Simulation of biogas synthesized via co-digestion processes

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Abstract

The AM2 model was able to accurately predict gas production in anaerobic digestion, with methane production increasing from 0.015 to 0.018 m^3/day as organic loading rates (OLRs) increased. However, the model faced limitations in predicting volatile fatty acid (VFA) dynamics, especially at high OLRs, due to the presence of excess organic matter.In a 37-day experiment of maize silage digestion in a 50-liter anaerobic reactor, it was shown that the AM2 model accurately estimates biogas production, with feeding intervals of fifteen minutes and a pause during weekends.The extended AM2 model was calibrated to ADM1 for grass silage simulation in $MATLAB^{TM}$ 2015b. The ADM1 simulation was unsteady initially, with inconsistent biogas flow and alkalinity output profiles, which were stabilized by increasing the disintegration process parameter,K_{hyd}, to 0.266 based on a literature review. The profiles demonstrated stability, and an identical initial parameter was suggested for K_{hyd}.The organic loading rate (OLR) and hydraulic retention time (HRT) were set at 3.58 kg ODM $m^{-3}d^{-1}$ and 33.09 days, respectively. The extended AM2 model successfully simulated biogas and methane flow rate profiles, indicating better performance than ADM1 for grass silage digestion simulation.Cattle manure digestion is simulated using an extended AM2 model calibrated to ADM1, based on literature parameters. Manure composition analysis determines the influent composition of organic fractions. Manure is valuable for agriculture, enhancing soil structure and nutrient availability, with some nutrients persisting despite cow digestion. Anaerobic digestion of manure can be affected by ammonia concentrations, with equilibrium digestion achievable by maintaining elevated rates, as detailed in the literature.In AM2's extended version, a sensitivity analysis of 24 parameters found that K_1 , K_4, K_7, K_8 , μ_{1max}, μ_{2max}, K_{s1}, K_{s2}, K_{1_2} , K_{d1}, K_{d2}, $K_{hyd,ch}$, $K_{hyd,pr}$, $K_{hyd,li}$, f_{ch,x_c}

,f_{pr,x_c} and f_{li,x_c} related to substrate degradation and CO2 yield, had the greatest impact on model output.The hydrolysis process and organic matter parameters also demonstrated high sensitivity.Sensitivity analysis data can improve model accuracy by removing parameters with low sensitivity.AM2 model extensions were made based on sensitivity analysis and AM2-ADM1 model comparisons, enhancing its applicability and accuracy. These modifications allowed AM2 to account for ADM1's combined factors, improving simulation results. While biogas generation and key variables showed agreement with ADM1 trends, AM2 responded more slowly to feedstock addition. Important findings include the consideration of inorganic nitrogen incorporated into organic matter, addressing a limitation in the original model.

Keywords:biogas; co-digestion; anaerobic digestion; modeling; simulation; optimization; Anaerobic Digestion Model (AM2); biomass.

1.Introduction

Since fossil fuels are running out quickly, bioenergy is expected to be the primary source of energy from renewable sources[1] [2].Biomass wastes from agricultural and forestry operations are regarded as carbon-neutral sources of energy[3] [4] . If the amount of carbon dioxide and oxides of sulfur emitted is decreased, using biomass is good for the ecosystem[5] .A possible technique that lowers pollution from carbon dioxide and other hazardous substances is biomethane[6] .

Anaerobic digestion (AD) is a process that turns biological material into methane, carbon dioxide, as well as digested matter using bacteria. The result is biogas, a renewable energy source with numerous advantages[7]. Utilizing agricultural waste along with other biomass, biogas is a source of clean energy with a wide range of uses, such as power production, heating, fuel manufacture, and the provision of raw materials for environmentally friendly chemicals. It can be used straight for cogeneration, cooking, lighting, and automobile fuel. Once purified, it can be pumped as biomethane into the gas supply grid[8] [9] [10]. Biogas may be processed into inexpensive syngas that is high in nitrogen. This syngas can then be utilized to produce liquid biofuel using the Fischer-Tropsch process[11] .

The process of co-digestion (AcoD) reduces carbon dioxide emissions by reducing them into carbonate molecules like magnesium carbonate (MgCO3), enhances process equilibrium, and increases biogas yield and quality. It also diversifies feedstock sources[12].Nevertheless, limited biogas production, high CO2 content, the environmental effects of digestate disposal, and the addition of complexity and

uncertainty to the AD process are some of the problems that face AcoD[13] .As a result, simulation was required to assess and enhance the effectiveness and viability of co-digestion[14] .Simulation can aid in understanding and improving the AcoD process by applying various models, including kinetic, feedstock, reactor, and optimization models, to simulate the performance of various co-digestion reactor types. These models can be applied using a variety of software packages, including Aspen Plus, SuperPro Designer, BioWin, CFD, and MATLAB [15].Several benefits come with co-digestion. In comparison with the process of anaerobic digestion alone, it can boost biogas output[16] [17] [18] [19] . This is due to the fact that co-digestion makes it possible to use various substrates, including microbe biomass, dung from animals, and waste from food, all of which can increase the total amount of methane produced. Moreover, co-digestion can raise the co-substrate's carbon-to-nitrogen ratio, which would enhance process stability. During digestion, it can also improve the volatile fatty acid, pH, as well as total ammonia nitrogen properties. By breaking down biological waste and retrieving nutrients, co-digestion can offer a sustainable waste management solution. Co-digestion has the ability to promote a circular economic model, produce biogas as a renewable biofuel, and aid in the decarbonization of the global economy[20] .

Anaerobic digestion's fundamental concept is the bacterial process that turns organic materials into biogas in the absence of oxygen. A wide range of bacteria, including methanogens and syntrophic bacteria, are involved in this process. The primary processes in anaerobic digestion include hydrolysis, fermentation, acetogenesis/dehydrogenation, as well as methanogenesis[21].By encouraging direct interspecies electron transfer (DIET) among syntrophic bacteria as well as methanogens, which increases electron transfer effectiveness and boosts the generation of methane, anaerobic digestion can be made more efficient[22]. Thermal pretreatment to increase biodegradability as well as recycling are two further methods to promote anaerobic digestion[23]. In order to overcome the difficulties posed by the existence of lipid in anaerobic reactors, bioreactors with membranes and flotation-based biological reactors have been created as well for treating lipid-rich effluent[24]. The weaknesses of each individual approach can also be addressed by mixing anaerobic digestion and electromethanogenesis, a procedure that bioelectrochemically transforms carbon dioxide into methane[25].Anaerobic digestion can be summed up by the chemical formula that follows: $H12\ O6\ C6 + 2H2\ O \rightarrow 3CH4 + 3CO2$

The organic substrate glucose ($C6H12O6$) represents a prime example of one that can be broken down anaerobically[26].

Several of the factors that affect biogas production are pressure, pH, temperatures, organic loading rate (OLR), hydraulic retention time (HRT), application of macro- and micronutrients, and suitable hybrid selection [27] [28] . The amount that can be produced of fresh maize mass, a popular substrate for producing biogas, can be increased by using macro- and micro-fertilizers [29].To increase biogas productivity, pH, temperature, OLR, and HRT must all be optimized. The generation of biogas can also be influenced by temperature, pH, and pressure. Producing more biogas and methane may result from lower internal gas pressure. Furthermore, pre-treatment techniques, substrate degradation, feedstock type, and the use of various microbes can all affect the production of biogas[30] .

As previously stated, these stages of anaerobic digestion are essential for effectively converting biological material into biogas and other useful products. Hydrolytic bacteria convert complex organic substances into simpler molecules through the process of hydrolysis [31]. Acidogenic bacteria continue to break down the simpler compounds into volatile fatty acids (VFAs) throughout the acidogenesis stage[32].Following this, acetogenic bacteria transform VFAs into acetate in a process known as acetogenesis[33]. At the final stage of anaerobic digestion, methanogenic archaea convert hydrogen and acetate into methane gas. The switch from acidogenesis into methanogenesis, which is essential for recovering energy, is influenced by the microbial ecology and gene expression[34].The process as a whole is affected differently by the various stages of anaerobic digestion. The diversity of microbes and composition, as well as the amount and quality of extracellular polymeric substances (EPS), were all impacted by the kind of substrate, which in turn affected the toxicity of aromatic compounds, according to a study by Prem et al. [35]. In their investigation of a two-phase anaerobic digestion process, Valentino et al. discovered that a mesophilic temperature combined with a 5.0-day hydraulic period of retention produced a VFA-rich stream with a high acidification yield, while a thermophilic second methanation stage enhanced the equilibrium of energy as well as the generation of biogas[36]. Optimization of anaerobic co-digestion (AcoD) was covered by Inayat et al., who highlighted temperatures, concentration of co-substrate, the inoculum ratio, and the C/N ratio as crucial variables[15]. Aeration can lower the accumulation of volatile fatty acids and raise process yields, according to Girotto et al.'s assessment of research on the combined use of aerobic treatment as well as anaerobic digestion. However, they also noted that high soluble chemical oxygen demand (COD) consumption before the AD phase may diminish methane generation[37]. Wu et al. discovered that while the acidogenic stage was predominantly responsible for reducing the number of these genes, the two-phase

thermophilic digestion also lowered the presence of several antibiotic resistance genes (ARGs) [38].

Researchers have modeled the AcoD process for different substrates and conditions using various methods and tools, including temperature, co-substrate concentration, inoculum ratio, and C/N ratio, evaluating their influence on biogas yield and quality. Deng, Y. et al. used response surface methodology (RSM) to optimize the operational parameters and biogas yield of AcoD[39], Sendjaja, A. et al. developed a state-space model and an adaptive identifier for controlling the biogas generation from AcoD [40], Harun, N., et al. simulated the AcoD reactor for three substrates using SuperPro Designer software and optimized the process parameters[41], Wang, X. et al. developed and validated an online alkalinity monitoring system for AcoD processes using an artificial neural network (ANN) model with oxidation and reduction potential (ORP), pH, and electrical conductivity (EC) as inputs and two hidden and one output neurons[42]. Employed the ADM1 model by Bułkowska et al. to delve into the influence of various co-substrates and their subsequent impacts on hydrolysis, propionate degradation, and hydrogen inhibition[43]. To increase the production of biogas from maize silage and its co-digestion with other substrates, a number of models and tactics were studied [44]. Studies on co-digestion that have already been conducted have concentrated on building kinetic models for a variety of feedstocks, predicting biogas potential models, and designing simulation models to maximize reactor performance [45].Even with the advancements in co-digestion modeling, there are still shortcomings in the modeling of dynamic reactors and the forecasting of feedstock effects and operating conditions on the composition and quality of biogas.Most experiments are small-scale or isolated, and most models are unrealistically simplistic.More dynamic and realistic models, as well as representative and doable experiments, are needed to make co-digestion more scalable and sustainable. Finding a balance between the theoretical model's complexity and its practical application is crucial for applying knowledge to biogas production systems that are both sustainable and scalable[15] [46] [47].

Present anaerobic digestion models have difficulties and constraints when it comes to accurately representing real system conditions. They don't consider the effects of many factors on the quantity and quality of biogas and are predicated on irrational assumptions. [14] [48] .High complexity, high computing cost, high value of parameter sensitivity, and limited precision are some of these limitations [48].The majority of models are limited in their applicability and generalization to various scenarios because they were designed and calibrated for certain substrates and conditions.Furthermore, they are not supported by a variety of experimental findings[49].Comprehensive modeling that explains the dynamics

and interactions of different substrates and bacteria is severely lacking [50]. Although the dynamics and interactions of current research in co-digestion processes are not fully understood[51], it reduces the intricacies of these systems and ignores the complex microbial communities that are essential to the production of biogas[52].There are currently few studies being conducted to create comprehensive models that fully capture the intricate relationships between various substrates in co-digestion systems [14].Current studies often ignore the precise interplay between multiple feedstocks and lack the depth required to simulate and improve the potential synergistic and negative effects of different substrate combinations[14] [53].Although various models exist for anaerobic digestion, they often overlook the special opportunities and problems presented by scenarios of co-digestion[52].Our capacity to forecast co-digestion systems' performance, efficiency, and stability with any degree of accuracy is hampered by the absence of appropriate modeling tools[54].The lack of standardized measurement protocols for measuring and monitoring biogas production hinders the comparison of results between different studies[55].A number of the existing models are overly complicated and call for a high number of parameters that are challenging to measure or estimate[56].Previous studies have not tackled the modeling and optimization of co-digestion with seasonal substrate changes[57].The integration of biogas production with other renewable energy sources, known as biogas hybridization, has not yet been thoroughly studied[58].The ideal parameter configurations—such as changing substrate compositions, mixing ratios, and operation conditions—remain inadequately investigated and thus contribute to the knowledge gap[59] [60].This is further hindered by the lack of strong models that take into account the synergistic effects of different feedstocks[61]. The lack of attention to comprehensive evaluations of co-digestion also affects economic and environmental decisions.The potential of alternative substrates, especially lignocellulosic materials, remains largely untapped due to limited understanding and challenges in their effective utilization .The dynamic population of microorganisms and the complexity of metabolic pathways also affect this gap[62].Because of a lack of variety among the places researched, anaerobic digestion studies face geographic gaps, mostly focused on industrialized countries and agricultural waste substrates. This narrow focus fails to consider the influence of various environmental and climate conditions on co-digestion systems worldwide, ignoring organic variety in industrial and urban environments and impeding thorough modeling of anaerobic digestion processes[63] [64]. The rules and regulations governing the generation of biogas differ across nations and areas. These measures in European nations are evaluated using a biogas policy model. This model takes into account a number of factors, such as the kind of policy, the administrative

level, the administrative region, the value chain segment that is being targeted, and changes as time passes[65].

It's important to create sophisticated and accurate models that can accurately represent the system's dynamic behavior, forecast biogas production and quality under various conditions, and be verified by experimental data. This will facilitate the design of complete systems that account for various organic material kinds and operating conditions, as well as the improvement and management of co-digestion processes. Since pretreatment effects increase organic matter's bioavailability, they must also be incorporated into the models. To give a thorough understanding of the whole biogas generation process, current models must be improved, as they frequently overlook the effects of pretreatment techniques on microbial communities[66].There are obstacles to overcome, including infrastructural shortages, poor government support, and technological shortcomings. However, there are also opportunities for improved waste management, pollution reduction, energy recovery, and economic gains when biogas systems are implemented in developing nations [67].

The goal of this study is to increase the co-digestion processes' efficiency and applicability in the production of biogas. The primary objectives are to tackle the current obstacles in this field, specifically the absence of all-encompassing and precise forecasting models for biogas production and quality under diverse circumstances. The study includes evaluating several parameters that affect the yield and quality of biogas and validating these models. It highlights the application of simulation methodologies to enhance co-digestion procedures. The anticipated advantages encompass amplified biogas generation via process optimization, the transformation of organic waste to reduce carbon dioxide emissions, and the attainment of equilibrium by regulating pH, temperature, and substrate composition. It also seeks to verify experimental results and optimize operational factors, including feedstock composition and mixing ratios. In addition, the study looks at using co-digestion procedures to produce biogas, which has drawbacks such as low biogas output, environmental issues, and complicated processes. It also looks into how biogas hybridization may be used to improve the sustainability and scalability of biogas production systems employing substrates including cattle manure, grass silage, and maize silage.

2. METHODOLOGY

2.1 AM2 Model Test

The digestion of maize silage over a period of 37 days in a 50-liter experiment was studied. Maize silage was used as an organic material to produce biogas. Every feeding into the reactor took place every fifteen minutes. The feeding was stopped over the weekend, on days 5, 13, 20, 27, and 34. Silage is a preserved animal feed produced by the fermentation of green plants under anaerobic conditions.

2.2 Enhanced AM2 Model Outperforms ADM1 in Simulating Grass Silage Anaerobic Digestion

For grass silage in $MATLAB^{TM}$2015b, the extended version of AM2 was likewise calibrated to ADM1.The parameters for ADM1 were taken from the literature.The model's equations were applied in the same way as they were in the previous studies. The organic loading rate (OLR) and hydraulic retention time (HRT) were taken into consideration as operating parameters; they were 3.58 kg ODM$m^{-3}d^{-1}$ and 33.09 days, respectively.The production of biogas and methane, alkalinity (Z), methanogenic and acidogenic bacteria (X1, X2), organic material (S1), volatile fatty acids (S2), and inorganic carbon (C) are the output variables that needed to be improved.Fmincon, a $MATLAB^{TM}$ optimization function, was employed.

2.3 The Development of a Simulation for Co-Digestion Processes in the Production of Biogas

The AM2 model aims to address challenges in co-digestion systems by providing accurate predictions of biogas production and quality under various conditions. It considers substrate characteristics, pH, temperature, and mixing ratios, while also evaluating the impact of pretreatment on microbial communities. The model employs simulation techniques and different models to simulate co-digestion reactor performance. It offers the potential to optimize co-digestion processes, enhance biogas yield, and achieve stability through operational factor control, contributing to a sustainable and efficient solution.

3. Results and Discussion

3.1 Simulation's Use in Anaerobic Digestion

Anaerobic digestion processes are difficult to comprehend and optimize without the use of simulation. This method offer practical guidance for addressing the technological difficulties associated with anaerobic digestion[68]. Using MATLAB, dynamic models using modified Hill's model may be created to accurately estimate biomethane production for batches as well as continuous processes with varying

substrates and circumstances[69].With a variance of fewer than ±7.6% from values found in the scientific literature, such models have demonstrated great precision as well as durability. The production of biogas can be optimized by using modeling and simulation of anaerobic digestion processes[70].For accurate predictions, sensitivity analysis techniques like Shannon's entropy can help identify parameters that are sensitive in anaerobic digestion models[71].When it comes to lowering overall summary error, automatic parameter optimization in anaerobic digestion models typically performs better than human optimization [72]. For parameter estimation, a sensitivity-based hierarchical as well as sequential individual parameter optimization technique was suggested, which is followed by a correlation-based approach. By using this technique, the total error and computation times are decreased, and fewer parameters need to be fitted to the data[73]. The accuracy and effectiveness of the calibration of the anaerobic digestion model are being improved by sophisticated parameter estimation methods such as particle swarm optimization-based smart algorithms[74].

3.2 AM2 Validation

Using experimental data from two anaerobic digesters running at varied organic loading rates (OLRs), the AM2 model was validated by comparing its predictions of gas output and volatile fatty acid (VFA) concentration.The purpose of the study was to validate the predictive accuracy of the AM2 model with reference to anaerobic digester settings. Though there were a few small variations from the actual numbers, the AM2 model accurately anticipated the system's behavior.When it came to replicating the creation of VFA, researchers found that the model performed rather accurately.It is crucial to remember that the model's accuracy is dependent on a number of variables, including the OLR.The model predicted a rise in methane production in tandem with an increase in OLR.But from days 5 to 11, there was an adaptation phase, during which the methane production rapidly increased to 0.024 m^3d^{-1}.Additionally, the model correctly predicted that methane production in the area of trials 1 and 2, which had measurements of 0.015 m^3d^{-1} and 0.016 m^3d^{-1}, respectively, would drop to 0.018m^3d^{-1}. Nevertheless, in comparison with the experimental findings, the model was unable to correctly forecast the dynamics of VFA concentration.Because of the excess organic matter at high OLRs, the variation is explained. Therefore, even though the AM2 model is a useful resource for comprehending anaerobic digestion, there are situations in which it is not ideal.The AM2 model is a helpful tool for understanding anaerobic digestion, but it should be used with caution, especially when forecasting the concentration of volatile fatty acids, the study concluded after comparing the model's output with the real anaerobic digestion results. See papers[75] [76].

3.3. AM2 application on substrates

3.3.1 maize silage

A study was done on the 37-day digestion of maize silage in a 50-liter anaerobic reactor. In Figure 1a, because of the brief feeding duration, multiple peaks corresponding to the gas generation rate emerge during digestion. Every feeding into the reactor took place every fifteen minutes. The feeding was stopped over the weekend, as evidenced by the observations made on days 5, 13, 20, 27, and 34. Figs. 1b and 1c, respectively, display the results of the biogas as well as the methane production rate and the AM2 simulation. The results show that AM2 does a good job of estimating the generation of biogas (paper[75]).

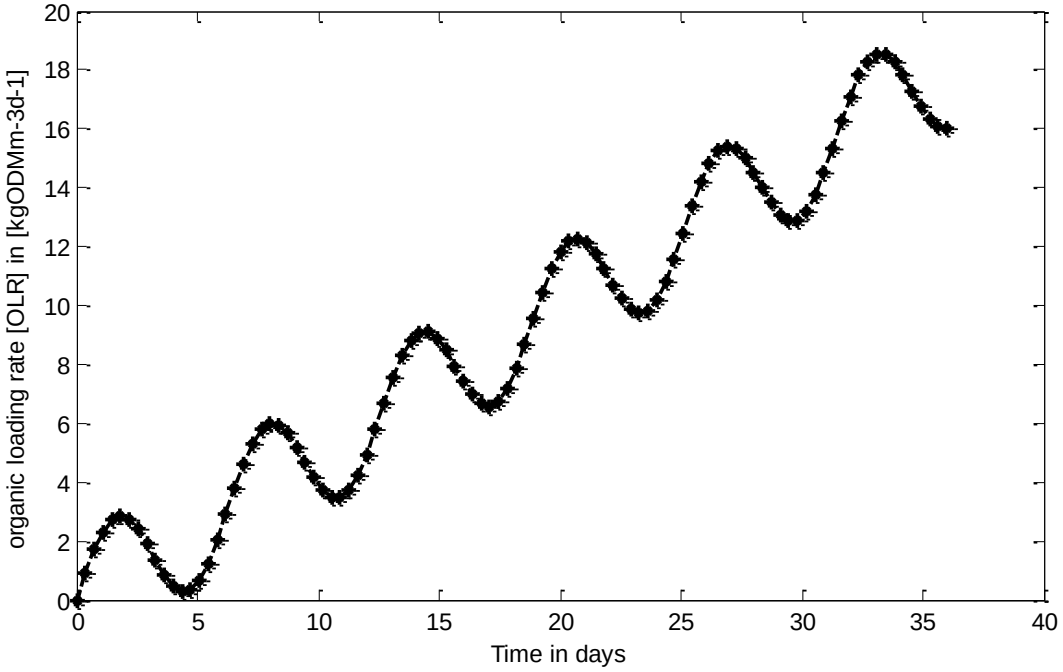

Figure 1. a) In a 50-L scaled anaerobic digestion process, the organic loading rate was observed throughout 36 days with an alternating feedstock load.

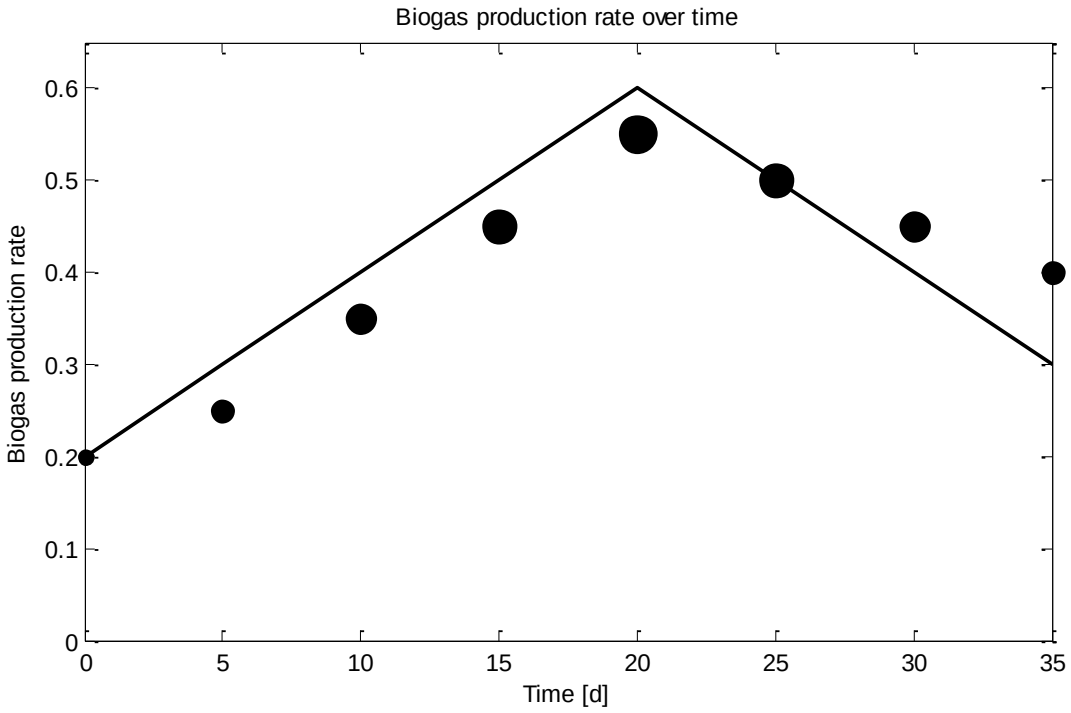

Figure 1.b): Biogas production using online experimental data and AM2 simulation.

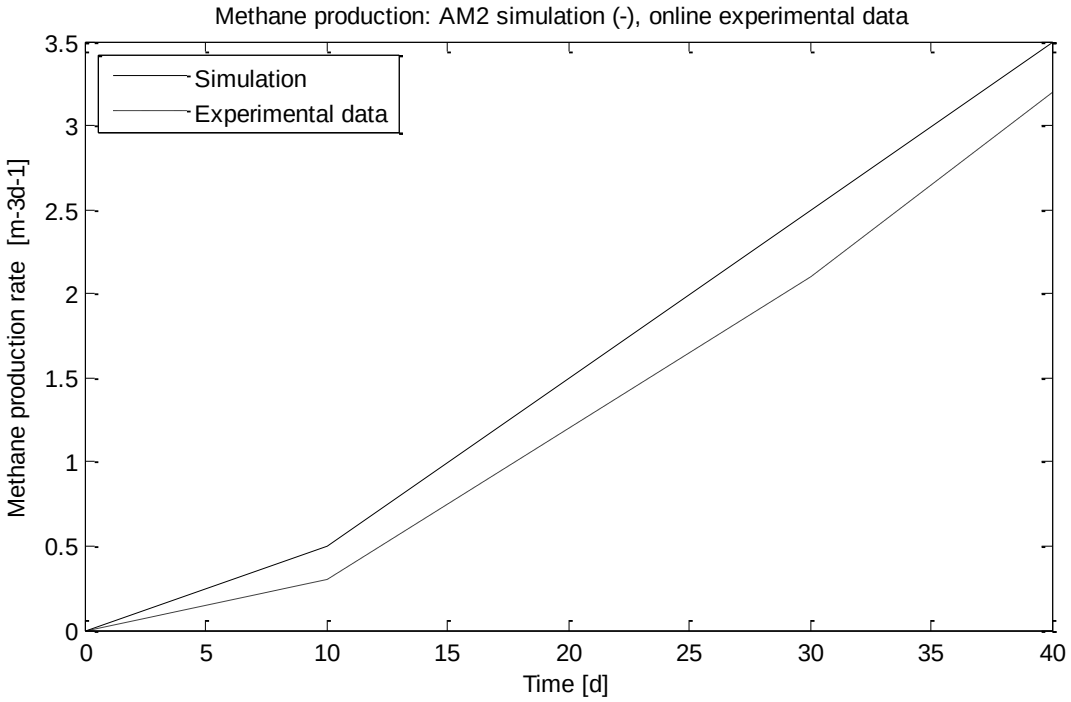

Figure 1.c): Methane generation using online experimental data and AM2 simulation

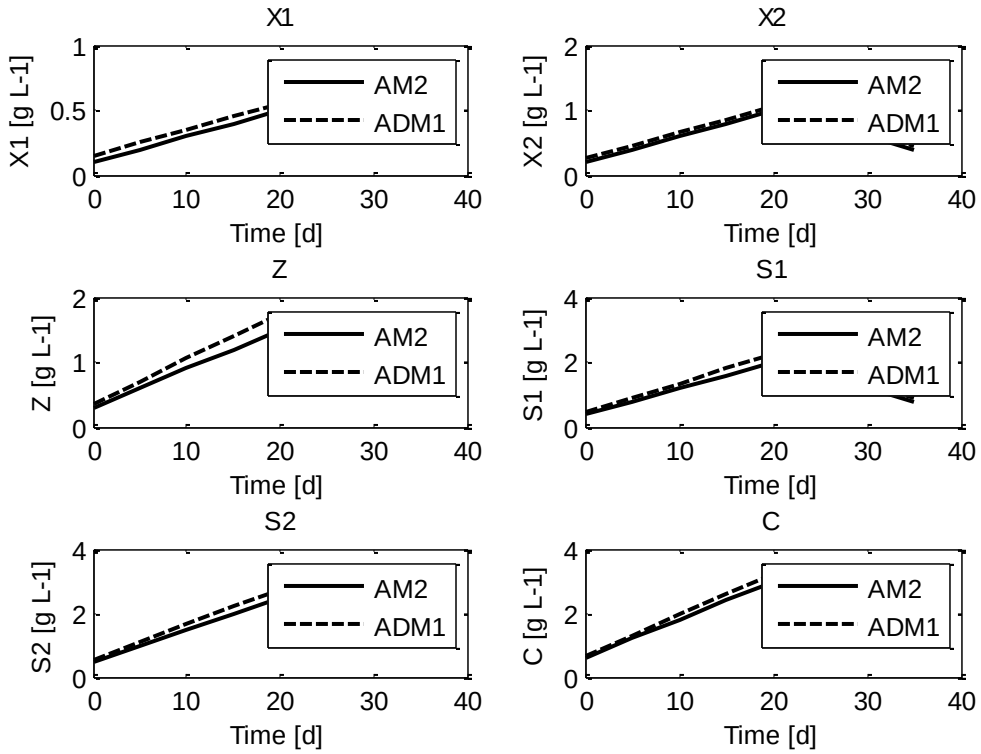

Figure 2. Analyzing the differences between the 36-day simulation of the modified AM2 and ADM1 at varying feedstock loads in a 50-L scaled process of anaerobic digestion.

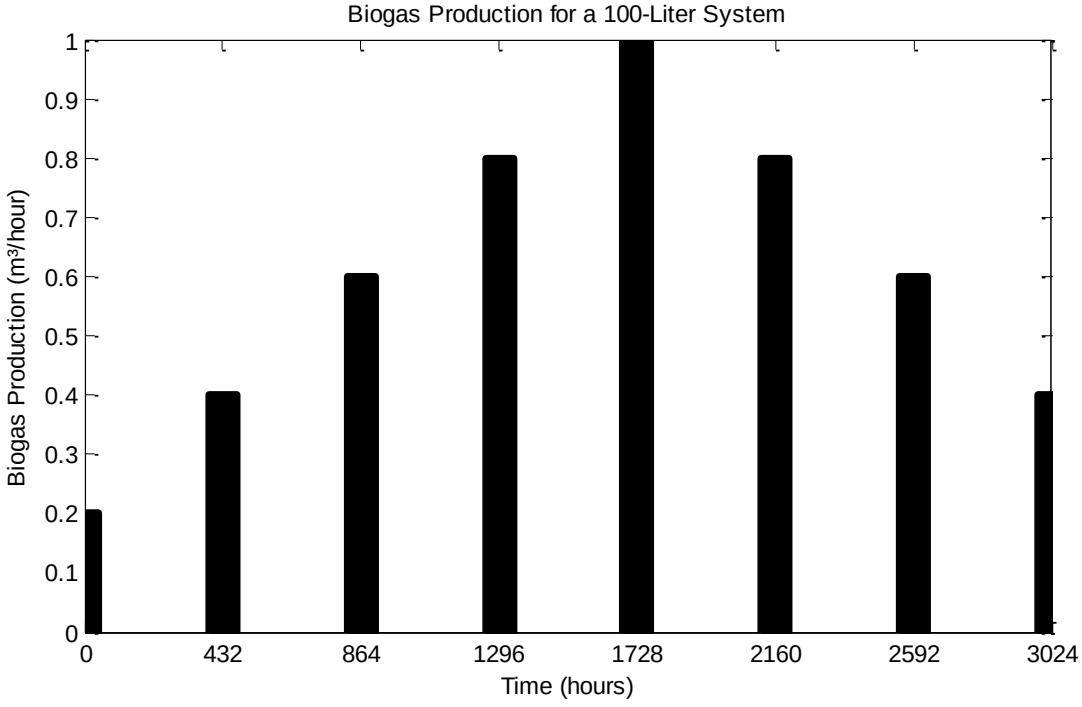

Figure 3) Biogas production rate in a 100-L scaled anaerobic digestion process.

3.3.2 The lumping variables

Lumping variables, grouped elements in a system, simplify research and analysis. They're vital to understanding complex interactions in processes like digestion. In the context of anaerobic digestion, variables like bacteria concentrations and chemical characteristics are considered lumping variables. In AM2, these include X1, X2, Z, S1, S2, and C, representing bacterial concentrations and chemical constituents. AM2 offers a streamlined approach, breaking digestion into steps and highlighting the acidogenic and methanogenic bacteria roles.While the ADM1 model is more detailed, it's complex due to its extensive equations and parameters. AM2's mathematical simplicity aids in simulating waste conversion using equations dependent on bacterial growth and environmental factors. ADM1, in contrast, offers detailed representations but is harder to analyze (paper[75]).

3.3.3 Grass silage

For grass silage in $MATLAB^{TM}$2015b, the extended version of AM2 was likewise calibrated to ADM1. The parameters for ADM1 were taken from Paper[77] .The model's equations were applied in the same way as they were in the paper[75] .The ADM1 simulation was unsteady at first, with inconsistent output profiles for alkalinity and biogas flow. The parameter of the process of disintegration, $K_{hyd}[day^{-1}]$, might be increased to a value of 0.266, as mentioned in the papers[78] [79]. This was discovered after examining the literature.Both profiles demonstrated sufficient stability following alteration, as shown in paper[80] . As a result, an identical value was suggested for the initial parameter of K_{hyd} for the estimation of parameters. After the process was completed, 0.5 was the result.The organic loading rate (OLR) and hydraulic retention time (HRT) were taken into consideration as operating parameters; they were 3.58 kg ODM $m^{-3}d^{-1}$ and 33.09 days, correspondingly.The production of biogas and methane, alkalinity (Z), methanogenic and acidogenic bacteria (X1, X2), organic material (S1), volatile fatty acids (S2), and inorganic carbon (C) are the output variables that needed to be improved. Fmincon, a $MATLAB^{TM}$optimization function, was employed.The ADM1 model output is in good agreement with the AM2 biogas and methane flow rate profiles, as shown in paper[80] .The results of the simulation suggest that the extended AM2 model works better than the ADM1 model to simulate the anaerobic digestion of grass silage.

3.3.4 Cattle manure

The identical process that was described for grass silage was used to estimate the parameters of AM2 on ADM1 for cattle manure.Finding the calibrated parameters that would bring the model variables as well as simulation outputs as close to the process's ADM1 profiles as feasible was the optimization's goal function. The source of the parameters for ADM1 was the paper [77]. The chemical contents of cattle manure were examined in order to determine the influent composition of each of the feedstock's organic fractions. This information is provided in Table 1. Based on the calculation described in the paper [75], the influent composition of the substrate is displayed in figure 4.

Manure is useful for agricultural use because it improves the structure of the soil, microorganisms, pH neutralization, and nutrient availability.Although the cow has gone through four stomachs, cow dung usually still retains a large portion of the nutrients it has consumed. Sometimes the grass, feed, as well as nutrients are just transformed, and as a result of passing through the digestive system, they break down more quickly. In anaerobic digestion, methane output per digester volume can be raised by using crops in the feedstock as opposed to just digesting the manure alone (paper [81]).Cattle manure's anaerobic digestion may be hindered during digestion by ammonia concentrations.After some operating time, ammonia concentrations at specific elevated rates could be maintained to maintain an equilibrium digestion. But as acetate concentration rises, methane is decreased, and volatile fatty acid concentrations rise (paper [82]). Additionally, ammonia toxicity in populations that use hydrogen and acetate has demonstrated a greater susceptibility of the aceticlastic in comparison to the hydrogenotrophic methanogens (paper [82]).

Table 1: Chemical composition of maize silage, grass silage and cow manure

Contents	Maize [%]	GrassValue [%]	Cattle manure Value [%]
Dry matter (DM)	33.4	37.4	9.3
Organic dry matter (ODM)	81.7	89.8	81.7
Water	66.6	62.6	90.7
Crude protein (CP)	2.8	4.0	12.2
Crude fiber (CF)	4.8	8.8	17.8
Crude ash	1.1	3.1	–

Crude lipids (CL)	1.1	0.97	4.3
Neutral detergent fiber (aNDF)	11.2	17.9	–
Sugar as sucrose	3.1	6.8	–
Acid detergent lignin (ADL)	0.55	0.97	–
Acid detergent fiber (ADF)	5.7	10.4	–

The table illustrates that cattle manure contains the highest amount of protein and fiber. It contains a large amount of organic matter, but it also has the highest water content. On the other hand, maize silage has the lowest amount of protein and fiber content. Grass silage contains the highest percentage of dry matter and a higher percentage of protein compared to maize silage, but less than cattle manure.

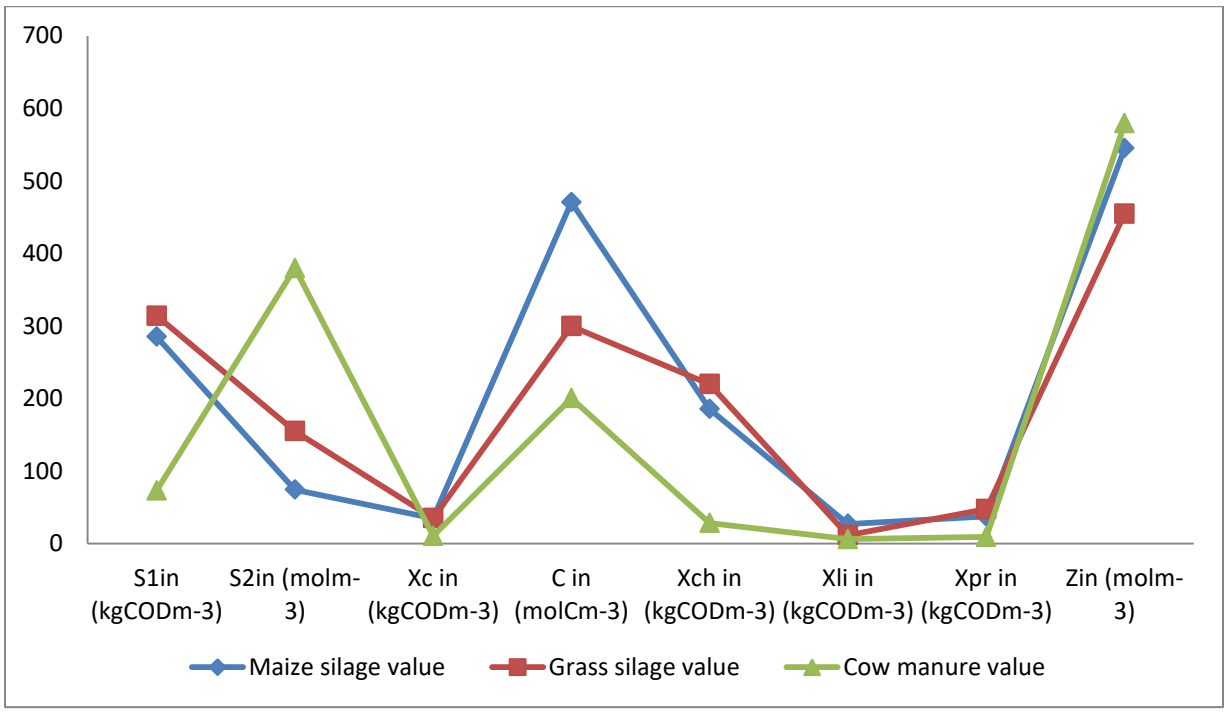

Figure 4. Cow manure, maize silage and grass silage content influence the AM2 simulation.

3.4 Estimating parameters

Table.2 provides the calibrated parameters for manure from cattle, grass silage, and maize silage. The input values used for maize silage in the parameter estimation method were derived from papers [83] [84] [77] .

Table 2: Cattle manure, grass, and maize characteristics calibrated using AM2.

Parameter	Unit	Grass silage	Maize silage	manure
The maximum growth rate of acidogenic bacteria, or μ1max	d^{-1}	0.7	0.6	0.7
The maximum growth rate of methanogenic bacteria,or μ2max	d^{-1}	0.4	0.3	0.4
Inhibition constant, $K_{1,2}$	$molm^{-3}$	991.3	998.2	250.0
Coefficient of volumetric gas-liquid mass transfer,or K_{La}	d^{-1}	22.1	22.0	80.4
Constant of half-saturation,or K_{S1}	kgm^{-3}	1.3	3.5	9.0
Constant of half-saturation, or K_{S2}	$molm^{-3}$	34.4	34.5	33.7
Degradation yield of the substrate, or k1	[-]	24.0	25.5	26.0
Generation yield of VFA, or k2	$molkg^{-1}$	220.7	309.7	226.6
Consumption yield of VFA, or k3	$molkg^{-1}$	874.0	1074.0	637.6
Generation yield of CO2, or k4	$molkg^{-1}$	90.0	90.0	34.9
Generation yield of CO2, or k5	$molkg^{-1}$	200.0	200.0	24.8
Generation yield of CH4, or k6	$molkg^{-1}$	488.2	575.0	155.0
Bacterial fraction in the liquid phase, or α	[-]	1.0	1.0	1.0
Ficara's extension's parameters				
The amount of nitrogen in the biomass,or Nbac	$molkg^{-1}$	9.0	11.0	34.4
The amount of nitrogen in the substrate,or Ns1	$molkg^{-1}$	$1.9X10^{-2}$	$1X10^{-4}$	$2.4X10^{-2}$
Biomass degradation rates, X1 and X2, k_{d1} and k_{d2}	d^{-1}	4.4%μ1max 4.4%μ2max	5.3% μ1max 5.3% μ2max	7.9%μ1max 15 %μ2max
parameters, the process of hydrolysis				
Hydrolyzing carbohydrates, $k_{hyd,ch}$	d^{-1}	10	10	10
Hydrolyzing lipids, $k_{hyd,li}$	d^{-1}	10	10	10

Hydrolyzing proteins, $k_{hyd,pr}$	d^{-1}	10	10	10
Disintegration, k_{dis}	d^{-1}	0.5	0.5	0.2
Rate of biomass degradation X1 and X2 $k_{dec,x1}$ and $k_{dec,x2}$	d^{-1}	0.033	0.032	0.032
Disintegration yield coefficient of the substrate,or k7	[-]	12.7	12.7	25.0
Disintegration yield coefficient of the carbohydrates,or k8	[-]	0.01	0.01	0.01
Disintegration yield coefficient of the proteins, or k9	[-]	0.03	0.01	0.01
Disintegration yield coefficient of the lipids, or k10	[-]	0.01	0.01	0.01

3.5 Sensitivity Analysis

Sensitivity analysis is a statistical technique or method that's used to assess how much a given parameter or set of variables influences a mathematical model's output.It's a means of researching how variations in model parameters impact its output.It indicates which parameters are highly relevant and have a big influence on the anaerobic digestion result, and which ones don't really matter that much.As a result, this analysis can assist in refining the model and lowering the quantity of estimations needed.To ascertain which parameters are important and to what degree, the values of each parameter are changed one at a time.Every time, the final result is tracked to observe any changes. The parameter is sensitive if there are significant changes in the outcome. The parameter is insensitive if there is little variation in the outcome. All parameters go through this process again, and the outcomes are then compared.

In AM2's extended version, 24 parameters were subjected to a sensitivity analysis in order to determine which ones affected the model's output. In Figure 5, the prescribed procedure for parameter analysis is displayed.It is evident that the following primary parameters have a considerable impact on the model results:K_1, K_4, K_7, K_8, μ_{1max},μ_{2max} ,K_{S1} , K_{S2}, K_{1_2}, K_{d1} , K_{d2}, $K_{hyd,ch}$, $K_{hyd,pr}$, $K_{hyd,li}$,f_{ch,x_c} ,f_{pr,x_c} , f_{li,x_c} .

-However, the levels of sensitivity for parameters K_3, K_6 as well as $K_{dec,x1}$ remain lower.

-Lastly, it has been shown that the parameters K_2, K_5 as well as K_{dis} are the least responsive to the model (refer to Figure 5).

-The original AM2 is the source of several highly sensitive parameters, including K_1,K_4 ,K_{S1} ,K_{S2} and K_{1_2} which are associated with substrate degradation, CO2 yield, as well as half-saturation constants, respectively.Their correlation with the model's equations for organic substrate, volatile fatty acids, and organic carbon is significant. The hydrolysis process's parameters K_8, $K_{hyd,ch}$, $K_{hy,pr}$, $K_{hyd,li}$, f_{ch,x_c}, f_{pr,x_c} , f_{li,x_c} and $K_{dec,x2}$ exhibit a strong correlation with the organic matter. The decay rates of biomass, $K_{d1}$and K_{d2}, are the crucial parameters of the extension that determine the alkalinity.

Figure 5 demonstrates that the amount of fermentation gas generated is less affected by factors with smaller normal variation, or those that are near 0 on the graph. On the other hand, values that are closer to 0.25 on the graph and have a higher normal variation have a bigger effect on the amount of fermentation gas generated. This implies that, generally speaking, characteristics with smaller normal fluctuations have less significance in estimating the volume of fermentation gas generated. By eliminating parameters with less normal variation, the extended AM2 model's accuracy can be raised with the help of this data.

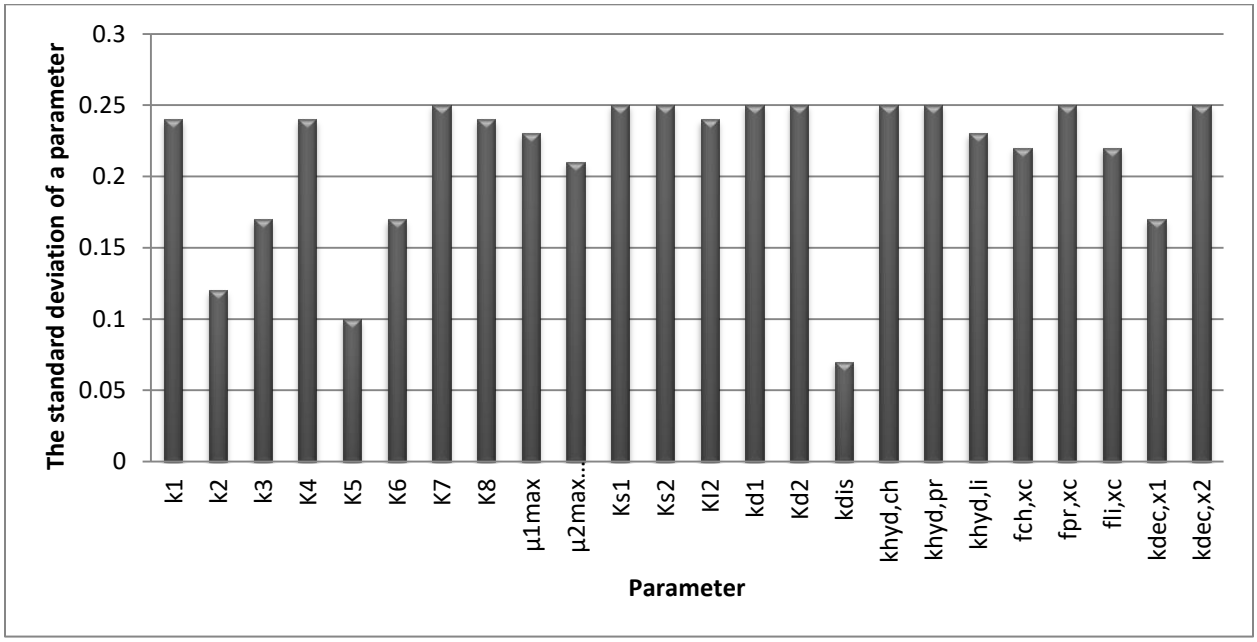

Figure 5. Sensitivity study of the enlarged AM2's 24 parameters. The normal parameter variance ranges from 0 to 0.25. (paper [75])

3.6 Am2 Extensions

There were additions made to the original AM2 model in order to increase the model's applicability and performance simulation accuracy. These additions were made

in light of the findings from the sensitivity study and the AM2 vs. ADM1 comparison.At first, the AM2 model was unable to account for all of the ADM1 model's combined factors. This constraint was addressed by adding additional elements to the AM2 model, as described in the paper [85], and was applied especially to silage made from maize. The model's outputs were then contrasted with the ADM1 model's, encompassing biogas generation, methane levels, as well as its internal elements.

Results show that, according to the results reported by Arzate et al.[75] , biogas generation in AM2 generally responded more slowly to the addition of feedstock than in ADM1. In addition, because the model lacked precise hydrolysis-related equations, it tended to overstate the presence of organic material. However, according to the results reported by Arzate et al.[75] shows, important variables such as biomass, VFA (volatile fatty acids), alkalinity, as well as inorganic carbon agreed well with the ADM1 model's trends. One important finding of these studies is the precise incorporation of inorganic nitrogen into organic matter by taking alkalinity into account.

3.6.1 Biomass Extension

Recent studies on maize silage have utilized the original AM2 model[83] to simulate the flow rates of methane and biogas production. To optimize state variables and accurately predict biomasses (x1, X2), organic substrate (S1), volatile fatty acids (S2), inorganic carbon (C), and alkalinity (Z), adjustments are necessary to the model. Modifications were therefore made to the fundamental framework of the model to improve its capabilities[86] [87].The AM2 model was modified to account for nitrogen and alkalinity in a biogas process. The model uses differential equations (1, 2) to simulate the dynamics of two types of bacteria.

$$\frac{dX1}{dt} = (\mu_1 - \alpha D_{in} - k_{d1})x1 \quad (1)$$

$$\frac{dX2}{dt} = (\mu_2 - \alpha D_{in} - k_{d2})x2 \quad (2)$$

A new method for calculating alkalinity in anaerobic digestion processes was developed. This was achieved by creating a new equation, Equation 3, which is an extension of the AM2 model.It takes into account a variety of factors, including nitrogen content in biomass and substrate,as well as dilution rate, bacterial growth rates, and decay rates[88].

$$\frac{dz}{dt} = D_{in}(Z_{in} - Z) + [(K_1 N_{S1} - N_{bac})\mu_1 X1] - N_{bac}\mu_2 X2 + (k_{d1} N_{bac}\mu_{1max} X1)$$

$$+ (k_{d2} N_{bac}\mu_{2max} X2) \quad (3)$$

Equations 1 and 2 in the context of the Advanced Microbial Model AM2 describe the growth and decay dynamics of acidogenic and methanogenic bacteria involved in anaerobic digestion processes. These equations provide insights into understanding the behavior of biomass concentrations (X1 for acidogenic bacteria and X2 for methanogenic bacteria) over time. Regarding the choice of time span in equations 1 and 2, there isn't a rigid limitation on the length of the time interval. Instead, researchers should select a suitable timeframe that adequately captures the essential features of the targeted biogas process. For instance, if investigating short-term phenomena such as start-up or shock loading events, shorter time intervals might suffice. Conversely, long-term trends, such as those related to nutrient cycling or seasonal variations, require longer time spans.

The range of possible values for X1 and X2 varies substantially depending on the type and conditions of the biogas process being examined. In small-scale laboratory reactors, where precise control over operating conditions is achievable, typical biomass concentrations lie within the range of a few grams per liter (g/L) to tens of grams per liter (for example, 5–50 g/L). On the contrary, industrial-scale digesters operate under harsher conditions and generally exhibit higher biomass concentrations, sometimes exceeding several hundred grams per liter.

The rate of change of biomass concentration for acidogenic microorganisms, denoted as dX1/dt in equation 1, depends on the unique properties of the biogas process being analyzed. In a well-performing anaerobic digestion system, the rate of change exhibits a quick rise during the acclimation phase, eventually settling down to a constant value known as the steady state. Typical steady-state values for dX1/dt range between -0.01 g/L/day and +0.01 g/L/day. However, when dealing with transient situations, such as alterations in feedstock composition, the rate of change may display considerable variability.The rate of change of biomass concentration for methanogenic microorganisms, indicated as dX2/dt in equation 2, follows similar patterns as described above for acidogenic microorganisms. A well-functioning anaerobic digestion process displays an initial surge in the rate of change during the acclimation stage, subsequently reaching a consistent value around the steady state. Steady-state values for dX2/dt also remain within the same order of magnitude (-0.01 g/L/day to +0.01 g/L/day). When confronted with transient scenarios, such as shifts in feedstock composition, the rate of change may demonstrate noticeably greater fluctuations.

The decay rate terms, represented as k_d*X1 and k_d*X2 in equations 1 and 2, respectively, account for the natural decay or degradation of biomass over time for acidogenic and methanogenic microorganizations in a biogas process. The specific range for these variables can vary depending on factors such as experimental setup, system

characteristics, and operational parameters. It is recommended to consider experimental data, literature references, and constraints specific to the biogas process when determining the allowable range for these terms.

The variables in equation 3, which models the alkalinity dynamics in a bioreactor system, can also affect an anaerobic digestion system.Alkalinity (Z) represents the concentration or amount of substances that can neutralize acids in the system. The rate of change of alkalinity over time (dz/dt) is influenced by several factors, including the influent flow rate of substrate (Din), influent alkalinity (Zin), and the nitrogen content (N_{S1}) of the biomass or microorganisms (N_{bac}) present in the system. Bacterial growth, particularly of acidogenic bacteria and methanogenic bacteria, also plays a significant role in affecting alkalinity dynamics.The growth rates ($\mu_1 X_1$and $\mu_2 X_2$) for these bacteria are described by specific equations. Additionally, there are terms that consider the maximum growth rates ($k_{d1} N_{bac} \mu_{1max}$X1 and $k_{d2} N_{bac} \mu_{2max}$X2) and how they impact changes in alkalinity based on nitrogen content.

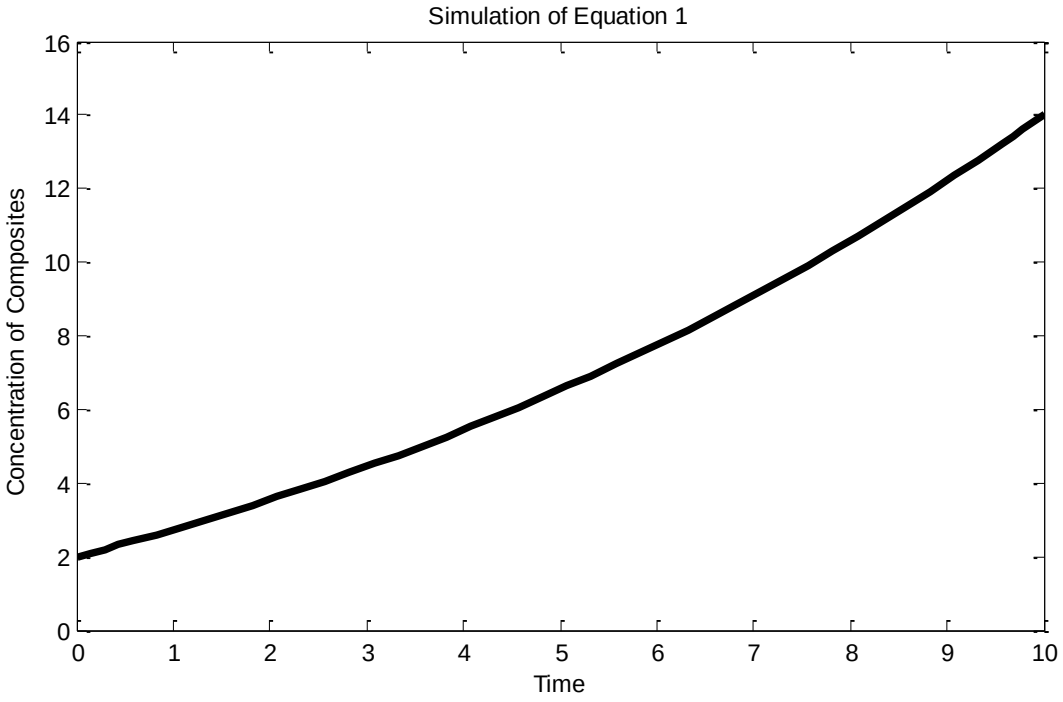

Figure 6: Simulation of Equation 1:The Effect of Nutrient Concentration on Biomass Growth (Increase the concentration of composites linearly with time in seconds according to the simulation of equation 1)

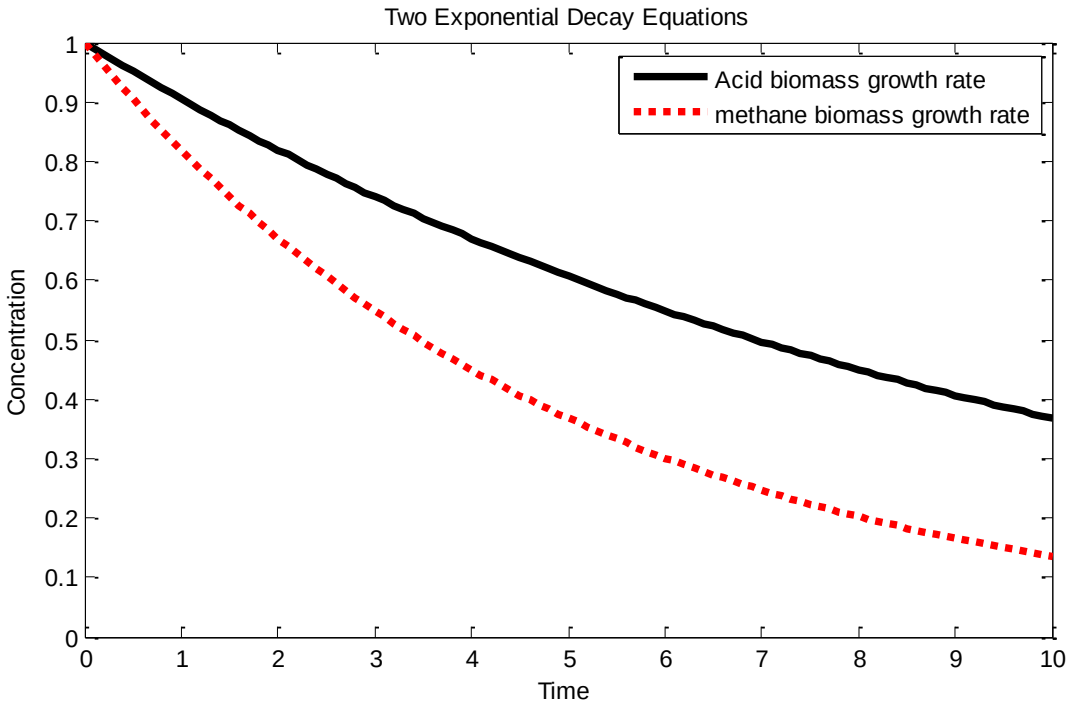

Figure 7: Effect of nutrient concentration on acid and methane biomass growth rates and exponential decay of acid and methane biomass over time(s)

-For stable biomasses with slow decay rates over time, k may be small (e.g., between 0.001 and 0.01 per day).

-When k1=0.01 per day. and k2 = 0.02 per day. The results will be as follows in Figure 9

-When k1=0.001 per day. and k2 = 0.002 per day. The results will be as follows in Figure10

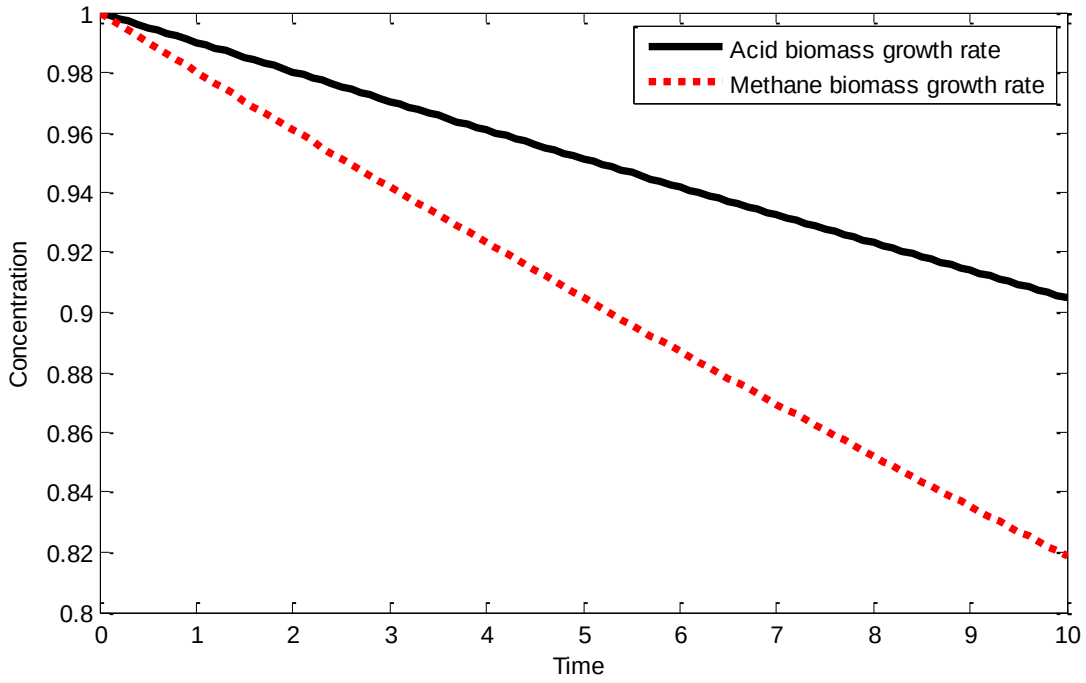

Figure 8 shows that k may be minimal (k1 = 0.01 and k2 = 0.02) per day when stable biomass with slow degradation rates over time is present.

For more labile biomasses with faster degradation rates, k may be larger (e.g., between 0.05 and 0.5 per day).

-When k1=0.005 per day. and k2 = 0.006 per day. The results will be as follows in Figure11

-When k1=0.5 per day. and k2 = 0.6 per day. The results will be as follows in Figure12

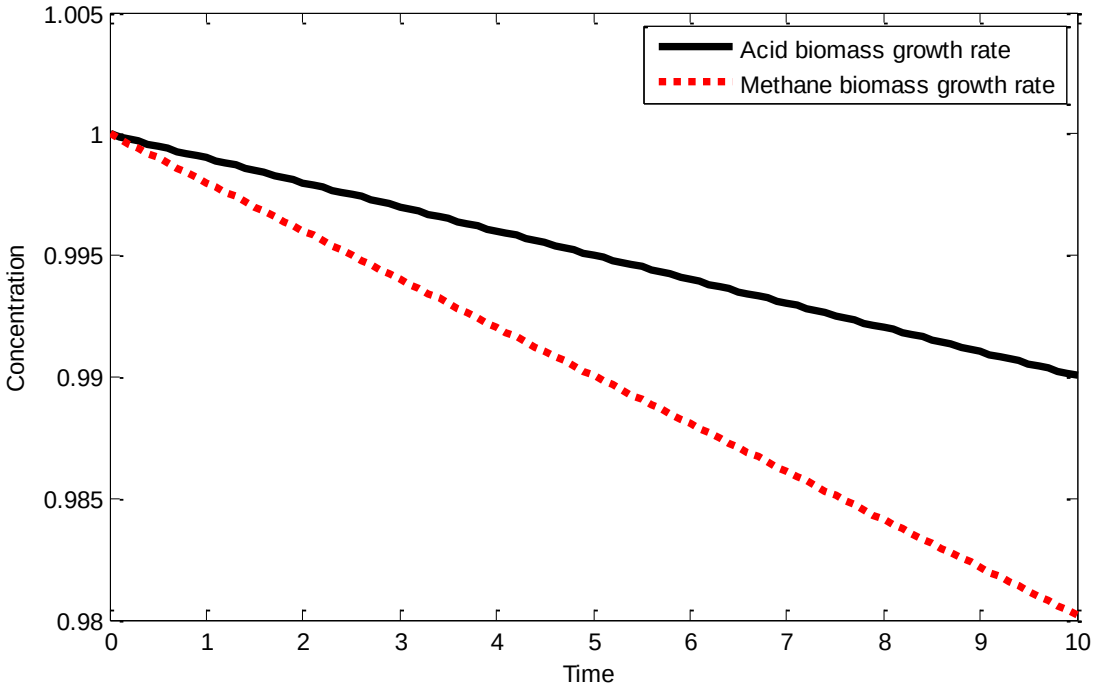

Figure 9 shows that k may be minimal (k1 = 0.001 and k2 = 0.002) per day when stable biomass with slow degradation rates over time is present.

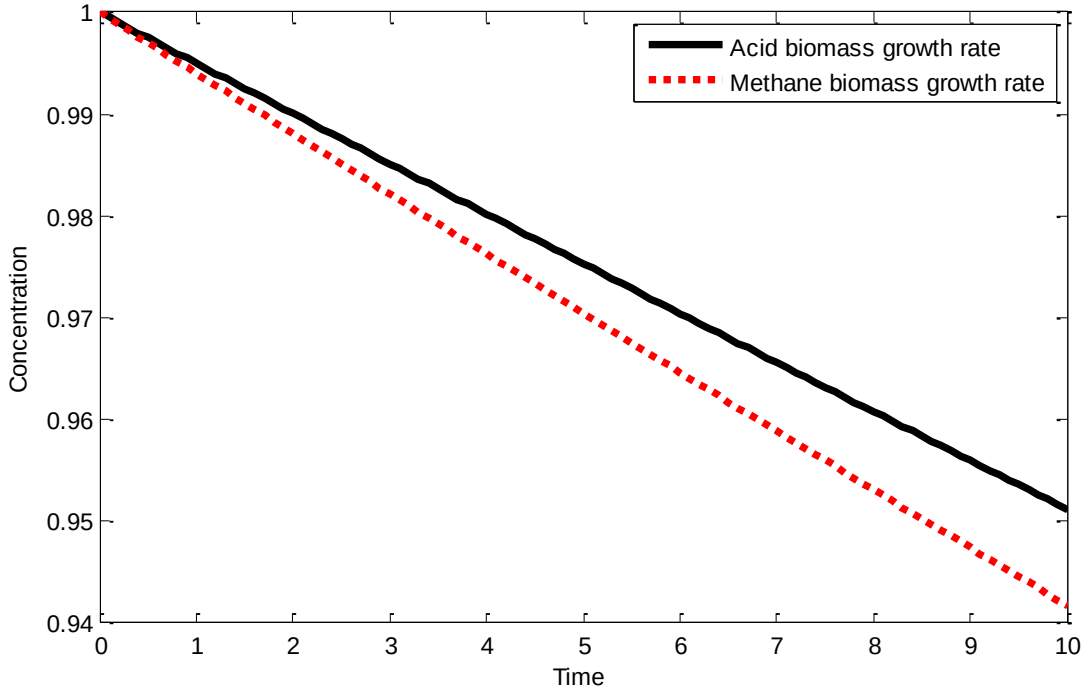

Figure 10 shows that k may be more labile biomass (k1 = 0.005 and k2 = 0.006) per day when lable biomass with more degradation rates over time is present.

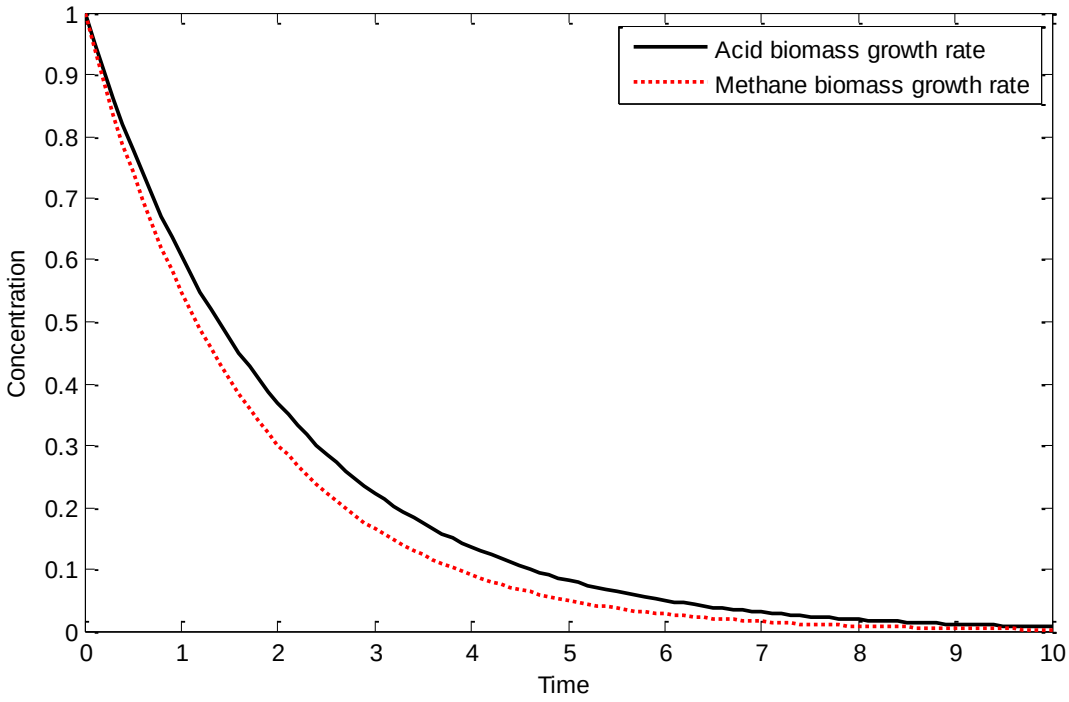

Figure11 shows that k may be more labile biomass (k1 = 0.5 and k2 = 0.6) per day when lable biomass with more degradation rates over time is present.

3.6.2 Hydrolysis Extension

The hydrolysis extension was added to the AM2 model (paper[75]). During substrate degradation, composites, carbohydrates, proteins, and lipids are broken down into smaller components—a process known as hydrolysis. Additionally, some equations were added to illustrate how the rate of hydrolysis varies over time based on variables such as the energy available, the amount of water present, and the speed at which the waste is mixed. This work contains equations that represent the rate of change of these components over time, taking into account variables like yield coefficients, hydrolysis, and disintegration. The hydrolysis stage is characterized by Eq. 4 and involves the partial disintegration of degradable particulate organic substrates or composites, Xc, into carbohydrates (Xch), proteins (Xpr), and lipids (Xli) (paper[89]). Eqs. 5, 6, and 7 define the hydrolysis of Xch, Xpr, as well as Xli.

$$\frac{dX_C}{dt} = - K_{dis}X_C + D_{in}(X_{C_{in}} - X_C) + K_{dec,x_1}X_1 + K_{dec,x_2}X_2 \qquad (4)$$

$$\frac{dX_{ch}}{dt} = - K_{hyd,ch}X_{ch} + D_{in}(X_{ch_{in}} - X_{ch}) + f_{ch,x_c}K_{dis}X_C \quad (5)$$

$$\frac{dX_{pr}}{dt} = -K_{hyd,pr}X_{pr} + D_{in}(X_{pr_{in}} - X_{pr}) + f_{pr,x_c}K_{dis}X_C \quad (6)$$

$$\frac{dX_{li}}{dt} = - K_{hyd,li}X_{li} + D_{in}(X_{li_{in}} - X_{li}) + f_{li,x_c}K_{dis}X_C \quad (7)$$

Equation 4 describes an extension for high organic loading rates in the AM2 model, which is used to simulate the acidification of anaerobic digestion processes. The equation incorporates a term related to the yield-coefficient of substrate disintegration and the yield-coefficient of carbohydrates, proteins, and lipids. This extension is incorporated into the AM2 model from previous work by Ficara et al. [87] and is specifically applied when high organic loading rates, up to 5.0, are present during the process. This extension is crucial for accurately simulating the behavior of the anaerobic digestion process under high organic loading rates, providing a more comprehensive and accurate representation of the system dynamics.Equation 4 outlines the rate of change in the composite's concentration (dXc/dt) over time.Variables involved include the current composite concentration (Xc), the disintegration rate constant for composites (K_{dis}), the initial input concentration of composites in the substrate ($D_{in}X_{C_{in}}$) and decay rate constant for X1 component and its interaction with X1

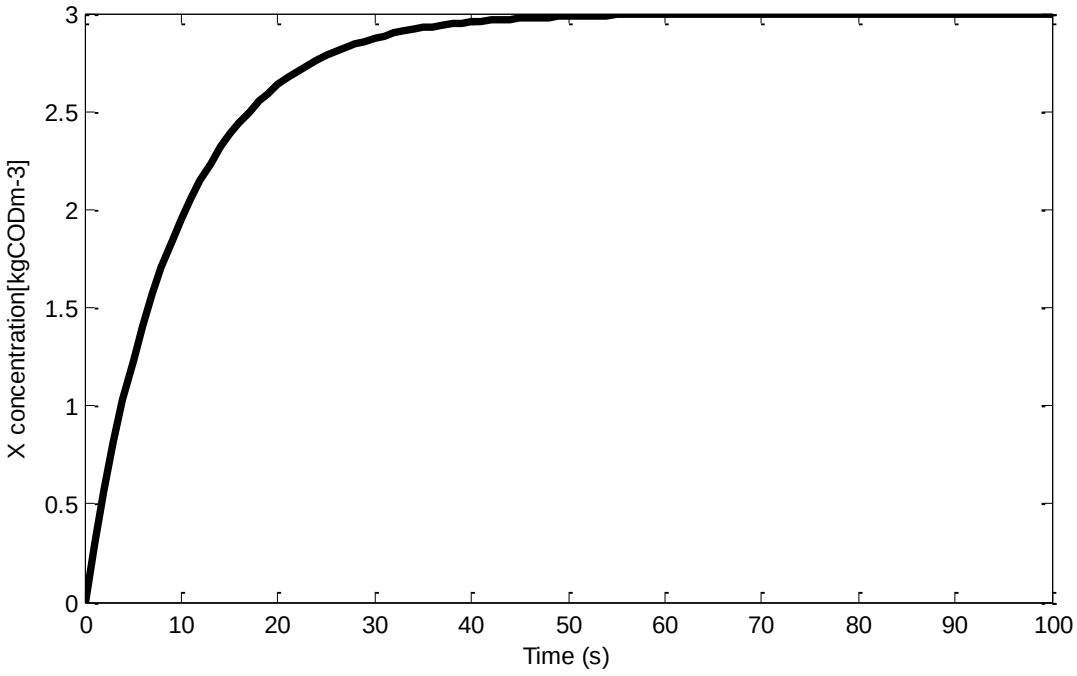

Figure 12: The Effect of Time on X Concentration in a Hydrolysis

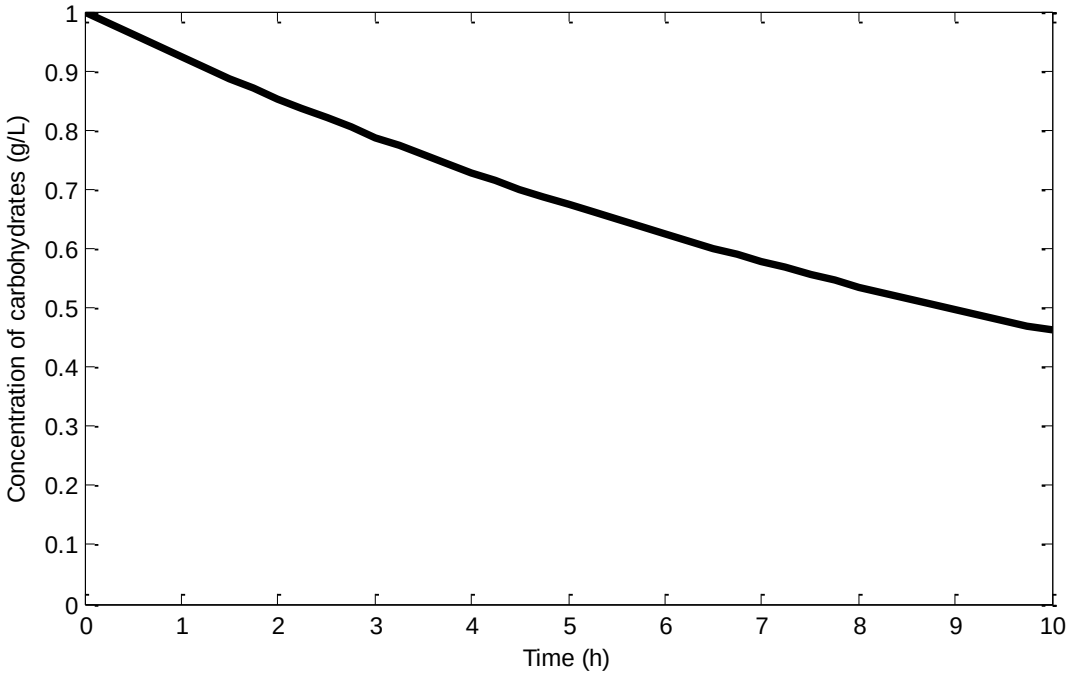

Figure 13: The Effect of Time on the Concentration of Carbohydrates in a Hydrolysis

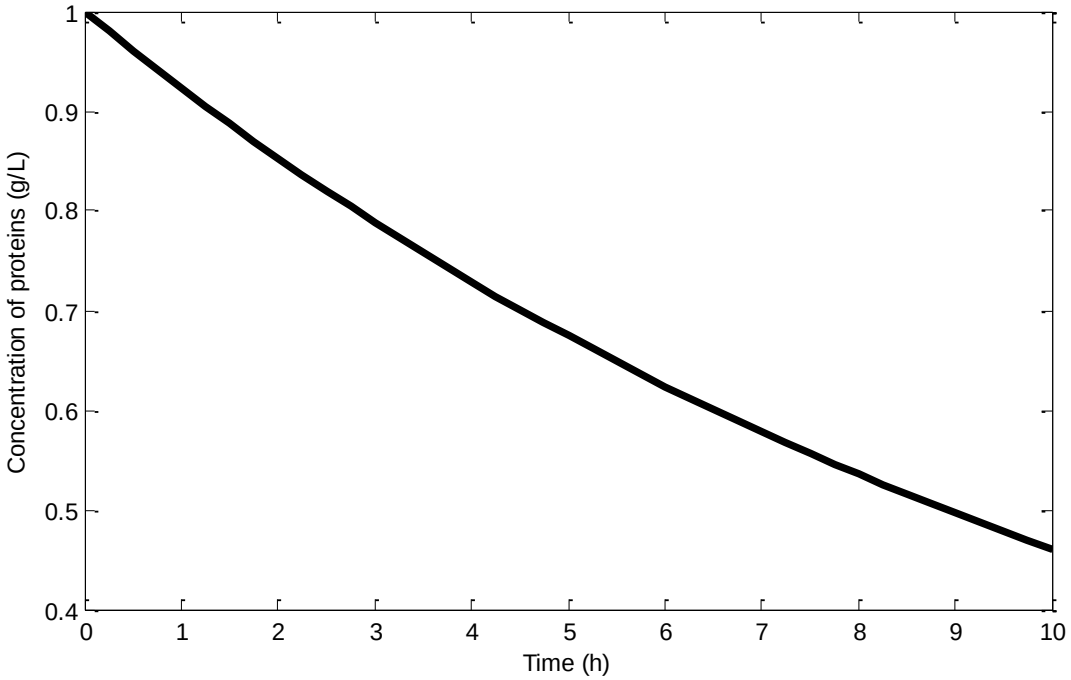

Figure 14: The Effect of Time on the Concentration of Proteins in a Hydrolysis

Equations (5), (6), and (7) represent the hydrolysis of carbohydrates, proteins, and lipids, respectively, into volatile fatty acids (VFAs) during anaerobic digestion. All equations consider degradation rate, pH, and temperature as influencing factors.

4.Conclusions

The extended AM2 model developed in this study provides a more accurate and detailed description of the anaerobic digestion process compared to the original model.Experimental data from two anaerobic digesters operating at organic load rates are used in a variety of ways to better accept the model.The biogas generation rate and methane content were precisely anticipated by the model; however, the dynamics of the volatile fatty acid (VFA) concentration were not well predicted. This occurred especially at high organic loading rates (OLRs) due to the presence of excess organic matter.There are multiple reasons why the AM2 model cannot precisely predict the dynamics of VFA concentration.Firstly, there are complicated metabolic pathways as well as microbial interactions that are involved in the creation and consumption of VFA.Secondly, there are differences in the composition of the substrates, data collection and monitoring, and environmental elements (such as pH and temperature) that impact microbial activity and the production of volatile fatty acids.Thirdly, the intricate relationships and feedback cycles between these variables are difficult for the model to accurately represent. Furthermore, it can be difficult to make precise projections because of the variety in the composition and quality of organic waste.To increase the precision of VFA production forecasts, these factors should be taken into account and investigated further.This explains that the AM2 model is a helpful tool in understanding anaerobic digestion but should be used with caution, especially when predicting VFA concentrations. Improving knowledge of microbial populations and their interactions in VFA generation and consumption, as well as identifying the critical variables influencing VFA dynamics, are necessary to improve the prediction of VFA concentration during anaerobic digestion. Furthermore, to accurately record the dynamics of VFA generation and consumption, complete models incorporating microbial dynamics, environmental parameters, and substrate features should be constructed and integrated with real-time monitoring. Also, advanced analytical techniques for continuous VFA concentration measurement plus model calibration should be investigated, and experimental research should be carried out to collect data on VFA concentration dynamics according to various conditions. Sensitivity analysis showed that the model output is highly sensitive to associated parameters such as substrate degradation, CO2 yield, and half-saturation constants. These parameters were further improved by adding additional factors such as nitrogen concentration and alkalinity, resulting in better agreement with the ADM1 model in terms

of biogas production, methane concentration, and content. Overall, the extended AM2 model provides a valuable tool for modeling and optimizing biogas production from various feedstocks. Maize, grass silage, and animal manure substrates were studied in this study.

Symbols used

K_1 [-]	yield for substrate degradation	K_{1_2} [molm^{-3}]	inhibition constant
K_2 [molkg^{-1}]	yield for VFA generation	K_{d1} [d^{-1}]	decay rate of biomass X1
K_3[molkg^{-1}]	yield for VFA consumption	K_{d2} [d^{-1}]	decay rate of biomass X2
K_4[molkg^{-1}]	yield for CO2 production	K_{dis} [d^{-1}]	parameter for disintegration process
K_5[molkg^{-1}]	yield for CO2 production	$K_{hyd,ch}$[d^{-1}]	parameter for hydrolysis carbohydrates
K_6[molkg^{-1}]	yield for CH4 production	$K_{hyd,pr}$[d^{-1}]	parameter for hydrolysis proteins
K_7 [-]	yield for substrate disintegration	$K_{hyd,li}$[d^{-1}]	parameter for hydrolysis lipids
K_8 [-]	yield for carbohydrates, proteins and lipids	f_{ch,x_c} [kgCODkgCOD^{-1}]	yield of carbohydrates on composites
μ_{1max}	Max growth rate of acidogenic bacteria	f_{pr,x_c} [kgCODkgCOD^{-1}]	yield of proteins on composites
μ_{2max}	Max growth rate of methanogenic bacteria	f_{li,x_c} [kgCODkgCOD^{-1}]	yield of lipids on composites
K_{S1} [kgm^{-3}]	half-saturation constant	$K_{dec,x1}$[d^{-1}]	decay rate of acetogenic bacteria X1
K_{S2} [molm^{-3}]	half-saturation constant	$K_{dec,x2}$[d^{-1}]	decay rate of methanogenic bacteria X2
ADM1	Anaerobic digestion model No. 1	AM2	Anaerobic digestion model two steps
X1 [kgCODm^{-3}]	Concentration of acidogenic bacteria	X2 [kgCODm^{-3}]	Concentracion of methanogenic bacteria

dX1/dt	rate of change of biomass concentration for acidogenic bacteria	dX2/dt	rate of change of biomass concentration for methanogenic bacteria
μ_1 $[d^{-1}]$	growth rate of acidogenic bacteria	t	Time
μ_2 $[d^{-1}]$	growth rate of methanogenic bacteria	N_{S1}[mol kg^{-1}]	nitrogen content of substrate S1
α [-]	fraction of bacteria in the liquid phase	N_{bac} [mol kg^{-1}]	nitrogen content in the biomass
D_{in} $[d^{-1}]$	dilution rate	in	Influent
X_C[kgCODm^{-3}]	particulate composite	dXc/dt	The rate of change of the concentration of composites over time.
X_{ch}[kgCODm^{-3}]	particulate component of carbohydrates	$K_{hyd,ch}$ $[d^{-1}]$	parameter for hydrolysis carbohydrates
X_{pr}[kgCODm^{-3}]	particulate component of proteins	$K_{hyd,pr}$ $[d^{-1}]$	parameter for hydrolysis proteins
X_{li}[kgCODm^{-3}]	particulate component of lipids	$K_{hyd,li}$ $[d^{-1}]$	parameter for hydrolysis lipids
Z [mol m^{-3})]	Total alkalinity	S1[kgCODm^{-3}]	Organic substrate concentration
Z_{in} [mol m^{-3}]	influent value for alkalinity	S2[molem^{-3}]	Volatile fatty acids concentration
C [mol C m^{-3}]	Total inorganic carbon concentration	$S1_{in}$[kgCODm^{-3}]	influent value for organic substrate
C_{in} [mol C m^{-3}]	influent value for total inorganic carbon	$S2_{in}$[molm^{-3}]	influent value for volatile fatty acids

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