 II CHNS/O Elemental Analyzer, PerkinElmer, USA). The cellulose, hemicellulose, lignin, and moisture contents estimated methods adopted from Vu et al. [28]. The higher calorific values (HCV) and lower calorific values (LCV) were calculated according to Chuanchai and Ramaraj [2].

2.3 Biochemical methane potential evaluation methods

In this study, theoretical biochemical methane potential (TBMP) of the material was used to predict the biogas methane productivity through the constants of chemical elements and potential COD of feedstock. Therefore, the theoretical production of elemental compositions ($TBMP_{ThEC}$) and theoretical production of COD ($TBMP_{ThCOD}$) were applied in terms of calculation. However, the methane potential of material through $TBMP_{ThEC}$ and $TBMP_{ThCOD}$ is presented by volume of methane (CH_4) per amount of volatile solid added (VS) as a unit of formula ($mlCH_4/gVS$) and assumed under STP (standard temperature and pressure) conditions. The flow chart of this work is given in Fig. 2.

Fig. 1 Collection and preparation of material. **a** Grass field. **b** Cutting grass. **c** Dried grass. **d** Shredder machine. **e** Particle grass. **f** Grass powder

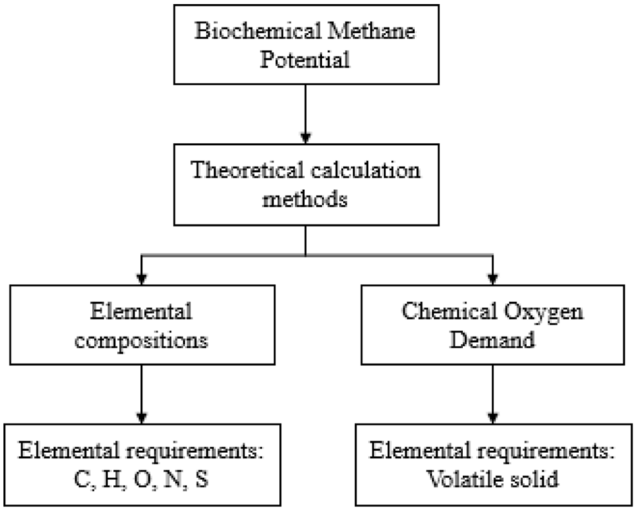

Fig. 2 Conceptual work of this paper

2.4 Theoretical production of elemental compositions ($TBMP_{ThEC}$)

The constants of chemical elements compute TBMPThEC are given by ratios of C/H/O/N/S from the stoichiometric formula. Buswell and Mueller developed the principle chemical equation of methane production [29]. Moreover, O'Rourke [30] was also agreed with Buswell and Mueller's developed equation. It was given in Eqs. (1) and (2), respectively.

$$C_aH_bO_c + \left(a - \frac{b}{4} - \frac{c}{2}\right)H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4}\right)CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4}\right)CO_2 \quad (1)$$

$$TBMP_{ThEC}\left(mlCH_4g^{-1}VS\right) = \frac{22.4 \times \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4}\right)}{12a + b + 16c} C_aH_bO_cN_d + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4}\right)H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8}\right)CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8}\right)CO_2 + dNH_3 TBMP_{ThEC}\left(mlCH_4g^{-1}VS\right) = \frac{22.4 \times \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8}\right)}{12a + b + 16c + 14d} \quad (2)$$

However, it was improved and modified by Boyle [31], to estimate the potential of materials due to the presence of ammonia (NH_3) and hydrogen sulfide (H_2S). The equation was presented in Eq. (3)

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2}\right)H_2O \rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right)CO_2 + dNH_3 + eH_2S TBMP_{ThEC}\left(mlCH_4g^{-1}VS\right) = \frac{22.4 \times \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)}{12a + b + 16c + 14d + 32e} \quad (3)$$

Nevertheless, in order to achieve exact results, the molar mass of the substrate should be presented as its nature without rounding. It was modified by Achinas and Euverink [32] and followed Eq. (4).

$$TBMP_{ThEC}\left(mlCH_4g^{-1}VS\right) = \frac{22.4 \times \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)}{12.017a + 1.00794b + 15.999c + 14.0067d + 32.065e} \quad (4)$$

where the constants of the chemical elements such as a, b, c, d, and e, these elements are equal to results from elemental analysis determination of material (EAD) divided by the molar

Table 1 Characteristics of common reed

Parameters	Compounds (wt%)
Total solid (TS, % d.b)[a]	92.48 ± 1.6
Volatile solid (VS, % d.b)[a]	87.64 ± 1.47
pH	7.49 ± 0.04
COD (g/L)	290.66 ± 21.00
Ash content (%)	6.01 ± 0.03
Moisture (%)	7.52 ± 1.6
Carbon (C)	46.872 ± 0.03
Hydrogen (H)	6.775 ± 0.00
Oxygen (O)	45.167 ± 0.04
Nitrogen (N)	1.058 ± 0.20
Sulfur (S)	0.131 ± 0.00
Cellulose	31.958 ± 0.11
Hemicellulose	29.034 ± 0.06
Lignin	18.634 ± 0.01

[a] Based on dry basis matter

Table 2 The atomic number of chemical elements (%, d.b)

Composition $C_aH_bO_cN_dS_e$ of common reed				
a	*b*	*C*	*d*	*e*
3.900	6.722	2.823	0.075	0.004

Based on dry basis matter

mass of the chemical element, and 22.4 is the volume of 1-mol gas at STP condition.

$$a = \frac{\mathrm{EAD_{Carbon}}}{\mathrm{MolarmassC}} = \frac{\mathrm{EAD_{Carbon}}}{12.017}; b = \frac{\mathrm{EAD_{Hydrogen}}}{\mathrm{MolarmassH}}$$

$$= \frac{\mathrm{EAD_{Hydrogen}}}{1.00794}; c = \frac{\mathrm{EAD_{Oxygen}}}{\mathrm{MolarmassO}} = \frac{\mathrm{EAD_{Oxygen}}}{15.999}$$

$$d = \frac{\mathrm{EAD_{Nitrogen}}}{\mathrm{MolarmassN}} = \frac{\mathrm{EAD_{Nitrogen}}}{14.0067}; e = \frac{\mathrm{EAD_{Sulfur}}}{\mathrm{MolarmassS}} = \frac{\mathrm{EAD_{Sulfur}}}{32.065}$$

The accuracy of results above depended on the precision of elemental analysis determination of material. Hereafter, it exposes biodegradability and manufacturing capability of the material.

2.5 Theoretical production of COD ($\mathrm{TBMP_{ThCOD}}$)

The chemical oxygen demand (COD) concentration of feedstock is considered a pathway to expose methane potential using Eq. (5) [33] that depends on the amount of organic material (volatile solid—VS).

$$\mathrm{TBMP_{ThCOD}}\left(\mathrm{mlCH_4g^{-1}VS}\right) = \frac{n_{\mathrm{CH_4}} \times R \times T}{p \times \mathrm{VS}} \tag{5}$$

where $\mathrm{BMP_{ThCOD}}$ is the theoretical production of methane based on COD, $n_{\mathrm{CH_4}} = \frac{\mathrm{COD}}{64}$ is the amount of molecular methane (mol), R is the gas constant (R = 0.0821 atm L/mol K), T is the temperature of the reactor (308 K), p is the atmospheric pressure (1 atm), and VS is the volatile solids of the substrate (g).

$\mathrm{TBMP_{ThCOD}}$ is a method that reveals the methane potential by calculation. However, according to Raposo et al. [34], calculating this method on solid waste often provides erroneous results due to the direct analysis of COD. Thus, the results from Eqs. (5) and (6) will show the inaccuracy of computing based on COD concentration. Hypothetically, 1 g removal of COD can produce 0.35 L of methane at STP and 1 atm [35]. The reaction of oxidation for organic material is shown:

$$\mathrm{C_aH_bO_c} + \left(a + \frac{b}{4} - \frac{c}{2}\right)\mathrm{O_2} \rightarrow a\mathrm{CO_2} + \frac{b}{2}\mathrm{H_2O}$$

Hence, to calculate methane production, Eq. (6) [34] can be applied.

$$TBMP_{ThCOD}\left(mlCH_4g^{-1}VS\right) = VS_{add} \times (gCOD/gVS) \times 350 \tag{6}$$

where, according to Angelidaki and Sanders [35], the ratio of COD/VS can be calculated based on atomic compositions and is determined as Eq. (7):

$$\mathrm{gCOD/gVS} = \frac{\left(a + \frac{b}{4} - \frac{c}{2}\right) \times 32}{12.017a + 1.00794b + 15.999c} \tag{7}$$

3 Results and discussion

3.1 Characteristics of common reed

The characteristic of common reed is presented in Table 1. Additionally, compositional analysis of the lignocellulose contents such as cellulose, hemicellulose, and lignin was detected via elemental composition investigation of carbon (C),

Table 3 Elemental of common reed and seasonal changes

No.	Element		C (%)	H (%)	N (%)	O (%)	S (%)	References
1	China	Stem	45.5 ± 0.4	6.0 ± 0.0	0.7 ± 0.0	40.3 ± 0.2	0.10 ± 0.01	[36]
		Leaves	44.6 ± 0.5	6.1 ± 0.0	2.7 ± 0.0	31.6 ± 0.5	0.40 ± 0.02	
	Italy	Stem	45.5 ± 0.4	8.0 ± 0.1	0.5 ± 0.0	39.5 ± 0.6	0.07 ± 0.00	
		Leaves	50.0 ± 0.7	7.0 ± 0.2	1.5 ± 0.2	33.4 ± 1.0	0.11 ± 0.01	
2	Winter		47.0–48.3	5.5–5.6	0.2–0.3	42.8–43.8	0.03–0.09	[21]
	Summer		46.1–47.1	5.9–6.4	0.6–1.2	39.7–42.2	0.12–0.45	
3	Summer		46.872 ± 0.03	6.775 ± 0.00	1.058 ± 0.20	45.167 ± 0.04	0.131 ± 0.00	This study

hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) of common reed.

The characterization of material depends on several conditions such as temperature, nutrient, climate, and weather. So, the variation of composition in the material has various types. Moreover, common reed, a semi-aquatic grass, is an agricultural waste with a complex structure, which is investigated as excellent feedstock for bioenergy. The elemental forms used for this study are representative of the common reed of North Thailand with high precise parameters.

3.2 Estimation of masses of atoms and molecules on biomass

The elemental determination of material after an analysis shown in Table 1 is an effective factor to the BMP. Dividing of elemental analysis determination of material (EAD) by molar mass of chemical elements into the atoms as constants of chemical elements is shown in Table 2.

The results from Table 2 represent the matter that consists of complex organic composed of available material, and it plays an essential role in determining energy production; a comparison of common reed from this study with another research paper was gathered and is presented in Table 3.

3.3 Biogas estimation

The results are obtained from theoretical methane potential dissimilar with experimental results; it provides numbers through the calculation to predict methane production. The standard temperature and pressure (STP) were used as a condition for production in this study. Indeed, anaerobic digestion of raw materials needs assistance from inoculums. Therefore, the results express the potentials of feedstock and present by $mlCH_4$ per amount of organic material added (VS). Consequences of TBMP are presented in Table 4, and gas composition content was of CH_4 (51.88%), CO_2 (26.22%), and NH_3 (1.90%).

Equations (4), (5), and (6) will be used to detect the based on the accompanying calculation methods to achieve the result, and these results will be compared to identify the potentials that are not fully utilized in energy conversion. The result of methane yield shown in Table 4 based on Eq. (5) was 130.88 $mlCH_4$/gVS which quite fits with the experiment which was conducted by [37] in different months. Materials were sampled in July and October; results obtained were 107.6 and 172.4 $mlCH_4$/gVS, respectively.

This proves that the use of Nielfa et al.'s [33] formula has high reliability due to application from this equation including COD and VS, and other conditions such as temperature and the pressure of the reactor are expressed as well. Therefore, the results obtained from the formula in this study are acceptable. Nonetheless, besides the above factors, there are still many other factors affecting the production of biogas that inhibit the ability to produce optimal methane yield of raw materials, which is verified through Achinas and Euverink [32] and Raposo et al. [34]. As shown in Table 4, the maximum methane yield from elemental composition was 460.890 $mlCH_4$/gVS, while the combination of COD content and fraction of gCOD/gVS lower was 414.160 $mlCH_4$/gVS; though the disparities from both results exist, it is negligible.

Besides that, these results that compare with data obtained from Nielfa's equation proved that the experimental methane yield is obstructed during anaerobic digestion, and the potential maximum methane production available in raw material can get higher. Moreover, different biomass sources [38–40] proved that TBMP revealed similar results to this study. The experimental results shows that achieving the approximate numerical result with theoretical estimation. But the results from the other calculation methods have a relatively large deviation because the experiment has barriers that prevent absolute efficiency and demonstrates gas leakage or inhibition that leads to the difference [41]. Nevertheless, the leakage of gas is considered insignificant in this case. In other words, the main reason is

Table 5 Lignocellulose of common reed

No.	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
1	38.13	20.51	23.02	[23]
2	32.80	19.90	24.90	[47]
3	31.96	29.03	18.63	This study

Table 4 Results of theoretical biochemical methane potential methods

Methods	Measurement	Methane yield	References
$TBMP_{ThEC}$	$mlCH_{4}g^{-1}VS$	460.890	This study
$TBMP_{ThCOD}$	$mlCH_{4}g^{-1}VS$	414.160	This study
$TBMP_{ThCOD}$	$mlCH_{4}g^{-1}VS$	130.88	This study
Practical experiments	$mlCH_{4}g^{-1}VS$	107.6–172.4	[37]
TBMP (pig manure)	$mlCH_{4}g^{-1}VS$	230–360	[38]
TBMP (corn stove–chicken manure)	$mlCH_{4}g^{-1}VS$	437.6–476.9	[39]
TBMP (swine and buffalo manure)	$mlCH_{4}g^{-1}VS$	392–399	[40]

inhibition, which may be caused by heavy metals, accumulation of ammonia (NH_3) and volatile fatty acids (VFAs), which flourishes at low pH value [42–44]. According to Khalid et al. [45], the C/N ratio was detected a common reason effect to gas production; the high C/N ratio causes rapid depletion of nitrogen to lead to lower productivity. Kwietniewska and Tys [46] revealed the optimal range for C/N ratio from 20 to 35:1.

According to Nielfa et al. [33] when Eq. (5) is applied, the productivity of materials increases with a high content of COD that explains this study; the $TBMP_{ThCOD}$ methods are applied to bring results consistent with what was obtained in the experiment. Besides, the lignocellulose of material is also a factor that needs to be considered. The lignocellulose content such as cellulose, hemicellulose, and lignin from common reed has been reported [23, 47] and shown in Table 5.

Several studies are published about accessible surface area for cellulose and its benefits. The lignin and cellulose components of common reed in this study are lower, whereas hemicellulose is higher than the others. Although the lignin content is easier, however, the relatively high hemicellulose content, and therefore the accessibility and degradability of microorganism to cellulose in practice are more challenging with the protection of crystallinity of lignin or hemicellulose [48]. As a result, the accessible surface area in lignocellulose of bacteria that interacts with the enzymes can be limited. However, it can be entirely solved by pre-treatment methods before the feedstock participates in the anaerobic digestion process [49].

The useful part of the energy of biogas is the calorific value of its CH_4 content. The calorific value of the biogas is a function of the CH_4 percentage, the temperature, and the absolute pressure. From this study, biogas HCV was 20.69 MJ/m^3, and LCV was 18.64 MJ/m^3. It was much higher than biogas production from traditional anaerobic digestions [2]. The calorific value of the biogas is a vital parameter for the performance of an engine, a burner, or any other application using biogas as a fuel.

4 Conclusions

The methodology used in the TBMP test is essential. Using $TBMP_{ThCOD}$ calculation for common reed in this study was 130.88 $mlCH_4/gVS$, although this result is consistent with effective effects. However, based on the results, highest from elemental composition was achieved 460.890 $mlCH_4/gVS$. This can be explained by the theory that there is no inhibition during the process. Assumptions are taken into account, simplifications are made, and the results for different feedstocks may vary, but the model provides basic predictions that can aid agricultural farmer decisions. Finally, the theoretical study can give overall details and substrate information and usage of anaerobic technology as a sustainable waste treatment option and a viable alternative to other energy production processes.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Abbreviation TS, total solid; VS, volatile solid; COD, chemical oxygen demand; GHG, greenhouse gas; TBMP, theoretical biochemical methane potential; $TBMP_{(ThEC)}$, theoretical production of elemental compositions; $TBMP_{(ThCOD)}$, theoretical production of COD; EAD, elemental analysis determination; VFA, volatile fatty acids; STP, standard temperature and pressure; CR, common reed

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