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Operational Conditions affecting Biohythane Production in Anaerobic Digestion and its Kinetic Model: A Review

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Abstract

Recently, the global carbon footprint issue is rising significantly due to fossil fuel demand. Biohythane, which is produced from anaerobic digestion is found as an alternative fuel to address this problem. Even though quite a number of reviews have been done before on the biohythane production process, an in-depth review particularly onbiohythane kineticstudy is not available until now. Therefore, this review paper discusses the general anaerobic digestion process of biohythane production as well as its operating factors such as temperature, pH, and microbial population in improving productivity. In addition, this paper also discusses kinetics modeling, which is commonly used in biohythane production to improve or analyze the effect, relationship, and function of the parameter, as well as to investigate the performance of biohythane during the process. These kinetic models provide a variety of functional goals depending on the experiment's objective, such as determining the kinetics of cell growth, discussing the effect of different operating parameters on biohythane production, studying substrate utilization and inhibition, and product formation. All models are classified in a table by their equation for further reference.

Keywords: Biohythane; Anaerobic Digestion; Kinetic Modeling; Hydrogen; Methane.

1.0 INTRODUCTION

In the past few years, the usage of fossil fuels as an energy resource has become crucial for many countries [1]. Despite the fact that fossil fuel is a significant source of energy, however, it has been generally acknowledged as the main contributor to emissions leading to the global climate disaster [2]. This issue becomes more critical since energy consumption is expected to grow greater than 300% by the end of the century [3]. These global issues and the associated environmental implications, both on the environmental and energy security aspect have encouraged research and development of alternative green fuels [4]. The biogas industry, which acts as an alternative green fuel has dramatically grown in recent years [5], [6]. This biogas technology has appeared as a promising source owing to its ability to resolve several issues of energy due to its renewable and cleaner energy potential [7].

Hydrogen (H_2) and methane (CH_4) are the main two carriers of energy that have been utilized in the biogas sector today [8]–[11]. According to Song et al. [12], H_2 and CH_4 are discovered to be the two prominent gaseous energy carriers, and their high calorific values have been commonly used and exploited in the chemical industry and processing. CH_4, an abundant renewable gas, is regarded as a desirable power energy source and heating generation, and it may also be utilized as automotive fuel for transportation [13]. However, the narrow flammability range and slow flame speed of methane limitfuel efficiency [14]. Since H_2 has a higher flame speed than CH_4, the presence of small the amount of H_2 significantly improved the flame speed and extends the lean flammability range of the fuel [15]. Owing to its stable molecule, CH_4 is difficult to be ignited but hydrogen in contrast has an ignition energy that is 25 times lower than CH_4 [16]. Combustion of CH_4 in an engine and catalyze in the exhaust is difficult after treatment converters mean while H_2 is a powerful stimulant for combustion which facilitate the acceleration of CH_4 combustion within an engine [16], [17].

Hythane, a hydrogen-methane mixture with 10% to 30% hydrogen concentration by volume, is getting prominence as a valuable fuel for vehicles due to the complement of both H_2 and CH_4 advantageous that compensate for each other's drawbacks and problems [18], [19]. Hythane has been produced to maximize heat recovery and increase hydrogen utilization [20]–[22]. It is regarded as a transition fuel in order to accomplish the evolution from a fossil fuel-based economy to an H_2-based economy [23], [24]. The gases produced at various phases of the process can also be combined to produce an upgraded fuel known as biohythane [25]. In the current scenario, hythane has been generated by a thermochemical process rather than a biological process, with natural gas as the substrate. This process consumes high energy and relies completely on current fossil fuels. To prevent this problem, nowadays, "hythane" is changed to "biohythane," in which the substrate used is based on organic wastes (biowastes) under anaerobic conditions for its production [26].

In the automotive industry, adding 10-25% of H_2 into CH_4 will effectively enhance the performance of CH_4-fueled engines for automobiles [27]. Due to these advantages, hythane has been commercialized in the automobile sector for hythane-fuelled vehicles in the US, India and China [28] and has also received high attention from individual companies such as Volvo, Fiat, and Ashok Leyland [16]. Although the current usage of hythane in automobile sector helps to reduce GHG emission released in the atmosphere, as being said earlier the commercialized hythane used today are produced thermo-chemically based on fossil fuel (natural gas as a starting material) therefore making it unsustainable and the process is energy intensive. As claimed by Mamimin et al. [29], biohythane could be produced in the purification process as a green and effective vehicle fuel after extracting CO_2. As can be seen, converting organic waste into biohythane through anaerobic digestion (AD) helps to alleviate the energy crisis and pollution concerns. As a result, AD has become one of the best alternatives for producing hythane in a sustainable and environmentally friendly manner using biological processes.

2.0 ANAEROBIC DIGESTION

Anaerobic digestion (AD) is a natural process that happens biologically when there is no oxygen present and serves as one of the main waste management techniques that eliminate trash while also producing bioenergy [30]–[33]. Organic waste can be converted to renewable energy such as H_2 and CH_4 to alleviate the burden of energy shortage and diversify fuel sources [34]. AD has many advantages and is regarded as one of the most successful ways of treating bio-wastes intorecovering renewable energy through biogas production [35]. It is gaining popularity in the scientific community and among the general public due to its effective performance in waste reduction and energy recovery [36]. The biological pathways for both hydrogen and methane production share similarities. Both consist of four-generation phases (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) [37]–[40]. Each phase is dominated by different microbial groups which results to several products.

Hydrolysis consists of the degradation of complex polymeric matters, such as polysaccharides, proteins, carbohydrates, nucleic acids and lipids (fat and grease) into soluble monosaccharides, sugars, amino acids, purines and pyrimidines, glycerol and LCFAs [18], [41], [42]. The importance of the hydrolytic stage understanding is critical since it is regarded as the process's limiting step [43]–[45]. During this phase, a group of microorganisms known as hydrolytic and fermentative bacteria that release extracellular enzymes such as cellulase, lipase, protease and others break down complex organic polymers [46]. Based on the author, these enzymes are also released by certain types of saprophytes, which are classified as hydrolytic microorganisms. The length of the polysaccharides chain, such as cellulose, has a significant impact on hydrolysis. Polymeric sugars derived from hemicellulose and cellulose will be more hydrolyzable into free monomers such as glucose and xylose after pretreatment [47].

Acidogenesis is the second step of the AD process in which acid-phase bacteria (*Clostridium, Peptococcus Anaerobus, Lactobacillus, and Actinomyces*) use both dissolved and bound O_2 in solution and carbon (C), respectively [48]. Acidogenic bacteria will further degrade the products which are soluble in the water together with the hydrolysis products (simple sugar amino acid and long-chain fatty acid) to form various intermediate products such as short-chain organic acids or VFAs (formic, propionic, acetic, butyric, and pentanoic), alcohols (methanol, ethanol), aldehydes, CO_2, and H_2 [49]. The low H_2 ion concentrations during this stage will favor the synthesis of all these fermentation intermediates thermodynamically [46].

In acetogenesis, the VFAs will be reduced by a restricted group of homoacetogenic microorganisms into acetic acid (CH_3COOH), H_2 and CO_2 with some other product traces [41], [48], [50]. Then, in methanogenesis phase, the two groups of methanogenic microorganisms will be responsible to convert the intermediate compounds into CH_4 where the acetotrophic microbes produce CH_4 by using CH_3COOH and the hydrogenotrophic ones produce CH_4 by using CO_2 and H_2 [25]. Usually, this process is separated and brought to the second stage due to their different nutritional and pH requirements [51]. The rapid decomposition of substrate components such as carbohydrates and proteins generally results in the formation of volatile fatty acids (VFAs), which substantially reduces the pH during the process [52]. The dropping of pH outside of the ideal range results in methanogenesis inhibition since it is commonly operated at pH 7–8 [53]. Therefore, pH control should be utilized during this stage in order to maximize the yield production. The summarized pathway for biohythane production via AD is displayed in **Figure1.**

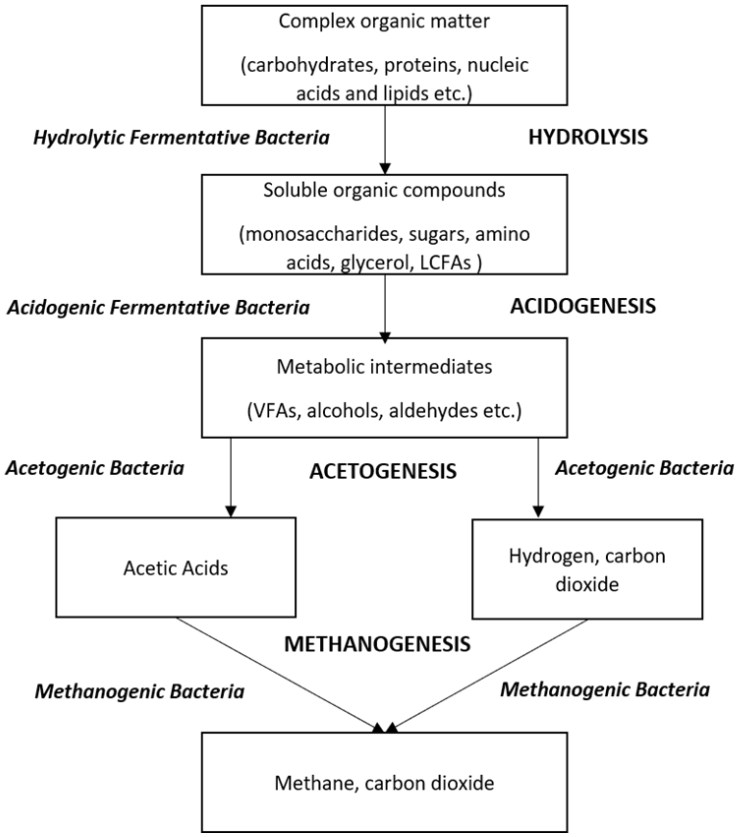

Figure 1. Anaerobic digestion process

3.0 OPERATIONAL CONDITIONS AFFECTING ANAEROBIC DIGESTION

Several factors affecting the efficiency of an anaerobic digestion have been analysed and depicted due to the complexity of the bioconversion processes as well as the complexity of specific requirements for optimum microbial process. This section will go through the operating factors that are commonly affected the process (temperature, pH, and microbial population).

3.1 Temperature

Temperature is a significant operating condition in anaerobic digestion (AD) since it affects microbial communities and influences the performance of AD process stability [54]. Due to that, microorganisms' sensitivity to temperature fluctuations outside of their optimum range has been indicated to have a substantial impact on their metabolic activity and development [54]. It is one of the important operational factors to be analyzed in order to maximize industrial waste biogas [55], [56]. It plays aimportant role in maintaining the rate of a digestion and has to be kept constant at all time throughout the process. The AD plant needs a consistent and optimal temperature since it has a big influence on numerous aspects such as substrate pH, methane concentration in biogas production, biogas yield rate, ammonia concentration, and volatile fatty acid concentration [57].

In general, AD process can be operated under three main categories of temperature which are psychrophilic (10-20 ^{o}C), mesophilic (35-37^{o}C) and thermophilic (55-60 ^{o}C) [58]–[60]. Despite, most of the AD processes are designed to operate under mesophilic and thermophilic environments in order to ensure stability and a high rate of decomposition as shown in Table 1. This is supported by a study fromde Diego-Díaz [55] which stated that the most common industrial scale for mesophilic and thermophilic are 35^{o}C and 55^{o}C respectively. This temperature has a good correlation with microbial intracellular enzyme activity during anaerobic digestion where it influencing microorganism metabolic activity and finally determine the process efficiency [61].

Table 1. Previous study on biohythane production

No	Reactor type		Substrate	pH		Temperature		H_2 yield	CH_4 yield	References
	H_2	CH_4		H_2	CH_4	H_2	CH_4			
1	Continuous stirred anaerobic bioreactors		Pineapple peel waste juice	5.5	7.0	37	37	9.3 mL H_2/g COD	174.6 mL CH_4/g COD	[23]
2	Batch bioreactor		Food waste	7.2	7.2	35	35	6.17 mol H_2/kg COD_{added}	1.22 mol CH_4/kg COD_{added}	[62]
3	Continuous stirred anaerobic bioreactors		Pineapple peel waste juice	5.5	7.0	37	37	266.91 mL/g COD	10.77 mL/g COD	[58]
4	Continuous stirred anaerobic bioreactors		Food waste	7.0	7.0	35	35	760 mL/L/d (rate)	10.2 mL/g COD	[18]
5	Batch bioreactor		Mixed fruit and vegetable waste	7.0	7.5	37	37	61.70 ± 1.47 $mL/gVS_{initial}$	208.6 ± 4.43 $mL/gVS_{initial}$	[63]
6	Serum bottle		Sugarcane bagasse and water hyacinth	6.5 ± 0.14	7.5 ± 0.16	37	37	303 mL/g COD	142 mL/g COD	[64]

Several studies have been done to investigate the temperature fluctuations' effect on the production yield. A study by Feng et. al [65] examines and compares sewage sludge anaerobic digestion (AD) at ambient and mesophilic temperatures. The results show that, in terms of process stability, removal of organic matter, and generation of methane, the performance of bioelectrochemical AD at ambient temperature (25ºC) is not significantly affected when compared to the mesophilic condition (35ºC). This implies that the ambient temperature may be used in the AD process to produce biogas without disrupting other factors. However, there are temperature ranges that must be taken into account tomaximise yield output. This is due to the fact that low-temperature AD processes may result in a lower yield percentage. This is supported by Kinnunen[66] who investigates the influence of temperature on AD of wastewater produced in order to minimize the process cost for wastewater-grown microalgae. The result shows that methane yields at low digestion temperatures (16-20ºC) were only 37-66% of the yields obtained by the standard mesophilic digestion temperature (37ºC).

A side from that, an earlier study has also focused on the thermophilic temperature, where it was discovered that this temperature can accelerate substrate breakdown, resulting in shorter operation periods compared to mesophilic [55]. This shows that high temperature promotes microbial growth and more efficient organic matter decomposition. In the AD system, two-stage thermophilic-mesophilic AD with a short-term thermophilic stage (55ºC) followed by a long-term mesophilic stage (35-37ºC) is commonly used [67]. As a result, the rate of cellulose hydrolysis at an early stage under a thermophilic environment becomes faster than mesophilic [19]. Based on the author, thermophilic environment is advantageous for AD since unwanted H_2 consumers are temperature sensitive and deactivate at high temperatures. Whereas most H_2 producers develop spores in stressful environments such as high temperatures, these desired H_2-generating microbes can live in thermophilic circumstances. However, failure to stabilize the thermophilic microbial population during the initial phase may lead to uncertain performance in a long run. The formation of thermophilic inoculum is difficult since most anaerobic wastewater treatment facilities function under mesophilic conditions [68]. Thus, the microbial community should be considered in the early stage while determining the temperature conditions of the process.

In conclusion, the temperature can significantly influence the anaerobic digestion performance since it affects the activities of extracellular enzymes. Generally, mesophilic condition operation is much more favorable than thermophilic and psychrophilic due to its large diversity of the microbial population that can degrade wide range of organic substrates and requires less energy for the operation to take place and is unsusceptible neither to additional inhibitors nor shock loading [58]. However, there are also studies that show that thermophilic works better in the AD process. Hence, the suitable temperature regime should be adjusted and explored to maximise the yield production while also lowering the energy cost.

3.2 pH

pH is one of the most significant biological parameters for anaerobic bacteria, since it may change the surface charge of microbial membranes. Apart from that, it has a significant impact on numerous enzymatic activities and nutritional absorption [69]. pH control is very important as a prominent technique to increase yield generation during AD. In the AD process, a change in culture pH can generate a shift in the dominant microbial populations, changing the primary organic acid products [70]. Therefore, maintaining an appropriate pH level is important for maximizing AD production. A number of authors have reported the effect of pH on the hydrolytic–acidogenic stage, indicating that a pH close to 6,

which is slightly acidic optimizes the working condition for hydrolytic–acidogenic bacteria [71]. Meanwhile, at pH more than 6.5, H_2 produced in the digester might be utilized by homoacetogens and methanogens in increasing the yield production of CH_4. This is supported by a study from Latif et al. [72] which investigates the influence of ph by lowering the ph from 7.0 to 5.5. The findings indicate that operating AD at low pH levels enhanced soluble product concentration while decreasing precipitation. The methane production at pH 5.5 is shown was reduced by 50% due to the aggregation of VFAs, particularly propionic and butyric acids, leaving a higher proportion of organic matter undegraded. This study observes that acidogenic predominated at low pH (6.0), while methanogens reduced by 88% at pH 5.5 compared to neutral pH. Furthermore, a study from Begum et al. [73] also found that methanogenesis is undesirable at both pHs less than 6 and pH more than 8.

Based on the previous study, it is found that a pH less than 6 was ideal for producing optimal hydrogen gas. However, the optimal ph for methane generation was discovered to be 6-8 in generating the highest yield production. The suitable pH range is very important in order to maximise yield production. Therefore, ph reading should be regularly monitored especially when it was conducted in a batch mode as it may affect the efficiency of the AD process.

3.3 Microbial Population

The selection of a suitable microbial community is critical for efficient AD [74], [75]. Hydrolytic, acidogenic, acetogenic, and methanogenic bacteria are the most common microbes found in the AD process [16]. The first microbial community, which is known as hydrolytic microorganisms will hydrolyze the complex polymeric substances comprising lipids, cellulose, and protein into basic structural building components like glucose and amino acids [76]. The hydrolysis of complex organic molecules depends heavily on hydrolytic enzymes [44]. Cellulase is another important hydrolytic enzyme generated by bacteria that catalyzes the conversion of lignocellulosic compounds (such as cellulose) into monosaccharides and endoglucanases, exoglucanases, and b-glucosidases are three essential cellulose components that catalyze cellulose degradation [77]. Meanwhile, cellulolytic bacteria such as *Cellulomonas, Clostridium, Bacillus, Thermomonospora, Ruminococcus, Baceriodes, Erwinia, Acetovibrio, Microbispora,* and *Streptomyces* generate cellulases, which hydrolyze cellulolytic biomass [77].

Following that, the second population (acidogenic bacteria) will consume the solubles produced by the hydrolysis reaction, creating several intermediates such as VFAs, CO_2, H_2, and alcohol [58]. According to current understanding, acetogenic microorganisms are made up of 23 distinct genera and over 100 species that may be found everywhere in nature. Despite this diversity, only a few microbes have been thoroughly studied. *Clostridium* strains are the most well-known and investigated. While *Clostridia* often have a diverse product range, *Acetobacteriumwoodii* has unusually high growth and acetate production rates, as well as acetate concentrations [78]. There are genera of microbes that are entirely acetogenic, such as *Acetobacterium* and *Sporomusa*, and genera that contain both acetogenic and non-acetogenic germs, such as *Clostridium, Ruminococcus,* and *Eubacterium*. AD is a naturally strong phenomenon due to the critical function of acetate as a methanogen substrate, as well as the prevalence and diversity of acetogens. However, because acetogenins are obligatory hydrogen producers that cannot sustain at high partial hydrogen pressures, a symbiotic interaction exists between acetogens that generate and consume hydrogen [16]. The reductive synthesis of acetate from CO_2 by acetogenesis is thermodynamically less favorable than methanogenesis under typical redox potential circumstances, which is the most often given cause for acetogen out-competition by methanogens in anaerobic sludge [79]. Nevertheless, it is now known that acetogens can undergo a wide spectrum of metabolic changes.

Methane is produced by methanogens that are highly vulnerable to small amounts of oxygen in the third stage of the AD process in two ways: cleavage of acetic acid molecules to produce CO_2 and CH_4, or reduction of H_2 and CO_2 [16]. Methanogenic bacteria are obligate anaerobic microorganisms that are extremely sensitive to environmental changes. They decompose the byproducts of acidic and acetogenic fermentation into CH_4 and CO_2. The breakdown of acetic acid produces around 70% of the CH_4, while a redox reaction of H_2 and CO_2 produces approximately 30% of the methane [58]. In general, the majority of the soluble organic material in the reactor medium is converted to volatile organic acids by fermentation and then converted into biogas via methanogenesis [23].

These methanogens are very essential for the AD process because they are slow to develop and highly sensitive to environmental changes [58]. *Methanobacterium, methanobacillus, methanococcus, and methanosarcina* are the examples of methanogenic bacteria. This methanogen can also be broken down into two groups: users of acetate and H_2/CO_2 (*Methanosarcina spp. and Methanothrix spp.)* and in AD, both users are considered to be essential (also, methanosaeta) [16]. As we can see, various bacteria produce different compounds. **Table 2** below depicts the type of commonly used bacteria to generate the yield.

Table 2. Type of bacteria used in AD process

No	Feedstock	Bacteria	pH	Temp	H_2 Yield	CH_4 Yield	References
1	Pineapple peels	*Clostridium sp.*	5.5	37ºC	599 mL/L_R-d	174.6 mL/L_R-d	[23]
2	Rubber Sheet Wastewater	*Desulfovibrio sp.* *Desulfitibacter sp.* *Dethiosulfatibacter sp.* *Clostridium sp.*	6	35ºC	14.53 mL/d	45 mL/d	[80]
3	Palm Oil Mill Effluent	*Clostridium sp.* *Methanosphaera sp.*	5.5	55ºC	53.1mLg/VS	259.1mLg/VS	[29]
4	Decanter Cake	*Clostridium sp.* *Methanosphaera sp.*	5.5	55ºC	51.2mLg/V	380.1mLg/V	[29]
5	Bioflocculants	*Methanosarcinaspelaei RK-23*	6.5	38ºC	-	17.4 mmol /mol acetate	[81]
6	Cow Manure and Corn Straw	*Clostridia*	7	35ºC	-	604.59 mL	[61]
7	Palm Oil Mill Effluent	*Thermoanaerobacterium*	7	55ºC	73 L/kg-VS	342 L/kg-VS	[50]

4.0 TYPE OF KINETIC MODELS APPLICABLE FOR ANAEROBIC DIGESTION PROCESS

The kinetic model is an important tool to understand the anaerobic digestion (AD) by assessing the performance of the process and accurately predicting the system's performance [82]. Kinetic model may be utilized to estimate the performance of feedstocks in AD system. Since AD is a dynamic system, it is interesting to develop mathematical formulations for the rates at which specific biochemical events in AD systems occur [83]. Understanding the response mechanism and optimising process variables require the kinetic model parameters produced by model fitting, which will also help with the estimation of biogas yield, hydraulic detention time, and energy consumption in the real-time applications. The parameters of every model were calculated by minimising the least square difference between the experimental and theoretical values. This reaction kinetics is useful in developing equations that describe the behaviour of complex feedstock in the modelled system since it is critical for evaluating anaerobic system behaviour and optimising biogas output [84].

In biohythane production, various models are evaluated in order to enhance or analyse the effect, relationship, and role of the parameter, as well as to study the performance of yield production during AD. These kinetic models provide a variety of functional goals depending on the experiment's objective. They can be used to determine the kinetics of cell growth, to describe the influence of different operating parameters on the gas production, to study substrate utilization and inhibition, and product formation. For biohythane production, each of the biohydrogen and biomethane yields are simulated independently by using the same equation. The model used for biomethane production is also applicable to biohydrogen production. Therefore, this section will explore prior studies that are relevant to either biohydrogen or biomethane and summarise which model is more appropriate to be used.

The Exponential model can be used in order to describe population growth [85]. This model could be represented by Eq. (1), where y(t) is the population size at time t and r is the proportional growth rate parameter.

$$\boldsymbol{y(t) = Y_0\, e^{rt}} \tag{1}$$

However, since the exponential growth model results in infinite population expansion, it is uncommon to use it to represent population growth. Consequently, the logistic growth model was used to improve this model [85].

The Logistic model was one of the first to be implemented in solid-state fermentation since it fits most microbial growth scenarios well, and it is now one of the most widely used models in diverse research projects [86]. In this model, a population grows until it attains a maximum capacity. In the AD process, this model is widely used to simulate cumulative biogas production over time due to the fact that it increases exponentially until it reaches a maximum value beforestaying constant [87]. This model has been utilized in a study by [88] which applying it as the kinetic model for biogas production from cattle manure. Besides, Senol et al. [89] also employed this model to estimate the potential of biogas generation potential of hazelnut (Corylus Colurna) husks. The result shows that this model give more accurate data to the experimental value compared to another model. The logistic growth model is given in Eq. (2), where; y is the estimated methane yield (mL/g VS), concerning time t (day); A is the maximum methane yield (mL/g VS); λ is the lag phase (day), and e is an Euler's function equal to 2.71828.

$$\boldsymbol{y(t) = \frac{A}{1+ e^{\frac{4\mu_m(\lambda - t)}{A}} + 2}} \tag{2}$$

In addition, several studies have also used conventional kinetic formulations, such as the AD process's Monod's equation [90]. A well-known kinetic model for comprehending microbial growth, this Monod equation shows a functional relationship between the particular growth rate and a required substrate concentration [91], [92]. Based on research done by Veshareh and Nick [93], a Monod equation may match the community activity with a certain initial substrate concentration in a batch experiment, but it cannot estimate the activity of the same community in another batch experiment with a different initial concentration of substrate. According to the findings, it shows that the proposed equivalent strain model can define the microbial community in non-isothermal reactive transport processes if the substrates are constrained, allowing for negligible microbial growth within the microbial process and consequently negligible microbial community development. However, the similar strain model is unable to predict the microbial population when substrates are in abundance. Eq. (3) shows the Monod equation. This model shows the relationship of the specific growth rate (μ) to a growth limiting substrate concentration (S) in bulk solution. Where: rate (μ) to a growth limiting substrate concentration (S) in bulk solution.Where: μmax ¼ maximum specific growth rate Ks ¼ Monod constant [94].

$$\boldsymbol{\mu = \mu_{max}\left(\frac{S}{S+K_s}\right)} \tag{3}$$

Among these 3 models, monod and logistic are observed to be more applicable in simulating the microbial growth than exponential equation in AD system. However, according to a study by Kong et al. [95], employing the Monod function by itself results in a deficient prediction of microbial growth, but combining the Monod and Logistic functions yields a more precise link between specific growth rates and nutrient concentrations.In this study, the modified Logistic function is appropriate to describe algal development. However, the relationship between specific growth rates and nutrient concentrations is not fully captured by the combination of modified Logistic and modified Monod functions, and necessitating further study. To summarise, the combination use of Logistic and modified Monod functions to analyse microbial development features is reliable and practical, and it is also expected that this technique might become an effective tool in the future.

For biogas production simulations, various cumulative single-equation kinetic models were constructed to estimate the entire volume of biogas generated from a feedstock, y ($mg.g^{1}$) over a given time period [96]. Most of these models are non-linear and were built on the presumption that the rate-limiting step in the AD is known (for example, the rate of microbial activity, the rate of hydrolysis, or the rate of biogas evolution). These kinetic models can be utilized to calculate the rate of maximum biogas production, production potential, as well as the delay phase of biogas production. As a result, the biogas potential and its production rate in batch procedures can be compared and analyzed. The first-order model, which has undergone extensive research, describes fundamental chemical reactions in which the rate of reaction is linearly proportional to the concentration of substrate [13]. For the AD hydrolysis step, this first-order kinetics is most frequently used [37]. It has the ability to provide more thorough details regarding the rate of hydrolysis constant [97]. However, various authors have modelled the other AD subprocesses using various kinetics [98]. The first order equation is given in Eq. (4) [99], where G_t is the cumulative yield of biogas (mL/gVS), G_0 is the maximum potential of biogas (mL/g VS), k is the rate of biogas production constant (1/day), and t is the BMP assay time (day).

$$G_t = G_0 \mathrm{x}(1 - e^{-kt}) \tag{4}$$

In contrast with the first order dynamic model, the modified Gompertz model was not able to provide additional information on hydrolysis rate, but it could provide a time delay for biogas production as well as the maximum methane generation rate [100]. The modified Gompertz model was demonstrated to be a suitable emperical non-linear regression model that accounts for the time delay in gas generation and depicts bacterial growth as exponential [100]. This model has been utilized extensively to simulate the biogas production performance in an AD process. Reported that, the modified Gompertz model could predict biogas yield more precise than first order kinetic models with only 0.00% – 3.78% percentage fitting error [49]. Although this model equation was commonly used to predict biogas production, however, in certain investigations, the Gompertz equation has been modified to account the rate of bacterial growth, common substrate degradation and biomass growth [90]. A study by Liew et al. [82] have reported a kinetic model to describe growth rate and product formation data by gompertz model. Similarly, a study from Meier et al. [101] also applied this model to determine the kinetic of biogas production. The model could be represented by the following Eq. (5):

$$\boldsymbol{P_t = P_m\left\{-e^{\left[\frac{R_m \mathrm{x}\, e}{P_m}(\lambda - t)\right]}\right\}} \tag{5}$$

Where P_t is the cumulative production of biohythane (mL) at culture time t, P_m is the maximum amount of biohythane production (mL), R_m is the maximum biohythane production rate (mL/L/h), λ is the lag phase time (h), and e is

2.71828 (constant).

A study from Abdel daiem et al. [87] did a comparison between Logistic kinetic model, modified Logistic kinetic, and also modified Gompertz model for biogas production from anaerobic co-digestion of waste activated sludge with wheat straw. From here, the logistic kinetic model was discovered to be more effective to all other models used in this study with R^2 0.9879 followed by modified Logistic kinetic 0.9845, and modified Gompertz 0.9815. However,a study from Mushtaq et al. [102] implemented and compared two distinct models, modified Gompertz and Logistic, for biogas data validation. According to the results, the modified Gompertz model suited the experimental data better than the Logistic function model. This is supported by a research from Zhang et al. [20] which shows that the data were all fit well to the modified Gompertz model that achieved a correlation coefficient (R^2) value higher than 0.99. A study from Armah et al. [99] also stated that the modified Gompertz model was found to be the most appropriate in explaining biogas production, with a good fit and connection to experimental results. It shows the smallest difference between measured and estimated yield production in this study. In addition, a study from Li et al. [83] also shows the correlation coefficient (R^2) obtained for biomethane production by the modified Gompertz was higher than that of the first-order model which are 0.974 and 0.968 respectively at organic loading 25 g-VS/L. These findings suggest that modified Gompertz may be a good fit for the biomethane production process.

A study from Ketsub et al. [13] investigates which model is suited the best among: First-order, Modified Gompertz, and Chen & Hashimoto. In comparison to the First-order model, the author claims that the modified Gompertz model, Chen & Hashimoto model, and these models are more advanced in correlating the proliferation of microorganisms, the effect of inhibitors, and yield production at various stages. However, among these 2 advanced models, it is indicated that Chen & Hashimoto model (Eq. (6)) is more appropriate model to be used in AD process compared to Modified Gompertz model. This study discovered that this model works well for simulating the production of biomethane using complete trash slurries prepared with three different types of pretreatments, which prior studies have rarely reported. However, due to the presence of HRT, this model is ineligible for batch processing. Follow is the model equation:

$$G_t = G_0 \left\{1 - \left(\frac{K_{CH}}{(HRT \times \mu_m) + K_{CH} - 1}\right)\right\} \quad (6)$$

Where G_t is the cumulative biogas yield (mL/g VS), G_0 is the maximum biogas potential (mL/g VS), K_{CH} is the Chen & Hashimoto constant (dimensionless), HRT (hydraulic retention time) is the BMP assay time (day), and μ_m is the maximum specific growth rate of microorganism (1/ day).

A study by Gulsen Akbay [103], found that models with the rate constant "k" such as Monod and Cone are preferred in conducting the potential of biogas production when comparing the same mixture's performance with various pretreatment applications, while models with the lag phase parameter like Transference function can be used to compare the various wastes co-digestion performance. This result shows that the cumulative biogas output (B(t)) predicted by the Cone and Transference Function models corresponded more closely to the experimental biogas production than the prediction of the Monod model. However, Som and Yahya [94] reported a good correlation of this model with experimental data. It indicates that UMAS is a potential therapy for POME since its computed kinetic coefficients of max and Ks are similar to theoretical values when the Monod Model (Eq. (3)) is used in this study. The Transference and Cone model are shown respectively in Eq. (7) and Eq. (8) below.

$$Y(t) = Y.\left\{1 - e^{-\frac{Rm\,(t-\lambda)}{Y}}\right\} \quad (7)$$

$$Y(t) = \frac{Y}{1+(k.t)^{-n}} \quad (8)$$

Where Y(t): cumulative production of biogas (mL) Y: ultimate biogas production potential (mL) Rm: maximal biogas production rate (mL/day) k: rate constant (d−1) λ: lag phase time in days (d) n: the dimensionless shape factor exp(1) = 2.7183

According to Emebu et al. [96], the cumulative models presented can be divided into two types: exponential models (Malthus model, First-order kinetic, Cone) and sigmoidal models (Gompertz, Logistic, Transference model). In addition to typically having a characteristic "S"-shaped curve in its function, sigmoidal models can be identified by the inclusion of a lag component in their equations. In contrast, as demonstrated by the first-order kinetic exponential function, exponential models have no lag factor and their data patterns approach curves with a negligible plateau at their ends.

In general, all of these models are tested in order to analyse the influence, relationship, and role of the parameter, as well as to estimate biogas performance during fermentation. Depending on the experiment's goals, these kinetic models are utilised for a variety of applications. According to the prior explanation, the criteria for selecting a kinetic model are reliant on the initial observation of displayed experimental data. Therefore, early observation with trial and error are crucial in determining the best suited model for application. Nonetheless, further research is required to

establish a kinetic analysis for anaerobic digestion based on biohythane generation. The **Table 3** below shows the type of model with its functions.

Table 3. Types of model function

Eq.	Models	Equation	Type of curve	References
1	Malthus Model/ Exponential Model	$y(t) = Y_0\, e^{rt}$	Exponential	[85]
2	Logistic growth Model	$y(t) = \frac{A}{1 + e^{\frac{4\mu m(\lambda - t)}{A}} + 2}$	Sigmoidal	[87]
3	Monod Model	$\mu = \mu_{max}\left(\frac{S}{S + K_s}\right)$	Sigmoidal	[94]
4	First-order Model	$G_t = G_0 \mathrm{x}(1 - e^{-kt})$	Sigmoidal	[99]
5	Modified Gompertz Model	$G_t = G_0\left\{1 - \left(\frac{K_{CH}}{(HRT \,\mathrm{x}\, \mu_m) + K_{CH} - 1}\right)\right\}$	Sigmoidal	[101]
6	Chen & Hashimoto Model	$Y(t) = Y.\left\{1 - e^{\frac{Rm\,(t-\lambda)}{Y}}\right\}$	Sigmoidal	[13]
7	Cone Model	$Y(t) = \frac{Y}{1 + (k.t)^{-n}}$	Exponential	[103]
8	Transference Model	$Y(t) = Y.\left(\frac{Y}{1 + (k.t)}\right)$	Sigmoidal	[103]

5.0 FUTURE PROSPECT AND CONCLUSION

The growth of biohythane from anaerobic digestion research has already shown its value as a technology with a wide range of applications from global demand. Given its clean architecture, enhanced heat and fuel efficiency using biohythane as a vehicle fuel contributes to a greener economy as it allows the combustion of engines to run effectively. Additionally, a biohythane mix with the sufficient amount of hydrogen is shown to minimize greenhouse gas emissions. From this review, it shows that the parameters condition should all be taken into account to provide a viable, efficient, and cost-effective end product. Since the manufacture of biohythane involves living microorganisms, the selection of ideal bacteria is essential for streamlining the procedure since they can facilitate substrate degradation. It is feasible to improve the quality and production rate of biohythane by selecting the most practicable substrates, controlling microbial growth, and employing metabolically engineered bacteria. This can be improved by studying the mixed microbial consortium and analyzing the unidentified microorganisms which aid in increasing the synthesis of biohythane. Besides, biohythane production can also be maximized by optimizing the bioreactor design. It was found that the pH and temperature condition especially in a single-stage anaerobic digestion process could not be controlled automatically, resulting in an inefficient fermentation process. It can therefore be modified by including a sensor to manage the operational settings. In addition, since the process requires anaerobic conditions with oxygen limitation, appropriate and adequate materials for the fermenter or bioreactor should be utilized to prevent leaks. To prevent gas from becoming entrapped in the fermenter, the gas collection part's design must be efficient. Apart from that, the productivity of this process also can be improvised by utilizing various kinetic models which are related to biohythane production depending on the objective of the study. In this review, it shows that all models stated are applicable to anaerobic digestion processes in biohythane synthesis.

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