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Biogas potential determination and production optimisation through optimal substrate ratio feeding in co-digestion of water hyacinth, municipal solid waste and cow dung

Tawanda Kunatsa[a,b], Lijun Zhang[a] and Xiaohua Xia[a]

[a]Center of New Energy Systems, Department of Electrical, Electronic and Computer Engineering, University of Pretoria, Pretoria, South Africa; [b]Department of Fuels and Energy, Chinhoyi University of Technology, Chinhoyi, Zimbabwe

ABSTRACT

Modelling and optimisation of biogas production from different substrate mixtures is lagging behind in research and development. Current biogas production processes are not fully exploiting co-digestion of multifaceted biomaterials with manures and other biowastes. A model is presented for the determination of biogas production potential from water hyacinth (WH), municipal solid waste (MSW) and cow dung (CD) as well as the subsequent optimisation of the co-digestion mix ratios of these substrates. In this study biogas is assumed to comprise of methane, carbon dioxide, ammonia and hydrogen sulphide. Baseline biogas potential yields of 747.4 ml/gVS, 790.83 ml/gVS and 884.24 ml/gVS were obtained from WH, MSW and CD, respectively. A linear programming mathematical optimisation was done. The objective is to find substrate blend ratios in the co-digestion mixture that maximises biogas production. Optimal co-digestion results in percentage substrate blending ratios of 53.27 : 24.64 : 22.09 for WH, MSW and CD, respectively in a case study. One kilogram of substrate mixture yields 124.56 m^3 of biogas which translates to 124,560 ml/gVS. Co-digestion and optimisation of substrate blend mix proportions increased the biogas output by 157.11%. The biogas fratenity benefits in having an informed optimal co-digestion model that foretells substrate blending ratios.

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Anaerobic digestion; co-digestion; substrate blend ratios; biogas modeling and optimisation

Introduction

Biofuels such as biogas have a potential to extend and diversify energy supply, thus reducing dependence on imported fuels and pollution levels [1]. Biogas is a biofuel produced by the process of anaerobic digestion. A wide range of waste streams, agricultural, municipal and food industrial wastes including industrial and municipal waste waters, as well as plant residues, can be feedstock for anaerobic digestion [2]. The substrate has to have the dietary rations for the microorganisms for it to be biodegraded optimally. Therefore, substrate composition is very crucial in the anaerobic digestion process to optimally produce biogas.

A number of ways ranging from experimental to theoretical tools are available for use to determine biogas potential of bio-materials [3]. Varied researchers [4,5] used the experimental biomethane potential prediction approach for different biomass materials. However, little is reported on biogas and/or biomethane potential of co-digestion mixtures. Dynamic, steady state and computational models based on individual substrates such as sludge, manures, organic waste and municipal solid waste (MSW) are the key existing anaerobic digestion models [6–9], nevertheless without accompanying optimisations and thus optimisation and modelling of biogas production from different substrate mixtures in co-digestion still remains an area of concern.

Tetteh et al. [10] employed a response surface methodology to evaluate and enhance biogas potential by optimising pH, temperature, hydraulic retention time (HRT) and feedstock to innoculum ratio (*F/I*) on biogas production from miscunthus fuscus and cow dung (CD) in a batch co-digester. They found the optimal parameters to be pH of 6, temperature of 30°C, HRT of 20 days and *F/I* ratio of 3 : 1. Feng et al. [11] and Jiya et al. [12] also optimised biogas production using the responce surface methodology, however none of them looked at the co-digestion feed mixture ratios. García-Gen et al. [13] used an experimental and heuristic methodology in an adaptive linear programming approach to optimise substrate blends from co-digestion of glycerine, gelatin and pig manure targeting at maximising chemical oxygen demand conversion into methane. Gaida et al. [14] developed an Anaerobic Digestion Model No.1 (ADM1) based simulation model, developed and applied a nonlinear model predictive control scheme with the incooperation of a state estimator to optimally control substrate feed of agricultural biogas plants. Álvarez et al. [15] applied the solver method from Excel^{TM} as a linear programming tool in combination with experimental methodology to maximise the substrate biokinetic potential from co-digestion of pig manure, fish waste and bio-diesel waste.

The search for appropriate models to be used in optimisation and control theory is now a high priority to optimise fermentation processes [16]. The modelling of biochemical processes remains difficult because there is no biological laws or universal models, unlike physics, where known and validated models exist for centuries which can

CONTACT Tawanda Kunatsa kunatsat@gmail.com Center of New Energy Systems, Department of Electrical, Electronic and Computer Engineering, University of Pretoria, Pretoria 0002, South Africa.
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be the basis for the construction of mechanistic models [16]. The bacteria involved in biogas production process are very sensitive to changes in their environment hence making it a challenge to predict and control the process [9]. Thorin et al. [9] concluded that for anaerobic digestion processes, the available detailed models such as the ADM1 among others are too complex for practical use and recommended the use of a combination of empirical and physical/biological models as a possible approach.

Major aspects in present-day anaerobic co-digestion, particularly interactions between system performance and co-substrate ratios for optimal biogas yields still remain underdeveloped [17]. Optimisation of anaerobic digestion processes for biogas production can be enhanced through mathematical models [18]. In addition to improving energy availability, modelling and optimisation of biogas production will also improve environmental sustainability [19]. Process monitoring and control have been noted as further improvements needed for the biogas production process [20].

Research on new types of substrates and co-digestion combinations in appropriate ratios has not been done adequately and this study seeks to make contribution to this gap by having this established so as to substantially increase biogas production. Of major importance is the carbon to nitrogen $(C:N)$ ratio. Different researchers reported different optimal $C:N$ ratio ranges in literature depending on substrate type and reaction conditions; 10–23 [21], 15–30 [22], 25–30 [23], 20–30 [24], 15.5–19 [25]. This entails the need of modelling and optimisation of the production process taking into consideration the substrates involved.

According to the authors' best knowledge, the three substrates: water hyacinth (WH), MSW and CD have not been co-digested together and no modelling nor optimisation for this trio substrate combination was done for biogas production enhancement. These wastes have been specifically chosen in a bid to deal with the negative implications they pose to the environment and atmosphere by way of value adding *via* anaerobic co-digestion and ultimately generating a biofuel in the form of biogas.

WH poses detrimental problems by infesting water bodies. It clogs within the rivers, lakes, ponds and dams forming intertwined mats. This hampers other activities such as fishing, boat riding and as well reduces biodiversity since other creatures which have water as their habitat can no longer survive. Proper management of MSW is paramount to both developed and developing countries in residential areas where the majority of the population has no access to waste collection services [26]. New legislation has to be put in place and existing policies revised so as to keep up with expected MSW environmental standards [26]. In addition to emitting hazardous greenhouse gases to the atmosphere, if not collected and dumped in a proper way, MSW also causes leaching and produces odours just like CD. Utilisation of MSW for biogas generation is a proven route of waste management that reduces the negative effects to the environment, [27–29]. CD and other animal manures emit $55-65\%$ methane into the atmosphere and tis affects global warming 21 times more than CO_2 does [30]. Of all the substrates for biogas production, CD is the major source, however, mordern researches on its co-digestion with other wastes has shown increased ultimate biogas yields [31–33]. WH and MSW are rich in nutrients for biogas production, however, their lignocellulosic recalcitrant nature renders them resistive to micro-bacterial degradation hence reduced gas yields. Co-digesting WH and MSW with CD gives enough access and potential to microorganisms to foster optimised degradation and digestion [34–36]. In addition, CD brings with it some buffering effect to the entire co-digestion reactions in the digester [37].

Literature shows that the enhancement and optimisation of biogas production for individual as well as co-digestions has mainly been done through heuristic, metaheuristic and artificial intelligence optimisation techniques and it appears that little work has been reported on the mathematical programming optimisation technique, and apparently no work in particular reports the co-digestion of WH, MSW and CD in one reactor chamber. For the heuristic experimental approaches, individual and/or combinations of substrates were considered without the use of informed mixing proportions. With due respect to such previous works, this study takes these as trial and error approaches.

This research reports an elemental composition mathematical programming modelling approach for biogas production and the respective novel optimisation methodology through co-digestion of WH, MSW and CD with the incooperation of substrate blending ratios. A stoichiometric (elemental composition) biogas prediction model is first developed and then a MATLAB tool based linear programming optimisation approach is developed and intergrated to maximise biogas production through determination and applilaction of optimal co-digestion substrate feed ratios. The purpose of this work is to provide an easy non-complex model for determining biogas potential from WH, MSW and CD as well as to provide the optimal co-digestion substrate mixing ratios of the same which lead to improved ultimate biogas yield. The methodology and approach used herein can apply to any other biomass residues.

This study finds application in determination of the feasibility of biogas projects as well as in already existing biogas plants in terms of co-digestion blend ratios and as such substitutes to a greater extend the necessity of using complex and time consuming models such as ADM1 and other experimental approaches needing sophisticated equipment and methodologies. This will go a long way in value adding to the decision making of individuals, communities as well as small-scale and big companies to venture and invest in biogas production. Biogas production *via* anaerobic digestion is a cost-effective route for waste-to-energy conversion, however, the abundant natural gas and liquid petroleum gas makes it less cost competitive [38]. The bigger the biogas plant, the huge the economic benefits attainable from it [39].

Section 2 of this article gives the materials and methods, section 3 gives a case study, section 4 gives the results and discussion and section 5 conludes the article.

Materials and methods

Theory and assumptions

This study assumes that:

- temperature is constant
- pH is constant
- the biomass material only consists of carbon, hydrogen, oxygen, nitrogen and sulphur

Table 1. Biochemical reactions in anaerobic digestion.

Stage	Reactions
Hydrolysis	$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + H_2$
Acetogenesis	$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2$ $C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O$ $C_6H_{12}O_6 \rightarrow 3CH_3COOH$
Acetogenesis	$CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2$ $C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2$ $CH_3CH_2OH + 2H_2O \leftrightarrow CH_3COO^- + 3H_2 + H^+$
Methanogenesis	$CH_3CH_2COOH \rightarrow CH_4 + CO_2$ $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $2CH_3CH_2OH + CO_2 \rightarrow CH_4 + 2CH_3COOH$

- methane, carbon dioxide, ammonia and hydrogen sulphide are the only products
- there is perfect mixing
- digestion goes to completion
- there is no ash accummulation
- for MSW, only the organic fraction of it from food wastes and market wastes among other biodegradables in combination is utilisable for biogas production

Biogas is a mixture of gases comprising mainly of methane and carbon dioxide and is produced by the process of anaerobic digestion. Table 1 shows the biochemical reactions in anaerobic digestion. The process consists mainly of four stages which are hydrolysis, acidogenesis, acetogenesis and methanogenesis [40].

Complex biomass materials are broken down into simple monomers with the aid of enzymes in the hydrolysis stage. Starch hydrolysis is catalysed by a combination of amylase enzymes while cellulose hydrolysis is catalysed by cellulases such as exo-glucanases, endo-glucanases and cellobiases. Enzymatic hydrolysis of proteins is aided by protease and peptidases collectively known as proteinases. Lipid hydrolysis is facilitated by triglyceride lipases [41,42]. In acidogenesis, the monomers produced in hydrolysis (amino acids, simple sugars and fatty acids) are fermented and anaerobically oxidised by acidogenic bacteria. Intermediate products such as volatile fatty acids are anaerobically oxidised by acetogenic bacteria in the acetogenesis stage. In methanogenesis, methane is produced from the products of acidogenesis and acetogenesis with the aid of methanogenic bacteria. These biochemical reactions are interrelated and depend on each other as depicted in Table 1.

In the course of biogas generation, there are a lot of multifaceted interlinks within the processes as the reactions progress. A number of different parameter conditions are required, consequently complicating the model development processes [43]. As such available models differ with respect to complexity and purpose. Buswell and Mueller, [44] developed a mechanism of methane fermentation which was a model for predicting methane and carbon dioxide. This model considered carbon, hydrogen and oxygen as the only elements present in the biomaterial. Equation (1) shows the Buswell and Mueller model equation.

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

Table 2. Ultimate analysis percentage composition by mass [47–49].

	WH (%)	MSW (%)	CD (%)
C	33.13	48.00	39.09
H	4.35	6.40	4.61
O	29.71	37.60	26.68
N	1.66	2.60	0.83
S	0.37	0.40	0.25

where n, a and b are the percentage composition by mass of carbon, hydrogen and oxygen, respectively, and obtained from ultimate analysis.

In 1977, Boyle, [45] modified the Buswell and Mueller equation and included nitrogen and sulphur as part of the elemental constuents of the biomaterial composition. Equation (2) shows the Boyle's biogas prediction equation.

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2}\right) H_2O \Rightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right)CO_2 + dNH_3 + eH_2S. \quad (2)$$

The constants a, b, c, d and e in $C_aH_bO_cN_dS_e$ are given by the ultimate analysis mass (or percentage composition by mass) of each of the elements devided by the relative atomic mass (Ar) of each of the elements as depicted below:

$$a = \frac{\text{Carbon ultimate mass}}{Ar_C} \triangleq \frac{\text{Carbon ultimate mass}}{12.017}, \quad (3)$$

$$b = \frac{\text{Hydrogen ultimate mass}}{Ar_H} \triangleq \frac{\text{Hydrogen ultimate mass}}{1.0079}, \quad (4)$$

$$c = \frac{\text{Oxygen ultimate mass}}{Ar_O} \triangleq \frac{\text{Oxygen ultimate mass}}{15.999}, \quad (5)$$

$$d = \frac{\text{Nitrogen ultimate mass}}{Ar_N} \triangleq \frac{\text{Nitrogen ultimate mass}}{14.0067}, \quad (6)$$

$$e = \frac{\text{Sulphur ultimate mass}}{Ar_S} \triangleq \frac{\text{Sulphur ultimate mass}}{32.065}. \quad (7)$$

Baseline study - biogas prediction and modelling

This subsection entails the methodology for the biogas prediction and modelling without co-digestion nor optimisation applied. In this baseline study, volumes are in (ml) and masses are in (g). The waste streams which are the raw materials for biogas production vary significantly due to seasonal and geographical location leading to a dissimilarity of biogas potentials among different studies for the same substrates [46]. For this reason, a single set of ultimate analysis results is used from literature for each of the substrates and it is assumed that this data matches with the Zimbabwe case presented in this research. Table 2 gives the ultimate analysis values used in this study.

The Boyle's modified Buswell and Mueller equation, represented by equation (Equation (2)) is adopted in this study.

Achinas and Euverink [50] reported that the relative molecular mass (Mr) of the biomass material with formular $C_aH_bO_cN_dS_e$ is given by:

$$\mathrm{Mr}_{C_aH_bO_cN_dS_e} = a*\mathrm{Ar}_C + b*\mathrm{Ar}_H + c*\mathrm{Ar}_O + d*\mathrm{Ar}_N + e*\mathrm{Ar}_S \,\mathrm{in}\, \frac{g}{mol}, \tag{8}$$

where Ar_C, Ar_H, Ar_O, Ar_N and Ar_S are constants defined in Equations (3)–(7). Similarly, the relative molecular masses (Mr) of the each of the reactants and products can be calculated as shown in Equations (9)–(13).

$$\mathrm{Mr}_{H_2O} = 2*\mathrm{Ar}_H + 1*\mathrm{Ar}_O \,\mathrm{in}\, \frac{g}{mol}, \tag{9}$$

$$\mathrm{Mr}_{CH_4} = \mathrm{Ar}_C + 4*\mathrm{Ar}_H \,\mathrm{in}\, \frac{g}{mol}, \tag{10}$$

$$\mathrm{Mr}_{CO_2} = 1*\mathrm{Ar}_C + 2*\mathrm{Ar}_O \,\mathrm{in}\, \frac{g}{mol}, \tag{11}$$

$$\mathrm{Mr}_{NH_3} = 1*\mathrm{Ar}_N + 3*\mathrm{Ar}_H \,\mathrm{in}\, \frac{g}{mol}, \tag{12}$$

$$\mathrm{Mr}_{H_2S} = 2*\mathrm{Ar}_H + 1*\mathrm{Ar}_S \,\mathrm{in}\, \frac{g}{mol}. \tag{13}$$

Biogas is assumed to comprise of methane (CH_4), carbon dioxide (CO_2), ammonia (NH_3) and hydrogen sulphide (H_2S) [45]. Given that at standard temperature and pressure 1mole of any gas occupies 22.4l [51], each of these biogas constituents can be calculated as shown in Equations (14)–(17) [50,52].

$$\text{Total biomethane } (CH_4) = \frac{22.4*1000*\left(\frac{a}{2}+\frac{b}{8}-\frac{c}{4}-\frac{3d}{8}-\frac{e}{4}\right)}{\mathrm{Mr}_{C_aH_bO_cN_dS_e}}, \tag{14}$$

$$\text{Total Carbon dioxide} (CO_2) = \frac{22.4*1000*\left(\frac{a}{2}-\frac{b}{8}+\frac{c}{4}+\frac{3d}{8}+\frac{e}{4}\right)}{\mathrm{Mr}_{C_aH_bO_cN_dS_e}}, \tag{15}$$

$$\text{Total Ammonia } (NH_3) = \frac{22.4*1000*d}{\mathrm{Mr}_{C_aH_bO_cN_dS_e}}, \tag{16}$$

$$\text{Total Hydrogen Sulphide } (H_2S) = \frac{22.4*1000*e}{\mathrm{Mr}_{C_aH_bO_cN_dS_e}}, \tag{17}$$

$$\text{Total Biogas production potential} = \text{Total}(CH_4) + \text{Total}(CO_2) + \text{Total}(NH_3) + \text{Total}(H_2S). \tag{18}$$

The adopted Boyle's modified Buswell and Mueller Equation (2) assumes 100% biomass disintergration and digestion which is not so with almost all biomasses. There is always some undigestible component within every substrate which is collected at the end of the digestion process as spent slurry. To cater for this descrepancy this study uses a factor of 0.8 adopted from [50] as an adjustment to the ultimate potential biogas yield.

Optimisation

This subsection entails the methodology for the codigestion, modelling and subsequent optimisation using the linear programming optimisation approach.

Problem formulation

Taking Equation (2) as the general reaction equation for the biogas production process, Equations (19)–(21) can be derived to represent WH, MSW and CD biogas production processes, respectively.

$$C_{a_1}H_{b_1}O_{c_1}N_{d_1}S_{e_1} + \left(a_1 - \frac{b_1}{4} - \frac{c_1}{2} + \frac{3d_1}{4} + \frac{e_1}{2}\right) H_2O \Rightarrow \left(\frac{a_1}{2} + \frac{b_1}{8} - \frac{c_1}{4} - \frac{3d_1}{8} - \frac{e_1}{4}\right) CH_4 + \left(\frac{a_1}{2} - \frac{b_1}{8} + \frac{c_1}{4} + \frac{3d_1}{8} + \frac{e_1}{4}\right) CO_2 + d_1 NH_3 + e_1 H_2S, \tag{19}$$

$$C_{a_2}H_{b_2}O_{c_2}N_{d_2}S_{e_2} + \left(a_2 - \frac{b_2}{4} - \frac{c_2}{2} + \frac{3d_2}{4} + \frac{e_2}{2}\right) H_2O \Rightarrow \left(\frac{a_2}{2} + \frac{b_2}{8} - \frac{c_2}{4} - \frac{3d_2}{8} - \frac{e_2}{4}\right) CH_4 + \left(\frac{a_2}{2} - \frac{b_2}{8} + \frac{c_2}{4} + \frac{3d_2}{8} + \frac{e_2}{4}\right) CO_2 + d_2 NH_3 + e_2 H_2S, \tag{20}$$

$$C_{a_3}H_{b_3}O_{c_3}N_{d_3}S_{e_3} + \left(a_3 - \frac{b_3}{4} - \frac{c_3}{2} + \frac{3d_3}{4} + \frac{e_3}{2}\right) H_2O \Rightarrow \left(\frac{a_3}{2} + \frac{b_3}{8} - \frac{c_3}{4} - \frac{3d_3}{8} - \frac{e_3}{4}\right) CH_4 + \left(\frac{a_3}{2} - \frac{b_3}{8} + \frac{c_3}{4} + \frac{3d_3}{8} + \frac{e_3}{4}\right) CO_2 + d_3 NH_3 + e_3 H_2S. \tag{21}$$

The objective is to find the substrate blend ratios in the co-digestion mixture that maximises the production of biogas. A linear programming optimisation approach is proposed in the following mathematical formulation.

$$\min_x f^T x \quad \text{such that} \quad \begin{cases} A.x \le b, \\ A_{eq}.x = b_{eq}, \\ lb \le x \le ub. \end{cases} \tag{22}$$

where f, x, b, b_{eq}, lb and ub are vectors, and A and A_{eq} are matrices, and $f^T x$ is called the objective function and the equalities and inequalities are called constraints.

Objective function and constraints

The objective is to maximise the biogas output from the substrate mixture and as such determine the optimal substrate mass blend ratios.

The objective function is expressed as:

$$f^T x = -(V_1 x_1 + V_2 x_2 + V_3 x_3), \tag{23}$$

where the number of moles of the substrates are the decision variables denoted by:

$$X(\text{moles}) = [x_1 x_2 x_3]^T \tag{24}$$

In the optimisations volumes are in (m^3), masses are in (kg) and the units of x_1, x_2 and x_3 are moles. In Equation (24), x_1 is the number of moles of WH, x_2 is the number of moles of MSW and x_3 is the number of moles of CD.

V_1 is the volume of biogas from WH expressed as:

$$V_1(m^3) = \frac{(22.4\times 10^{-3}) \times (CO_{2_1} + NH_{3_1} + H_2S_1 + CH_{4_1})}{\mathrm{Mr}_{WH}}, \tag{25}$$

V_2 is the volume of biogas from MSW expressed as:

$$V_2(m^3) = \frac{(22.4\times 10^{-3}) \times (CO_{2_2} + NH_{3_2} + H_2S_2 + CH_{4_2})}{\mathrm{Mr}_{MSW}}, \tag{26}$$

V_3 is the volume of biogas from CD expressed as:

$$V_3(m^3) = \frac{(22.4 \times 10^{-3}) \times (CO_{2_3} + NH_{3_3} + H_2S_3 + CH_{4_3})}{Mr_{CD}}. \tag{27}$$

$CO_{2_{1,2,\&3}}$, $NH_{3_{1,2,\&3}}$, $H_2S_{1,2,\&3}$ and $CH_{4_{1,2,\&3}}$ are the number of moles of carbon dioxide, ammonia, hydrogen sulphide and methane for WH, MSW and CD, respectively, and Equations (28)–(39) show how to determine these moles. Mr_{WH}, Mr_{MSW} and Mr_{CD} are as denoted in Equations (40)–(42), respectively.

$$CH_{4_1} = \frac{a_1}{2} + \frac{b_1}{8} - \frac{c_1}{4} - \frac{3d_1}{8} - \frac{e_1}{4}, \tag{28}$$

$$CO_{2_1} = \frac{a_1}{2} - \frac{b_1}{8} + \frac{c_1}{4} + \frac{3d_1}{8} + \frac{e_1}{4}, \tag{29}$$

$$NH_{3_1} = d_1, \tag{30}$$

$$H_2S_1 = e_1, \tag{31}$$

$$CH_{4_2} = \frac{a_2}{2} + \frac{b_2}{8} - \frac{c_2}{4} - \frac{3d_2}{8} - \frac{e_2}{4}, \tag{32}$$

$$CO_{2_2} = \frac{a_2}{2} - \frac{b_2}{8} + \frac{c_2}{4} + \frac{3d_2}{8} + \frac{e_2}{4}, \tag{33}$$

$$NH_{3_2} = d_2 \tag{34}$$

$$H_2S_2 = e_2, \tag{35}$$

$$CH_{4_3} = \frac{a_3}{2} + \frac{b_3}{8} - \frac{c_3}{4} - \frac{3d_3}{8} - \frac{e_3}{4}, \tag{36}$$

$$CO_{2_3} = \frac{a_3}{2} - \frac{b_3}{8} + \frac{c_3}{4} + \frac{3d_3}{8} + \frac{e_3}{4}, \tag{37}$$

$$NH_{3_3} = d_3 \tag{38}$$

$$H_2S_3 = e_3, \tag{39}$$

$$Mr_{WH}(\text{kgmol}^{-1}) = a_1 * Ar_C + b_1 * Ar_H + c_1 * Ar_O + d_1 * Ar_N + e_1 * Ar_S, \tag{40}$$

$$Mr_{MSW}(\text{kgmol}^{-1}) = a_2 * Ar_C + b_2 * Ar_H + c_2 * Ar_O + d_2 * Ar_N + e_2 * Ar_S, \tag{41}$$

$$Mr_{CD}\ (\text{kgmol}^{-1}) = a_3 * Ar_C + b_3 * Ar_H + c_3 * Ar_O + d_3 * Ar_N + e_3 * Ar_S. \tag{42}$$

The constraints are described in Equations (43), (56), (57), (58) and (59). Equation (43) is the reactor volume constraint which is fixed at $1 m^3$ specifically for the purpose of restricting the co-digestion substrate quantities to a unit volume for easy of determination of substrate blend mass ratios.

$$h(x) = V_A x_1 + V_B x_2 + V_C x_3 - 1 = 0, \tag{43}$$

where V_A is the volume of WH and its respective volume of water at any instant denoted as:

$$V_A(m^3) = V_{WH} + \left(\frac{(22.4 \times 10^{-3}) \times H_2O_1}{Mr_{WH}} \times V_{H_2O}\right), \tag{44}$$

where:

$$H_2O_1(\text{moles}) = a_1 - \frac{b_1}{4} - \frac{c_1}{2} + \frac{3d_1}{4} + \frac{e_1}{2}, \tag{45}$$

$$V_{WH} = \frac{m_{WH}}{\rho_{WH}}, \tag{46}$$

$$m_{WH} = Mr_{WH} \times n_{WH}, \tag{47}$$

ρ_{WH} is the density of WH.

V_{H_2O} in Equations (44), (48) and (52) is the volume of water to be added to each substrate per each mole of the respective substrate and has units of $m^3 mol^{-1}$.

V_B is the volume of MSW and its respective volume of water at any instant denoted as:

$$V_B(m^3) = V_{MSW} + \left(\frac{(22.4 \times 10^{-3}) \times H_2O_2}{Mr_{MSW}} \times V_{H_2O}\right), \tag{48}$$

where:

$$H_2O_2(\text{moles}) = a_2 - \frac{b_2}{4} - \frac{c_2}{2} + \frac{3d_2}{4} + \frac{e_2}{2}, \tag{49}$$

$$V_{MSW} = \frac{m_{MSW}}{\rho_{MSW}}, \tag{50}$$

$$m_{MSW} = Mr_{MSW} \times n_{MSW}, \tag{51}$$

ρ_{MSW} is the density of MSW.

V_C is the volume of CD and its respective volume of water at any instant denoted as:

$$V_C(m^3) = V_{CD} + \left(\frac{(22.4 \times 10^{-3}) \times H_2O_3}{Mr_{CD}} \times V_{H_2O}\right), \tag{52}$$

where:

$$H_2O_3(\text{moles}) = a_3 - \frac{b_3}{4} - \frac{c_3}{2} + \frac{3d_3}{4} + \frac{e_3}{2}, \tag{53}$$

$$V_{CD} = \frac{m_{CD}}{\rho_{CD}}, \tag{54}$$

$$m_{CD} = Mr_{CD} \times n_{CD}, \tag{55}$$

ρ_{CD} is the density of CD.

Equations (56), (57) and (58) show the the lower and upper bounds constraints for WH, MSW and CD, respectively.

$$V_{WH}^{min} \le x_1 \le V_{WH}^{max} \tag{56}$$

$$V_{MSW}^{min} \le x_2 \le V_{MSW}^{max} \tag{57}$$

$$V_{CD}^{min} \le x_3 \le V_{CD}^{max} \tag{58}$$

Equation (59) gives the *C:N* ratio constraint

$$(C:N)^{min} \le \frac{a_1.x_2 + a_2.x_2 + a_3.x_3}{d_1.x_1 + d_2.x_2 + d_3.x_3} \le (C:N)^{max}, \tag{59}$$

where a_1, a_2 and a_3 are the WH, MSW and CD carbon ultimate compositions, respectively; and d_1, d_2 and d_3 are the WH, MSW and CD nitrogen ultimate compositions, respectively.

Case study

WH, an invasive species is invading fresh water bodies thereby out-competing other species and decreasing biodiversity. MSW is currently being disposed of in waste dumps and landfills and this is resulting in the formation of landfill gas which is a more intoxicating gas than carbon dioxide such that its greenhouse effect is about 21 times greater over a 100 year time frame [53]. MSW and CD have been implicated in poor aesthetic quality of the environment and pollution of surface and ground water sources [54]. These wastes can be value added *via* the anaerobic digestion process to produce biogas thereby reducing direct CO_2 and CH_4 emissions into the atmosphere. However, if not properly managed, there are chances that these greenhouse gases can escape *via* leaks from the digester, field application of untreated slurry and uncovered

Table 3. Case data for volumes.

Parameter	WH (m^3)	MSW (m^3)	CD (m^3)
V_{min}	0	0	0
V_{max}	2.32×10^4	3.64×10^3	4.143×10^3

digestate storage tanks [55,56]. Overally GHG emissions are reduced by anaerobic digestion, however, proper management and efficient operation of the entire process is of paramount importance to achieve huge benefits in GHG reductions. The biogas has to be treated or purified so that CO_2 and other impurities such as H_2S can be captured and/or removed.

Lake Chivero in Zimbabwe near Norton is used as the WH resource base. The estimated total wet mass of WH in Lake Chivero is $197,400 t/yr$ and dry mass is $23,688 t/yr$ [19]. In this study, dried WH is used as it was proved to produce more biogas as compared to wet mass of the same [19]. The density of WH is $85 kg/m^3$ which gives a total available volume of $278,682.35 m^3/yr$ of dry WH.

Waste generation rate is estimated to be 0.5kg per person per day [57]. Norton, a peri-urban town in Zimbabwe is used as a case study area for this research and has a population of 52,054.[1] Total waste generated is therefore $0.5x52,054 = 26,027 kg/day = 9499.9 t/yr$. Computation using a density of $217.5 kg/m^3$ gives a volume of $43,677.7 m^3/yr$ for the MSW resource.

Norton is part of Chegutu district which has a total of 87,603 cattle. It is assumed that Norton owns 25% of Chegutu's cattle. Each cow produces 908kg/yr of dung. The total mass of CD is computed to be 19,885,881kg/yr. The density of CD is $400 kg/m^3$ which gives a volume of $49,714.70 m^3/yr$. The retention time is assumed to be 30 days implying that the digester has to be fed 12 times per year. As such each yearly volume of substrate is devided by 12 times yeilding maximum quantities of $2.32x10^4 m^3, 3.64x10^3 m^3 and 4.143x10^3 m^3$ for WH, MSW and CD, respectively. The minimum feed for each substrate is taken as zero.

Table 3 shows the minimum and maximum volumes used as part of the case data and these are as such also taken to depict the lower and upper volume bounds, respectively. Distinct researchers reported diverse ranges of *C:N* ratio for optimal biogas generation for specific substrates. The ranges reported are 15–30, 25–30, 20–30 and 15.5–19 [21–25]. This implies that each substrate and/or substrate combinations in co-digestions have perculiar *C:N* ratio range for optimality different from any other substrates. In this study, a minimum value, $(C:N)^{min}$ of 10 and a maximum value, $(C:N)^{max}$ of 35 were set and the simulations in the optimisation were allowed to pick an optimal *C:N* ratio for the substrate combinations (WH, MSW and CD) being co-digested.

To obtain the model parameters used in the determination of reacting moles for the co-digestion substrate mixture, the relative atomic masses were converted from $gmol^{-1}$ to $kgmol^{-1}$, Equations (3)–(7) were applied, the emperical formula concept was used (deviding each resultant value by the minimum of the resultant values) and finally the parameter values shown in Table 4 are arrived at by deviding the obtainable results by 1000 so as to be consistent with the units.

Table 4. Model parameters for determination of reacting moles.

WH		MSW		CD	
Parameter	Value	Parameter	Value	Parameter	Value
a_1	0.2389	a_2	0.3202	a_3	0.2687
b_1	0.3740	b_2	0.5090	b_3	0.4150
c_1	0.1609	c_2	0.1884	c_3	0.1219
d_1	0.0103	d_2	0.0149	d_3	0.0263
e_1	0.001	e_2	0.001	e_3	0.001

The relative atomic masses (Ar) used in the model are as defined in Equations (3)–(7) and then converted to units of $(kgmol^{-1})$. The densities used in the model are as shown in Table 5.

The final Linear Programming problem in the standard form as in Equation (22) with all the parameters is as shown in Equations (60)–(66).

$$f^T = 22.4 \times 10^{-3} \times \left[\begin{array}{c} -\frac{(CO_{2_1} + NH_{3_1} + H_2S_1 + CH_{4_1})}{Mr_{WH}} - \frac{(CO_{2_2} + NH_{3_2} + H_2S_2 + CH_{4_2})}{Mr_{MSW}} \\ -\frac{(CO_{2_3} + NH_{3_3} + H_2S_3 + CH_{4_3})}{Mr_{CD}} \end{array} \right] \tag{60}$$

where $CO_{2_{1,2,\&3}}, NH_{3_{1,2,\&3}}, H_2S_{1,2,\&3}$ and $CH_{4_{1,2,\&3}}$ are as denoted in Equations (28)–(39). Mr_{WH}, Mr_{MSW} and Mr_{CD} are as denoted in Equations (40)–(42).

The Carbon to Nitrogen ratio inequality constraint Equation (59), was linearised and two inequalities were arrived at as shown in Equation (61).

$$A = \begin{bmatrix} 10(d_1 - a_1) 10(d_2 - a_2) 10(d_3 - a_3) \\ (a_1 - 35d_1)(a_2 - 35d_2)(a_3 - 35d_3) \end{bmatrix} = \begin{bmatrix} -0.1362 0.1714 0.0062 \\ -0.1206 -0.2006 -0.6500 \end{bmatrix} \tag{61}$$

$$b = \begin{bmatrix} 0 \\ 0 \end{bmatrix}, \tag{62}$$

$$A_{eq} = \left[\begin{array}{c} V_{WH} + \left(\frac{(22.4 \times 10^{-3}) \times H_2O_1}{Mr_{WH}} \times V_{H_2O} \right) V_{MSW} + \left(\frac{(22.4 \times 10^{-3}) \times H_2O_2}{Mr_{MSW}} \times V_{H_2O} \right) \\ V_{CD} + \left(\frac{(22.4 \times 10^{-3}) \times H_2O_3}{Mr_{CD}} \times V_{H_2O} \right) \end{array} \right] = [7.5509 \times 10^{-5} \quad 4.0881 \times 10^{-5} \quad 2.3376 \times 10^{-5}], \tag{63}$$

where: H_2O_1, H_2O_2 and H_2O_3 are as denoted in Equations (45), (49) and (53), respectively.

$$b_{eq} = [1], \tag{64}$$

$$lb = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}, \tag{65}$$

$$ub = \begin{bmatrix} 2.32 \times 10^4 \\ 3.64 \times 10^3 \\ 4.143 \times 10^3 \end{bmatrix}. \tag{66}$$

The biogas production process has to be operated at a large scale for it to compete with conventional sources such as natural gas and liquid petroleum gas which are cheaper and at the same time have more calorific values. However, for the purposes of this study the digester volume is taken as unit $(1 m^3)$ as indicated in Equation (43) so as to arrive at the intended objective of ascertaining the substrate co-digestion blending ratios per unit volume of reactor.

Table 5. Densities.

Substrate/material	Density, ρ (kgm^{-3})	Source
WH	85	[58]
MSW	217.5	[47]
CD	400	[59]
H_2O	997	[60]

Results and discussion

The results presented are per dry WH, wet CD and wet organic fraction of MSW substrate feeds.

Baseline results

Table 6 gives the mono-digestion theoretical and adjusted biogas constituents as well as the total biogas potential (B_{tot}) for WH, MSW and CD, respectively. The theoretical values are arrived at using Equations (14)–(18) for each of the substrates and the adjusted values are obtained by multiplying the theoretical values by a factor of 0.8 so as to cater for the non-biodegradable fractions of the substarates which remain undigested [50]. Figure 1 is drawn from Table 6 and shows the quantity of each gas component constituent in the biogas for each of the substrates.

It can be deduced from the three substrates that CD produces the highest amount of biogas followed by MSW and WH produces the least as depicted in Table 6 and Figure 1. Biogas generation from CD is highest due to the fact that some partial digestion would have already happened on the bio-material in the stomach of the cattle and it is lowest in WH due to the complex lignin, cellullose and hemicelluloses within its structure which renders it to be recalcitrant in nature. Figures 2–4 display pictorial results of the percentage composition of the biogas constituent gases (methane, carbon doxide, ammonia and hydrogen sulphide) from WH, MSW and CD, respectively, as drawn from Table 6. A similar trend is observed from the results that methane constitutes the highest percentage, followed by carbon dioxide then ammonia and lastly hydrogen sulphide. This tallies with what was reported by Anuar [61], Rasi [62], Vanegas and Bartlett [63] as well as by Kossmann and Pönitz [64] among many other researchers.

Co-digestion and optimisation results

Table 7 shows the optimal substrate moles and the respective blend ratios for the co-digestion of WH, MSW and CD.

Linear programming optimisation using the linprog dual-simplex algorithm in MATLAB gave optimal substrate blends of $x_1 : x_2 : x_3$ as 9990.1moles : 3640moles : 4143moles for the co-digestion of WH, MSW and CD, respectively, for a $1m^3$ digester. The model gave the optimal $C : N$ ratio for the codigestion mixture as 17.57 : 1. The computed molar masses from the model are 0.006kg/mol, 0.0076kg/moland0.006kg/mol for WH, MSW and CD, respectively. Using these results and applying the stoichiometric relationship; mass = number of moles x molar mass [65], the quantities of each substrate to be fed for each cubic meter digester are found to be 59.9406kg : 27.664kg : 24.858kg. This translates to optimal percentage substrate mass blend ratios of 53.27 : 24.64 : 22.09 for WH, MSW and CD, respectively, for any digester volume.

Table 6. Biogas potential prediction for water hyacinth, municipal solid waste and cow dung.

Component	WH (ml/gVS)		MSW (ml/gVS)		CD (ml/gVS)	
	S_b	A_b	S_b	A_b	S_b	A_b
CH_4	455.11	364.09	502.38	401.91	543.95	435.16
CO_2	437.05	349.64	439.44	351.55	459.59	367.67
NH_3	38.35	30.68	43.77	35.01	98.03	78.42
H_2S	3.73	2.99	2.94	2.35	3.73	2.99
B_{tot}	934.24	747.40	988.53	790.83	1105.3	884.24

S_b: stoichiometric biogas yield.
A_b: adjusted biogas yield.

Discussion

From Table 6, with units converted from ml/gVS to m^3/kg, the total biogas potential predictions were found to be $0.747m^3/kg$, $0.790m^3/kg$ and $0.884m^3/kg$ for WH, MSW and CD, respectively. For the purpose of comparing the baseline biogas output to the optimised output, the baseline is subjected to the same masses of the individual substrates which were fed to a $1m^3$ digestion chamber. Table 8 shows the individual substrates' biogas yields as well as the total biogas or sum of these mono-digestion quantities.

In Table 8, the biogas potentials are taken from Table 6 and the individual substrate masses are taken from Table 7.

The optimised co-digestion system herein takes 112.46kg of substrate blend mixture and gives a biogas yield of $14,008.8m^3$. Upon applying the adjustiment factor of 0.8 to the yield as explained in the last paragraph of sub-section 2.2, 1kg of co-digestion substrate blend mixture yields $124.56m^3$ of biogas which translates to 124, 560ml/gVS. Equation (67) shows the calculation of the percentage increase from the baseline result to the optimisation result.

$$\text{Percentage increase} = \frac{\text{Optimised yield} - \text{Total baseline yield}}{\text{Total baseline yield}} \times 100 \tag{67}$$

$$\text{Percentage increase} = \frac{14{,}008.8 - 88.60}{88.60} \times 100 = 157.11\% \tag{68}$$

Based on the simulation results, this study reports that co-digestion of WH, MSW and CD as well as application of optimisation to the substrate feed ratios increases the biogas yield by 157.11% when compared to mono-digestion of the same. Varied percentage increases are reported in literature from co-digestion depending on the types and number of substrates as well as conditions the reactions are subjected to. Most of the reports are on co-digestion of only two substrates under thermophilic conditions. Astals et al. [66] reported an increase of 400% on output biogas from co-digestion of pig manure and crude gycerol. Yen and Brune [67] reported an increase of 104.2% from co-digestion of algal sludge and waste paper. Li et al. [68] reported an increase of 44% from co-digestion of kitchen waste and cow manure.

CD has a water content in the range of $70-90\%$ [69] and WH has a water content of about 90% [19]. These high percentages of water have a net positive effect on anaerobic digestion. However, cattle manure has residual lignin complexes from fodder which is somehow resistant to anaerobic digestion [70]. WH is constituted of lignin, cellulose and hemicelluloses which makes it recalcitrant in

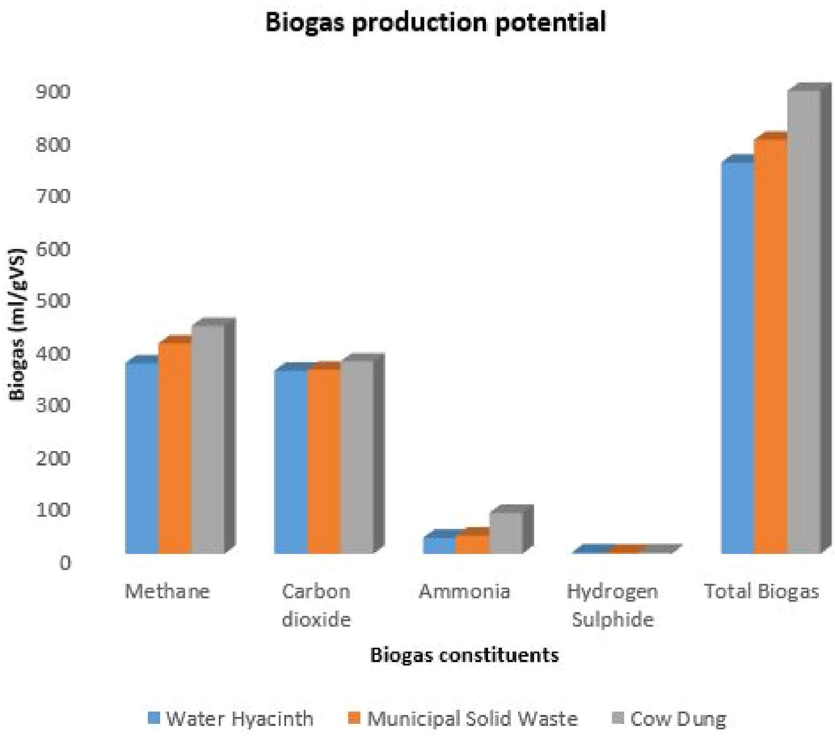

Figure 1. Biogas potential prediction.

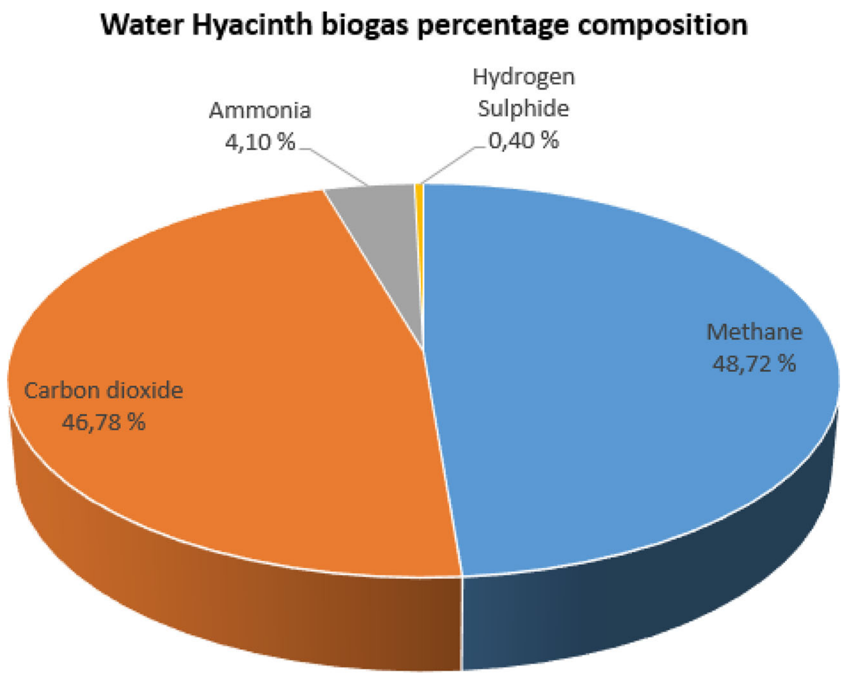

Figure 2. Water hyacinth biogas percentage composition.

nature leading to its poor digestion individually [71]. Co-digestion has a complimentary effect to the pros and cons of each of the substrates herein discussed leading to the higher combined biogas output realised.

Optimal substrate mix ratios realised from the optimisation done led to optimal carbon to nitrogen $(C:N)$ ratio within the substrate blend among other benefits such as stabilisation of the process. For this study, the optimal $C:N$ ratio was found to be 17.57 : 1. This agrees to the ranges reported by [21,25] and [22] even though the substrates are different. Different values were simulated for $(C:N)^{min}$ and $(C:N)^{max}$. $(C:N)^{min}$ values of 17 and below had no effect on the optimal $C:N$ ratio while on the other hand for values between 18 and 23 the optimisation picked that specific value set as the minimum of the range while at the same time reducing the proportion of the third substrate (CD) towards zero and increasing the mass ratios of the other two substrates. $(C:N)^{min}$ values of 24 and above led to infeasible solutions. $(C:N)^{max}$ values of 18 and above had no effect on the optimal $C:N$ ratio as well as the resultant mass ratios, the simulations picked a value of 17.57 as the optimal one. $(C:N)^{max}$ values of 17 and below led to infeasible solutions. The carbon to nitrogen $(C:N)$ ratio complimentary synergistic positive effect to the digestion process is one of the major explanations to the increase in biogas output from the co-digested substrates in comparison to the individual mono-digestion biogas output.

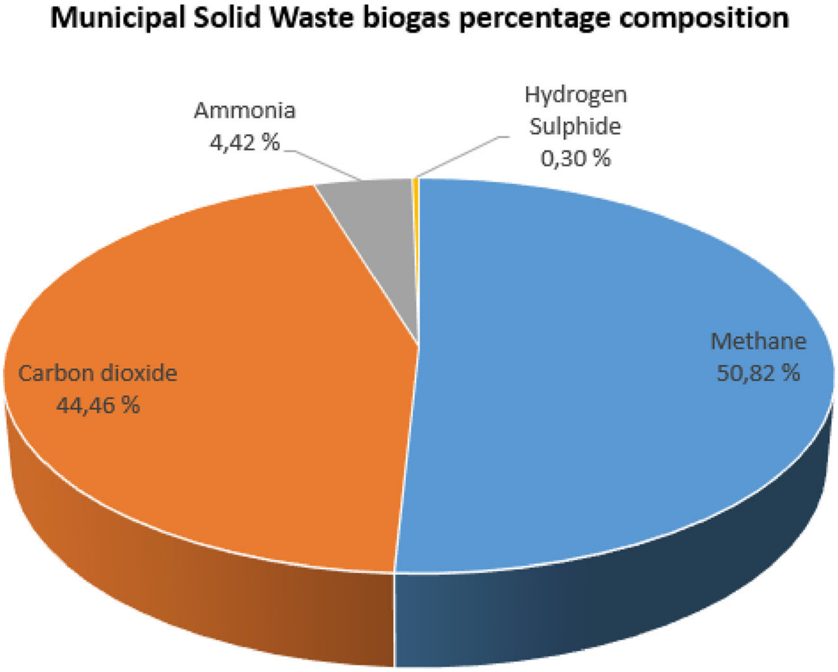

Figure 3. Municipal solid waste biogas percentage composition.

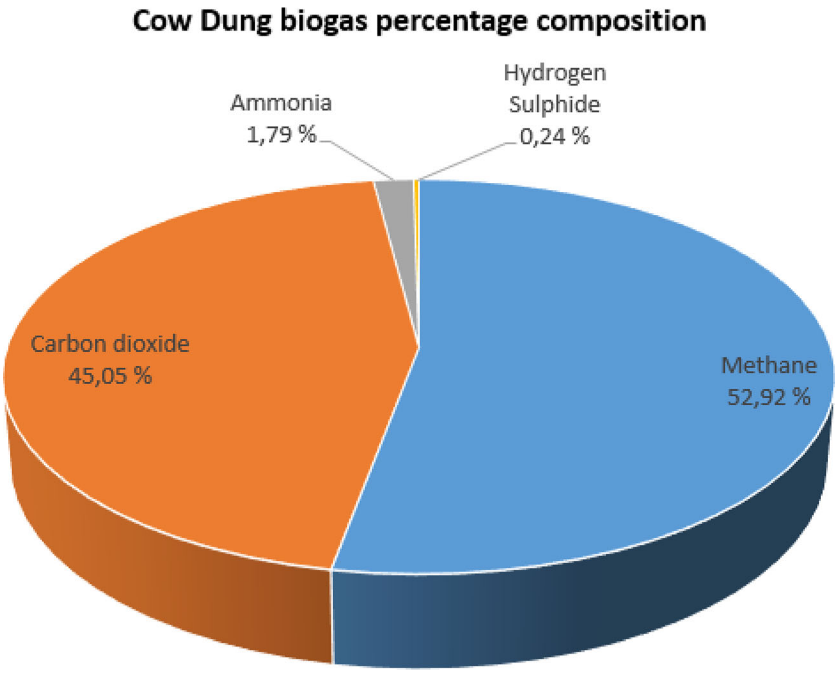

Figure 4. Cow dung biogas percentage composition.

Table 7. Optimisation results summary.

Parameters	WH	MSW	CD
Optimal substrate moles	9990.1	3640	4143
Molar masses (kg/mol)	0.006	0.0076	0.006
Optimal masses (kg)	59.94	27.66	24.86
Optimal mass ratios (%)	53.27	24.64	22.09
Optimal *C:N* ratio	17.57:1		
Optimal biogas (m^3)		17511	
Adjusted optimal biogas (m^3)		14008.8	

Table 8. Baseline biogas output.

Parameters	WH	MSW	CD
Biogas potential (m^3/kg)	0.747	0.790	0.884
Substrate masses (kg)	59.94	27.66	24.86
Substrate biogas yield (m^3)	44.78	21.85	21.97
Total biogas yield (m^3)	88.60		

Conclusion

Anaerobic digestion is an efficient and low cost technology for waste management that yields biogas – a high value biofuel. A more or less similar approach would be to use the same wastes and technology targeting the precursor chemicals such as carboxylic acids [38,72]. These chemicals would generate a lot of revenue but their demand and market is less than that of biogas. Proper management and handling of the produced biogas is key to mantaining the benefits of reduced GHG emissions. The digester has to be completely leak proof and the digestate slurry storage facilities have to be always covered to avoid the escaping of CO_2 and CH_4. CO_2 can be captured and used on site or channeled towards other beneficial uses such production of chemicals among others. Small scale biogas plants come with high costs as such biogas plants have to be operated at large scale to achieve benefits of reduced operational costs and matching in competitiveness with convenional liquid petroleum gas and natural gas.

This study investigated and established an optimal substrate blend ratio for the co-digestion of WH, MSW and CD and a model for the blend mixture which produces optimum biogas was developed from first principles. A prediction of the expected biogas yield from the individual substrates was done. The anaerobic biogas production process was optimised to give informed optimal substrate blend ratios for co-digestion using linear programming in MATLAB.

Optimisation of the biogas production process with respect to substrate blending ratios resulted in increased ultimate biogas yield from the optimised co-digestion combinations as compared to the individual mono-digestion total biogas yields from the same substrates. The informed feed mixing ratios from the optimisation helps in obtaining an efficient co-digestion of the substrates due to synergistic effects of the mixed organic wastes and ultimately giving the optimal quantity of biogas. This study concludes that co-digestion with subsequent optimisation of substrate feed ratios enhances the ultimate biogas yield.

The major caveats to this study are the seasonal variation of the substrates and the substrate constituent composition which differs with geographic location from which the feed materials are sourced. As such, the baseline and the optimised biogas yields would also differ accordingly if the caveats are taken into consideration. Future work will look into the optimisation of the methane component of the biogas and minimisation of carbon dioxide. Dynamic modelling with subsequent optimisation, regulation and control enco-operating other key parameters such as HRT, temperature and pH among others adds to the integral part of forseen future works.

Disclosure statement

No potential conflict of interest was reported by the authors.

Note

1. http://worldpopulationreview.com/countries/zimbabwe-population/

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