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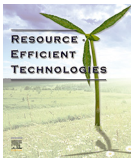

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Research paper

Theoretical analysis of biogas potential prediction from agricultural waste

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Abstract

A simplistic theoretical study of anaerobic digestion in order to predict the biogas amount of agricultural waste is proposed. A wide variety of models exist, but most of them rely on algebraic equations instead of biochemical equations and require many input parameters as well as computation time. This work provides a simplified model that predicts the biogas amount produced and could be applied for agricultural energy feasibility studies for instance dimensioning bioreactors digesting animal waste slurries. The method can be used for other feedstock materials and repeated for other similar applications, in an effort to expand anaerobic digestion systems as a clean energy source.

Keywords: Biogas; Anaerobic digestion; Animal slurries; Modeling

1. Introduction

Nowadays, the depletion of fossil fuels and the environmental compliance concerning the reduction of the greenhouse gases have attracted the interest in non-conventional fuel from bio-resources and -waste. Anaerobic digestion transforms waste material into valuable sources reducing in parallel the waste volumes [1,2]. Biogas is produced from anaerobic digestion and is considered a clean energy source for those who want an alternative energy pathway. Anaerobic digesters convert organic waste (waste water sludge, agricultural and food waste, animal and human manure) into energy (biogas). In addition, the digestate produced is a good soil additive and can be used by agricultural farmers in order to enhance crop production. The advantages from anaerobic digestion include energy production (biogas), material recovery (fertilizers) and waste elimination (waste treatment) [3,4]. Moreover, biogas production can enhance agricultural sector to overcome energy problems, increase the efficiency and of course to serve as a service taking account the environmental compliance [5–7] (Fig. 1).

The mathematical models can indicate digester performance capabilities and hence research efforts are currently focused on the development of advanced models with high accuracy level. Tomei et al. refer there is a wide variety of mathematical models for the description of anaerobic digestion ranging from steady-state to very complex dynamic models [9]. The most currently state-of-the-art model is the IWA ADM1 developed by the corresponding IWA Task Group. Batstone et al. described the capability of this model to predict the major processes occurring in an anaerobic digestion system, and acts as a unified base for modeling of anaerobic digestion [10]. Although efforts have been made in the modeling of anaerobic digestion by ADM1, various issues still remain unsolved. For instance, the kinetics involving hydrolysis is simplified in ADM1 by assuming first order kinetics. The majority of other parameters are assumed constant, given by the literature or by separate research. One specific case is the development of accurate models for the anaerobic digestion of solid waste. Moreover, issues like co-digestion or microbial community data have to be taken into account in order to develop more precise and accurate models [11,12].

However, our study focuses on biogas potential using a simplistic model in order to define the theoretical total amount of biogas that can be generated from agricultural material. The theoretical amount of biogas that can be produced from a feed can be calculated from the relative amounts of carbon, hydrogen, oxygen, nitrogen and sulfur in the material (Boyle's formula). Not all of the biomass materials can be processed. This model could help to achieve widespread utilization of the

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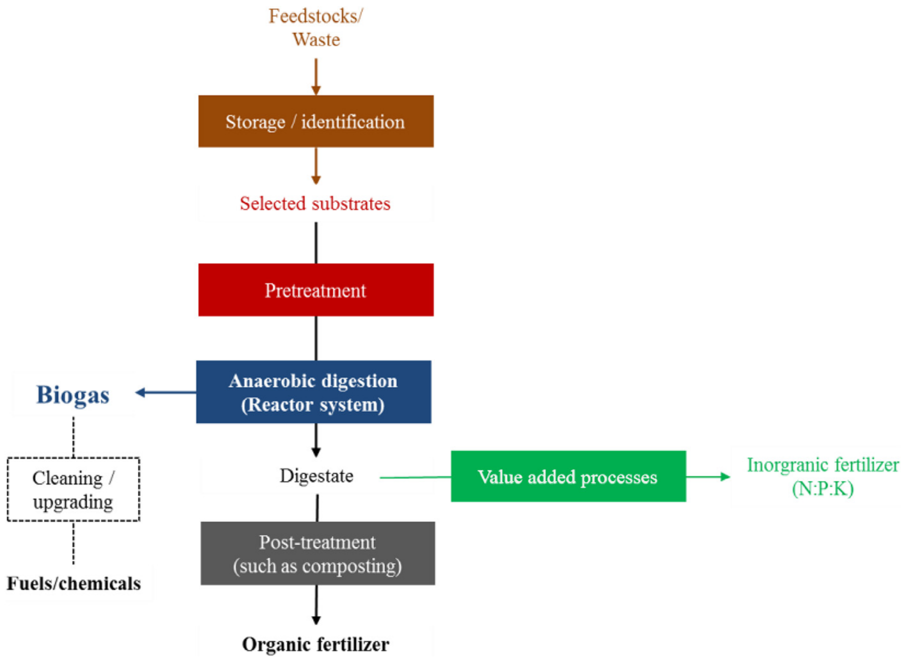

Fig. 1. Overview of AD technology [8].

large body of knowledge of anaerobic process available from research studies and operational experience in small agricultural farms.

2. Materials and methods

To apply this model to a specific feedstock, we need to know the chemical components of the feedstock. The model considers only carbon, hydrogen, oxygen, nitrogen and sulfur as input elements, and the relative ratios of these elements can be taken from published values for ultimate analyses of those waste. Table 1 below includes the values of ultimate analyses for the agricultural waste used in this study based on literature data.

Table 1
Composition of the feedstocks based on ultimate analysis from literature data [13–16].

Feedstock	Chicken litter (dried)	Swine solids (dried)	Feedlot manure (dried)
Ultimate analysis, %			
C	45.32	47.3	45.39
H	5.85	5.9	5.35
O	27.38	20.1	30.98
N	5.16	4.58	0.96
S	0.45	0.93	0.29
P	–	–	–
Cl	0.35	–	1.16

The composition of animal slurries depends on the type of animal, the feed they are given, and the external conditions that they are in. Because of the variation in waste composition for different types of each animal in different conditions, only one set of published values for ultimate analysis is used instead of averaging over published values. Agricultural wastes are very complex mixtures and different approaches are used to describe their composition. The elemental composition used here is the most basic method to describe the non-aqueous components of the waste. This model aims to provide a balance between simplicity and effective biogas prediction. The purpose is not to create a model that takes all factors into account and predicts biogas output to a very high level of precision (Fig. 2).

It can predict biogas output assuming that a reaction goes to completion. Knowledge on the biodegradation of organics and methane production is necessary in the prediction of reactor performance under varying operational conditions. In this study, a simple model is used in order to estimate the theoretical biogas potential. This model has to be applicable for agricultural small-scale activities in order to determine the digester size [17,18].

There is a wide variety of models developed so far and for this reason is required a convergent action to consolidate the

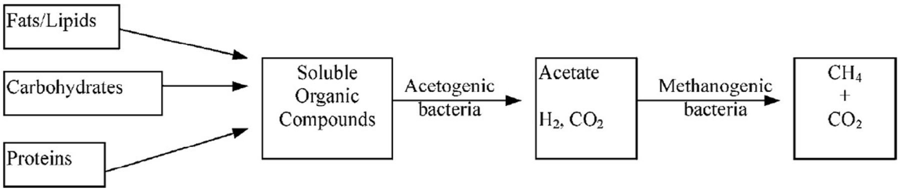

Fig. 2. Schematic biochemical process stages of anaerobic digestion. Adopted form the source [17].

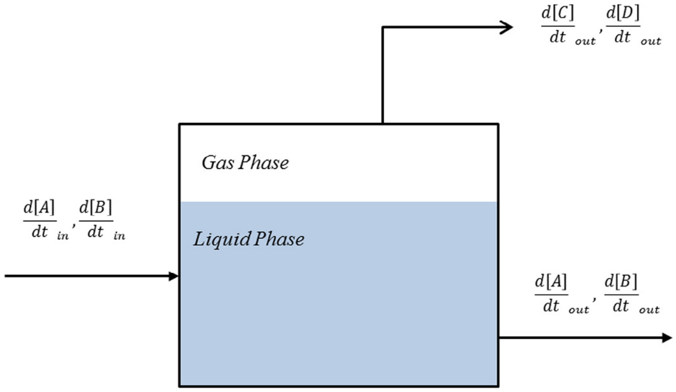

Fig. 3. Schematic of a typical well-stirred single tank reactor.

different approaches found in the different existing models. An anaerobic digestion system normally consists of a reactor with a liquid–solid volume, and a sealed gas headspace at atmospheric pressure with the gas removed to downstream utilization. A simple system consists of a stirred reactor with a single input and output stream, and constant feedstock volume (Fig. 3). This bioreactor is fed by reactants A and B which are converted through a series of biological steps into products C and D.

With knowledge of the chemical composition of a waste the quantity of methane can be predicted from the stoichiometric formula developed by Buswell and Hatfield in 1936 [19,20]:

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

Boyle modified the chemical reaction of Buswell and Mueller (1952) and included nitrogen and sulfur to obtain the fraction of ammonia and hydrogen sulfide in the produced biogas [21,22]:

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

or in simplistic form:

$$A + C_1B \rightarrow C_2C + C_3D + C_4E + C_5F$$

$$A, B \rightarrow reactants$$

$$C, D, E, F \rightarrow products$$

And constant equations are:

$$C_1 = a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} + \frac{e}{2}$$

$$C_2 = \frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}$$

$$C_3 = \frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}$$

$$C_4 = d$$

$$C_5 = e$$

The biochemical reaction is automatically balanced and can be applied to any input with known relative ratios of carbon, hydrogen, oxygen, nitrogen and sulfur. The model assumes that these elements are the only components of the feedstock. Moreover, the ultimate analysis is selected by the user of the model in order to determine the constants of the chemical reaction C_1, C_2, C_3, C_4 and C_5 by estimating firstly the chemical formula of our feedstock. The constant of each element is equal to the ultimate analysis-based mass divided by the molar mass of the element and therefore ultimate analysis gives mass ratios C:H:O:N:S (in grams) which are then defined as variables. Then, for molar masses of carbon (mm_C), hydrogen (mm_H), oxygen (mm_O), nitrogen (mm_N) and sulfur (mm_S) we have:

$$a = \frac{aultimass}{mm_C} = \frac{aultimass}{12.0107}$$

$$b = \frac{bultimass}{mm_H} = \frac{bultimass}{1.0079}$$

$$c = \frac{cultimass}{mm_O} = \frac{cultimass}{15.999}$$

$$d = \frac{dultimass}{mm_N} = \frac{dultimass}{14.0067}$$

$$e = \frac{eultimass}{mm_S} = \frac{eultimass}{32.065}$$

The molar mass of a compound with chemical formula $C_aH_bO_cN_dS_e$

$$mm_A = a * mm_C + b * mm_H + c * mm_O + d * mm_N + e * mm_S = 12.017a + 1.0079b + 15.999c + 14.0067d + 32.065e \quad in \quad \frac{g}{mol}$$

Respectively, the molar mass of each reactant and product can then also be calculated:

$$mm_B = 2 * mm_H + 1 * mm_O = 2 * 1.0079 + 1 * 15.999 = 18.0158 \frac{g}{mol}$$

$$mm_C = mm_C + 4 * mm_H = 12.017 + 4 * 1.0079 = 16.04 \frac{g}{mol}$$

$$mm_D = 1 * mm_C + 2 * mm_O = 1 * 12.017 + 2 * 15.999 = 44.02 \frac{g}{mol}$$

$$mm_E = 3*mm_H + 1*mm_N$$

$$= 3*1.0079 + 1*14.0067 = 17.03\frac{g}{mol}$$

$$mm_F = 2*mm_H + 1*mm_S = 2*1.0079 + 1*32.065 = 34.08\frac{g}{mol}$$

3. Theory/calculation

This model includes a number of simplifications and could be made more complex without adding excessive computation time if done correctly. The biogas amount, methane yield and water uptake are estimated theoretically in this study from the elemental composition of biomass, using Boyle's formula. The theoretical biochemical methane potential (TBMP) of the material is calculated from [23]:

$$TBMP\left(ml\ CH_4\ gVS^{-1}\right) = \frac{22.4\times\left(\frac{a}{2}+\frac{b}{8}-\frac{c}{4}-\frac{3d}{8}-\frac{e}{4}\right)}{12.017a+1.0079b+15.999c+14.0067d+32.065e}$$

In our study we have the following initial assumptions:

- constant temperature and perfect mixing;
- ideal bacterial conditions, meaning full digestion;
- input waste consists of only C, H, O, N and S;
- products of reaction include only CH_4, CO_2, NH_3 and H_2S;
- no accumulation of ashes.

These conditions affect the total amount of biogas produced in digester. For this reason, we added a limiting factor (*f*) that can give reliable results and eliminate the discrepancy between hypothetical and real biogas amount as hypothetical potential of complete reaction will not be reached. The reactions that take place in anaerobic digestion are not entirely completed and in order to eliminate high discrepancies in our calculations, a limiting factor is used incorporating issues such as presence of toxins, insufficient mixing, microbial population establishment, complexity of lignin structure and other process condition effects (pH, temperature and redox). The creation of a model which considers all possible effects and includes different many parameters would be complicated and out of the scope concerning small scale biogas production activities from farmers. We use a value for *f* (=80%) in order to adjust the gas produced under (unrealistic) ideal conditions to the gas produced under real conditions.

4. Results and discussion

The results are unlikely to match the true results because in practice no reaction goes to full completion and we do not have 100% breakdown of cellulosic materials. The model predicts ideal settings that are not found in the real world. This is why the model was adjusted with the limiting factor (f) to regulate the ideal conditions to more realistic ones (Table 2).

Table 2
Values of theoretical and adjusted (limiting factor) BMP values.

	TBMP values (ml CH_4/g VS)	Adjusted TBMP values (ml CH_4/g VS)	Methane values from different studies [24–26] (ml CH_4/g VS)
Chicken litter (dried)	544,05	435,24	437.6
Swine solids (dried)	641,88	513,50	487.9
Beef feedlot manure (dried)	551,41	441,13	360

The results only give a maximal biogas potential, and are very optimistic since neither non-degradable material nor energy demand of the microbes is considered. However, comparing the adjusted TBMP values with literature data, there is low discrepancy for chicken litter and swine solids. So, practical evaluation of methane production capacity can be further applied in practice. The equations of Buswell and Müller (1952) as well as Boyle (1976) assume a complete conversion of biomass. This results in an overestimation of gas yields and these models assume that substrates are individually fermented and are not part of complex feedstock mixtures as it is usually the case these days. From an economic perspective for the farmers, this means the methane that can be obtained from local husbandries is quite high. This makes sense as it motivates the farmer to invest in AD technology as AD provides energy (biogas) and fertilizer (digestate). Finally, the main use of the proposed model is methane potential prediction which is interesting when a small-scale single-stirred digester is used for the digestion of wastes.

For a wide variety of residues there are no sufficient data from lab experiments. The theoretical gas yields based on the Boyle model can provide useful information and allow comparing the potential of different materials based on their composition. This study provides simple model which does not require a large number of inputs and can be applied to a large number of feedstocks as long as the user has data from ultimate analyses for the elements of carbon, hydrogen, oxygen, nitrogen and sulfur.

5. Conclusions

A simple model can be used as a tool for the biogas amount prediction from animal slurries. Several advantages are expected from the application of a theoretical study like an increased interest for agricultural small-scale activities, a further development work on process modeling and an application of validation (experimental) procedures to make the results more comparable in order the AD technology to be generally related to practical, industrial applications and be transferred from research to SMEs.

This model outmatches as it is applied for different feedstocks if elemental analysis-based data are available. In order to make models simplistic enough to communicate ideas, some accuracy is lost but limiting factor used ($f = 80\%$) can reduce the deviation of the theoretical values from the experimental measurements. Moreover, this study makes up a simple and useful tool so that consultants and agricultural engineers can use in order to support farmers and other stakeholders.

Indeed, this is one of the areas where most benefits from the application of a simple model can be gained. 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. The theoretical study can support the increased application of anaerobic technology as a sustainable waste treatment option and a viable alternative to other energy production processes.

In the next decades, agricultural waste will be the most meaningful energy source as an alternative of fossil fuels. Lignocellulose-based biogas is a potential pathway for the global producers which provide renewable fuels. Although technological advances are still progressing, research efforts continue to support the development of efficient, sustainable and economically feasible bioprocesses and confront issues concerning the feedstocks and operations costs. Through a sustained research program and an emerging economic competitiveness, the anaerobic digestion technology for biogas production is poised for immediate widespread commercial applications.

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Abbreviations

IWA	International Water Association
ADM1	Anaerobic Digestion Model No. 1
BMP	biochemical methane potential
TBMP	theoretical biochemical methane potential
AD	anaerobic digestion
SMEs	small and medium enterprises

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