Improvements to the ADM1 based Process Simulation Model: Reaction segregation, parameter estimation and process optimization

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**Highlights**

- A robust process simulation model is constructed to simulate anaerobic digestion.
- The ADM1 model is the basis for kinetic reactions with associated inhibitions.
- Reaction parameters are optimized to fit literature and model results.
- pH, inhibition, and pre-exponential reaction factors differ from literature.
- Preliminary sensitivity analysis and process optimization are realized.

**Graphical Abstract**

**Abstract**

Anaerobic digestion is a sustainable organic waste treatment technique with energy recovery via biogas generation. This work presents a novel Aspen Plus ADM1-based flowsheet for this process. Three reactor segments were chosen: stoichiometric for the hydrolysis step, kinetic for acido-aceto-methanogenesis, and equilibrium for hydrogenotrophic methane production. Selected parameters- conversion ratios, kinetic pre-exponent and inhibitor factors- were controlled to best fit model and experimental results. The parity plot fitting had an $R^2 = 0.999$, a slope of 1.0058 and an intercept of $-0.8651$. Obtained parameter values stressed the importance of inhibitions, and simulation results showcased the bell-shaped curve for acetic and volatile fatty acid reduction. The model was used for a subsequent sensitivity analysis as well as an optimization runs, leading to a 50% higher methane production ratio. The proposed model presents itself as a significant contribution for optimal anaerobic digestion process design.

**Keywords:** Anaerobic digestion, Process modeling, Anaerobic Digestion Model 1, Aspen Plus, Process optimization, Parameter fitting

**1. Introduction**

Organic waste constitutes an important outcome of human activity, totaling 30% of waste with a 0.8% yearly increase. Traditional landfilling, predominant in developing countries [1], contrasts with the circular economy’s reduce, reuse, recycle, and add value philosophy. Raw organic waste has limited reuse/recycling possibilities, but it has significant energy potential [2]. Multiple value-additive methods exist: incineration, composting, pyrolysis, gasification, and anaerobic digestion (AD) [3]. AD stands out with its added energetic value, through biogas production, its operational efficiency and its competitive cost versus benefit ratio [3].

AD process yield is affected by feedstock characteristics like particle size, composition and total solids content [4], operating conditions like...
temperature, and pH [5], reactor design like volume, residence time and organic loading rate [6], and potential inhibitors such as ammonia, Volatile Fatty Acids (VFA), and long chain fatty acids (LCFA) [7]. Process modifications include co-digestion with two or more different substrates, bioreactor upgrade, inclusion of additives, and pretreatment [8]. The latter method, with multiple possible techniques: biological (by enzymes and fungi), chemical (acidic, alkaline), mechanical (ultrasound, liquid shearing, milling) and thermal, has the potential to significantly improve AD process yields.

Within this ongoing effort, modeling and simulation tools are valuable for process understanding and improvement [9], and constitute the core of this contribution. This introductory section recalls the development of such models and fits the present work within the global effort.

Different software programs were employed to implement AD modeling such as Aquasim®, MATLAB™, Simba# and process simulators [10]. The latter provide the advantage of possible sensitivity analysis, process optimization and economic analysis, with Aspen Plus regarded as a prominent software [11]. The use of process simulators is thus at the heart of this work.

Simpler models employed stoichiometric fixed time-independent conversion reactors [12], via a one-step waste to biogas reaction [13] or with reactors for hydrolysis, acidogenesis-acetogenesis, and methanogenesis respectively [14]. This approach provides an estimate of biogas potential but does not account for kinetics and inhibition among others.

In contrast, a kinetic model was adapted by Rajendran et al. [15] with a stoichiometric reactor for hydrolysis and a kinetic reactor for the remaining steps. This breakdown and corresponding equations were based off the International Water Association (IWA)’s kinetic Anaerobic Digestion Model No. 1 (ADM1) [12], a standard known for its accurate representation of various process aspects and its simplicity [16]. The Monod expression (Equation (1)) is at the heart of this model [17], capturing the non-linear relationship between the specific growth rate μ and the substrate content.

Equation (1) General Monod kinetic expression:

\[ \mu = \frac{S}{K_S + S} \]  

1st order Monod type reaction kinetic expressions were adopted for acidogenic, acetogenic, and methanogenic reactions, whereas equilibrium was assumed for hydrogenotrophic methane production. The different pre-exponential Monod-type factors were calculated before executing the reaction block. Calculations were based on post-hydrolysis product compositions to estimate the reaction rates. This approach was chosen because current process simulators only provide constant values for kinetics factors, independent of input contents.

This method paved the way for numerous subsequent works. Input ethanol and hydrogen were added by [18] and [19], whilst using a pre-heater to control reaction temperature along with partial digestate recycling and biogas-hydrogen filter separation. A single reactor was employed by [20] along with a gas separation unit, and CO₂ solubility via Henry’s Law coefficients. The work also considered the impact of pH and operating pressure. A hydrolyzed scrubber liquid output was considered by [21] as input to an anaerobic digester and employed two intermediary kinetic reactors and two stoichiometric reactors. A simulation four-reactor configuration was investigated by [22] for an up-flow anaerobic sludge blanket (UASB) reactor with the inclusion of a sulfate reduction step.

In all the simulations, input waste consisted of water, carbohydrates, proteins, lipids, and inert components. Complex compounds were approximated by simpler ASPEN compounds in line with literature. The NRTL (Non-Random Two-Liquid) thermodynamic method was the most widely adopted method for thermodynamic calculations, with the Electrolyte-NRTL (ELEC-NRTL) employed by [21, 22] to better capture electrolyte dynamics. The models were validated against experimental or industrial data and used in further sensitivity analyses, that measured changes in biogas production following variations in input parameters. Findings indicated the presence of an optimal feed rate for both biogas production and methane content [14], related to inhibition that increases with concentrations. Moreover, Harun et al. [18] found that a higher carbohydrate and/or lipid content increased methane composition. The opposite was true for high protein content, that lead to a greater ammonia inhibition.

Although promising, no single work included all input parameters, with typically omitted factors being temperature, pretreatment, pH and high input solid content. These works were not thus able to capture the full complexity of anaerobic digestion. Furthermore, the high number of considered components and corresponding reactions increased system complexity with noted inconsistencies in overall mass balance. This was the case for [14], where unbalanced chemical reactions were found, ultimately leading to unbalanced simulations. Moreover, most works considered a CSTR reactor which works as a black box converting input components into output contents, and operates under steady-state conditions and omits the time evolution of parameters within the reactor.

Considering the previous analysis, the current work’s proposes an improved, robust and versatile anaerobic digestion kinetic Process Simulation Model. This model includes multiple configurations, and successfully captures variations in process parameters like: the input stream composition and solid content (TS and VS), operating temperature, pH, the absence of pretreatment, and VFA inhibition of methanogenesis, which is important for high volatile solid (VS) anaerobic digestion [7]. Moreover, Aspen-based parameter fitting more closely approximates literature results. The use of built-in Aspen Plus R-Batch reactor enables dynamic simulation and tracking of components within the reactor. The model goes beyond the sensitivity analysis provided by previous works and makes use of computer-aided optimization of specific methane production, among other factors. Ultimately, the shown model provides a modular tool for the simulation and optimization of anaerobic digestion, readily available for future researchers and designers.

2. Materials and methods

The employed methodology is defined as follows. First, a process simulation model is constructed with different process steps and associated reactions. Next, model calibration and validation against literature results is delineated and key model parameters identified. Ultimately, a sensitivity analysis and optimization procedure are performed.

2.1. Model construction

The process model is simulated in Aspen Plus V9 and expands on the works of [15]. The chosen components are: (1) input components - water, inert compounds, carbohydrates, proteins (soluble and insoluble), and lipids (tri-olein, tripalmitin and linoleic acid), (2) decomposition products: carbohydrates (dextrose, glycerol, ethanol, xylose, acetic acid), proteins (phenylalanine, aspartic acid, ammonia), lipids (oleic acid, palmitic acid), volatile fatty acids (iso-butyric acid and propionic acid), methane, hydrogen, hydrogen sulfide and carbon dioxide. All nongaseous components were considered as dissolved in water. Thus, no solid phase was included.

The NRTL (non-random two liquid) method was employed, with methane, carbon dioxide and hydrogen sulfide as Henry Components. The process simulation elements are shown in Fig. 1 and detailed hereafter:

(1) The pump and pre-heater are additions to previous literature work and set the reaction pressure and temperature to the desired reaction level.

(2) A stoichiometric reactor was employed for the hydrolysis step. The employed reactions are indicated in Table 1.a.: Cellulose is converted to dextrose, hemi cellulose to acetic acid, xylose, and furfural, soluble protein to phenolic acid, insoluble protein to aspartic acid, and
finally lipids to LCFAs and glycerol. In contrast to approaches in literature, the amino-acid reactions were reduced to two for simplicity, in line with [23] which considered amino-acid kinetics. Component mole balance was respected in all considered reactions. The final conversion values were obtained from [15] for pretreated input waste. The effect of no pretreatment was introduced by the introduction of a pretreatment factor \( f_{\text{pret}} \). This factor is smaller than unity and thus reduces hydrolysis conversion by a proportional amount, leading ultimately to lower biogas production. This factor was chosen as an average value common to all biomass components, even though pretreatment may affect each component differently.

(3) The acidogenesis-acetogenesis-methanogenesis reactor was modeled as an R-batch reactor. This addition is a novelty of this work and was done in conformity with reaction conditions and literature [24]. This time-dependent unsteady-state reactor does not consider volume as a design condition. It also measures changes of variables and concentrations along reaction time. This reactor can be easily manipulated for subsequent parameter optimization and model fitting and can further be modified for semi-batch operations. It also integrates seamlessly with continuous flowsheets.

The occurring reactions are provided in Table 1 (b)-(f). Reactants are converted to products as follows: (b) dextrose and glycerol to propionic and iso-butyric acids with hydrogen generation through acidogenesis. (c) amino-acids to acetic-acid, ammonia, carbon dioxide and water through amino-aidogenesis. (d) Lipids to VFAs, ethanol and 1-ethoxy-2-propanol (E2P) to acetic-acid and hydrogen through acidogenesis. Finally, (e) acetic acid to carbon dioxide and methane through acetoclastic methanogenesis. These reactions, common to all previous works, were modified along with their stoichiometric coefficients to respect the mass balance. They are time dependent and follow the first order power law formula for kinetics, Equation (2).

**Equation (2) General Expression of First Order Kinetics:**

\[
\text{rate}_{\text{react}} = \frac{dC_{\text{react}}}{dt} = -k_{\text{react}} \cdot C_{\text{react}}(t)
\]

The reactant concentration \( C_{\text{react}} \) refers to the time dependent reactant concentration inside the batch reactor. The reaction factor \( k_{\text{react}} \) is a constant, based on the ADM1 model. Its expression is provided for each reaction in Table 1 and breaks down as follows: A constant pre-exponential factor \( (k_{\text{sub,0}}) \) specific for each operation is multiplied by the Arrhenius factor \( (e^{-\frac{E_{\text{act}}}{RT}}) \) and different reactant factors. The reactant factor, common to all reactions, is related to reactant concentration entering the batch reactor. It includes dextrose, glycerol, and amino acids for acidogenesis, LCFAs and VFAs for acetogenesis and acetic acid for methanogenesis. The Monod based expression (Equation (1)), with an increase in factor value with substrate contents, is common for all cases except for the oleic and palmitic acid. Their expression includes a second substrate inhibition term, reflecting the negative impact associated with high concentrations (Equation (3)).

**Equation (3) Modified Monod expression for LCFAs:**

\[
F_{\text{LCFA}} = \frac{1}{1 + \frac{c_{\text{LCFA}}}{k_{\text{LCFA}}} + \frac{c_{\text{LCFA}}}{k_{\text{LCFA}}^2}}
\]

Component concentrations were obtained from the post-hydrolysis simulation results, except iso-butyric and propionic acids. In fact, these components being absent from the output of the hydrolysis reactor, their corresponding concentration equaled zero and had minimal effect.
on kinetics. As a key contribution in this work, their hypothetical concentration was thus assumed equal to that obtained from a full dextrose conversion in line with reaction stoichiometry.

Employed inhibition factors include ammonia (\(NH_3\)), LCFA concentration, hydrogen, VFA, and ethanol. These expressions all follow Equation (4) that indicates that an increase in inhibitor concentration decreases factor value.

**Equation (4) Expression of inhibition factor:**

\[
I_{inhib} = \frac{1}{1 + \frac{C_{inhib}}{I_{inhib_{ref}}}}
\]  

pH inhibition is further expressed in Equation (5). The pH formula for the acidogenesis and acetogenesis cases indicates that inhibition occurs at low pH values and is non-existent for high pH values, whereas pH inhibition occurs for methanogenesis at both low and high pH values.

**Equation (5) Expression of pH inhibition factor:**

\[
I_{pH} = \begin{cases} 
1, & \text{if acido-aceto genesis and } pH > pH_{UL} \\
\frac{e^{-\frac{\gamma_{ac} (pH - pH_{UL})}{\Delta pH_{ac} + \gamma_{ac}}}}{1 + e^{\frac{\gamma_{ac} (pH - pH_{UL})}{\Delta pH_{ac} + \gamma_{ac}}}}, & \text{if acido-aceto genesis and } pH < pH_{UL} \\
\frac{e^{-\frac{\gamma_{ac} (pH - pH_{UL})}{\Delta pH_{ac} + \gamma_{ac}}}}{1 + e^{\frac{\gamma_{ac} (pH - pH_{UL})}{\Delta pH_{ac} + \gamma_{ac}}}}, & \text{methanogenesis}
\end{cases}
\]  

Table 2: Cases considered for validation: input conditions and output results.

| Waste     | PW | MSW | UCW | SW | BW | Ethanol | DW | FW | PM | RS |
|-----------|----|-----|-----|----|----|---------|----|----|----|----|
| Source    | [28]| [30]| [26]| [26]| [31]| [11] | [11] | [27] | [26] | [30] |
| Temperature (°C) | 55 | 35 | 35 | 35 | 2 | 2 | 2 | 2 | 2 | 2 |
| Days spent in reactor | 26 | 40 | 18 | 9 | 6 | 15 | 22 | 10 | 11 | |
| TS (%)    | 12 | 0.9 | 0.6 | 0.2 | 0.5 | 0.3 | 0.43 | 0.52 | 2.5 | 2 |
| VS/TS (%) | 88 | 85 | 87 | 98 | 92 | 100 | 96 | 95 | 20 | 95 |
| Carbohydrates/TS (%) | 22 | 60 | 64 | 5 | 53 | 100 | 79 | 54 | 7 | 49 |
| Protein/TS (%) | 11 | 15 | 13 | 30 | 30 | 0 | 15 | 18 | 7 | 30 |
| Lipids/TS (%) | 55 | 10 | 80 | 9 | 0 | 2 | 23 | 6 | 9 | |
| Pre-treatment | Y | Y | Y | |
| pH        | 7.5 | 5.5 | 7.6 | 7.0 | 7.4 | 5.5 | 7.2 | |
| SMP (l CH₄/kgVS) | 369 | 537 | 102 | 662 | 351 | 428 | 97 | 517 | 203 | 375 |

2.2. Basis for model fitting

For model calibration, ten different Anaerobic Digestion batch experiments were chosen, (Table 2). Some cases highlighted variations in input content such as total solids (Pig Waste-PW [28] and Rice straw-RS [26]), volatile solids (food waste-FW [27]), carbohydrates (Municipal Solid Waste-MSW [28]), lipids (slaughterhouse waste-SW [29]), protein (brewery wastewater-BWW [30]), ethanol (Et [30]), and free ammonia content (pig manure-PM [27]). Others presented various conditions such as: no pretreatment (untreated citric waste-UCW [28]) and low pH (dairy waste - DW [31]).

This diversity was reflected by an average coefficient of variation of 66% for the investigated parameters. All these works employed standard methods to calculate COD (Chemical Oxygen Demand), liquid displacement for biogas production and gas chromatographs for volatile fatty acids. The COD to TS conversion factors, obtained from [32] (1.06 g-COD/g carbohydrate, 1.5 g COD/g protein and 2.87 g COD/g lipid), helped convert from kg COD to kg VS. The observed output for each case was the Specific Methane Production (SMP, l CH₄/kgVS) measured as the ratio of overall methane production (l CH₄) to the overall input volatile solid content (kgVS). The resulting objective function (OF), expressed in %, is defined in Equation (7) as the algebraic average of the absolute normalized differences between literature and calculated SMP rates for each simulation.

**Equation (7) Expression of parameters objective function:**

\[
OF(\%) = \frac{\sum_{cases} \left(1 - \frac{SMP_{exp}}{SMP_{lit}} \right)}{n_{cases}} + 100
\]

With no associated constraints, model parameters were adjusted to minimize the OF value.

2.3. Sensitivity analysis and process optimization

This section employs model construction and fitting steps to predict process performance under varying input and operating conditions. This step is in line with previous bibliographic works [14, 18]. It further consolidates the model by verifying obtained results against prior knowledge and experience. It also gives the designer the possibility to explore novel configurations and settings. In this scope, a default case was considered to initiate this analysis. Therein, the values of different input stream parameters and reactor conditions were controlled and corresponding changes in methane production (Liter CH₄/kgVS) and biogas content (mol%) as well as COD reduction were recorded. The results were analyzed against prior knowledge and theory and recommendations were given.

This sensitivity analysis was supplemented with an optimization step to provide further insight into the process, and readily equip the design engineer with the best configuration given his input material. The goal therein is to control the value of preselected parameters that vary within predefined ranges in order to improve a selected objective function. The objective function in this article is to maximize the specific methane production (l CH₄/kgVS). Multiple input conditions were considered.
and the full range of results was compared, giving further insight into optimal anaerobic digestion process design.

3. Results and discussion

The result section splits as follows. First, model fitting is highlighted. Then, model specific results are discussed for selected cases. Finally, a demonstration sensitivity analysis and optimization are realized to emphasize the versatility and applicability of the model.

3.1. Model fitting

Through model fitting, reaction parameters are controlled to obtain a best fit between simulated and literature results [33]. In this context, 40 reaction parameters were available for control including: hydrolysis stoichiometric conversion rates, acido-aceto-methanogenesis parameters such as the substrate uptake rates, for proteins ($k_{\text{amin,0}}$), lipids ($k_{\text{lip,0}}$), VFAs ($k_{\text{VFA,0}}$), ethanol ($k_{\text{eth,0}}$), and acetic acid ($k_{\text{acet,0}}$), the pH parameters ($pH_{\text{L,0}}$ and $pH_{\text{U,0}}$), reactant parameters ($F_{\text{substrate}}$), and inhibition parameters for ammonia, VFA and hydrogen.

The Aspen Plus complex (Constrained Simplex) derivative-free algorithm was used for parameter optimization. The ranges for the different variables were based off the works of [15] and later approximated by multiple optimization runs. The minimized value of the objective function (OF, Equation (7)) was equal to 1%. Fig. 2 provides the parity plot for optimized model vs. literature results with the constructed trend line indicating a slope of 0.981 and an intercept of 5.4772 with a coefficient of determination, $R^2 = 0.994$. The average difference provides a closer approximation than [15] at 6.3% and [19] at 9.92%, indicating the accuracy of the proposed model and calculated parameters.

Discrepancies are greatest for MSW (4.9%), PM (2.5%) and SW (1.3%) cases, which are larger than the mean objective function. The difference is smaller than the mean objective function for all remaining cases with the UCW case having the smallest value at 0.04%.

3.2. Results analysis

Twenty optimization variables are presented in Table 3 along with their ranges, initial values, and final values. They were chosen thanks to their direct impact on the objective function as opposed to discarded variables. The results break down as follows:

The cellulose and keratin hydrolysis conversion rates were higher than in literature, stressing the contribution of these components to overall digestion.

### Table 3. Optimization results for model parameter.

| Parameter | Unit | Lower bound | Upper bound | Final value | Literature value |
|-----------|------|-------------|-------------|-------------|-----------------|
| $f_{\text{amin}}$ | - | 0.1 | 0.9 | 0.6010423 (−0.8%, +0.7%) | 0.3 |
| $f_{\text{lip}}$ | - | 0.1 | 0.9 | 0.578344 (−0.4%, 0.6%) | 0 |
| $pH_{\text{L,0}}$ | - | 5.8 | 6.5 | 6.04402 (−0.01%, 0.01%) | 4 |
| $pH_{\text{U,0}}$ | - | 7 | 7.3 | 7.20232 (−0.02%, 0.04%) | 5.5 |
| $k_{\text{amin,0}}$ | d$^{-1}$ | 1 | 12 | 8.54545 (±2%) | 70 |
| $K_{\text{amino}}$ | mol/l | 0.0001 | 0.1 | 0.00469 (±100%) | 0.3 |
| $k_{\text{lip,0}}$ | d$^{-1}$ | 10 | 60 | 44.58588 (±2%) | 10 |
| $K_{\text{lip}}$ | mol/l | 0.08 | 0.12 | 0.084729 (±2%) | 2.5 |
| $k_{\text{NH,0}}$ | mol/l | 0.01 | 0.1 | 0.088454 (±0.4%) | 0.05 |
| $k_{\text{VFA,0}}$ | d$^{-1}$ | 10000 | 80000 | 53057 (±5%) | 30 |
| $K_{\text{VFA}}$ | mol/l | 2 | 20 | 14.9091 (±5%) | 0.176 |
| $k_{\text{acet,0}}$ | d$^{-1}$ | 40 | 70 | 54.5806 (±0.1%) | 16 |
| $K_{\text{acet,0}}$ | mol/l | 0.01 | 0.04 | 0.02885 (±0.2%) | 0.26 |
| $k_{\text{eth,0}}$ | mol/l | 1 | 20 | 5.84469 (±30%) | |
| $K_{\text{eth,0}}$ | mol/l | 1 | 20 | 4.28901 (±2%) | |
| $k_{\text{NH,acet}}$ | mol/l | 0.15 | 0.25 | 0.177102 (±1%) | 5 |
| $K_{\text{NH,acet}}$ | mol/l | 420 | 460 | 428 (−82%, +1000%) | 0.00005 |
| $k_{e,0}$ | d$^{-1}$ | 10 | 100 | 42.9 (±0.1%) | |

![Fig. 2. Parity plot experimental vs. model optimized parameters.](image)

Upper and lower pH values were higher than in literature, providing a better depiction of the negative effect of low pH, and reducing the negative impact of increased pH values.

The amino acids’ pre-exponential and reactant factors were lower than in literature. This reduced the influence of amino-acid content, with a 50-fold increase in concentration only leading to a 6-fold increase in the kinetic factor versus a 1000-fold increase for the literature case. Amino-acid conversion in the fitted case can thus still occur in low concentration systems, with a kinetic plateau for increased amino-acid concentrations.

The pre-exponential factor for long chain fatty acids was greater in value than that of literature, and the reactant factor smaller. This translates into a decrease in the kinetic factor for high LCFA concentrations, depicting high LCFA content inhibition.

The Volatile Fatty Acids’ pre-exponential, reactant, and acetic acid inhibition factors were greater in the fitted case. This led to an average 70-times higher VFA conversion factor, with rates increasing with VFA concentrations. Acetic acid inhibition had also a smaller impact on VFA degradation in the fitted case.

The pre-exponential acetic acid degradation factor was three times greater in the fitted case, suggesting a conversion rate higher than in literature for similar acetic acid concentrations.

NH$_3$ and LCFA conversion factors were nine and thirty times smaller in the fitted case, with the opposite true for H$_2$ inhibition factors. This emphasized ammonia and LCFA inhibition in contrast to hydrogen. In
addition, the fitted case had two additional inhibition parameters in the form of ethanol and iso-butyric inhibition for acetic acid degradation.

The confidence intervals for each variable, beyond which the objective function value changes by more than 2%, were relatively narrow, indicating the criticality of associated values but also the preciseness of the optimization. Exceptions can be found for $K_{\text{amin}}$, $K_{\text{VFA,acet}}$ and $K_{\text{H,acet}}$ who have confidence intervals larger than the other parameters.

The evolution of digestion variables with time is provided in Fig. 3 for four cases: Citric Waste, Dairy Waste, Brewery Waste and Rice Straw. The choice was motivated by the different aspects provided by these cases: no pretreatment (UCW), low pH (DW), inhibitions (RS) and BWW presenting a nominal case. Two plots are provided for each case depicting the reactor content evolution of (a) phenylalanine, aspartic acid, oleic acid, glycerol, iso-butyric and iso-propionic acids and (b) acetic acid, dextrose, methane, carbon dioxide and hydrogen.

These plots indicate the rapid consumption of dextrose, phenylalanine, and aspartic acid, in line with [34]. Oleic acid, palmitic acid and glycerol exhibited a slower consumption rate, with glycerol having the slowest rate. Nonetheless, the near complete LCFA conversion is in line with [35]. Iso-butyric and iso-propionic acids highlighted a bell-shaped curve in line with [31], and linked to the two-reaction system: acidogenesis that produces these acids through dextrose conversion and acetogenesis that fully depletes them to acetic acid. An exception is however found in the DW case, linked to the low acetogenesis rate. Also, iso-propionic acid always exhibited a higher concentration than iso-butyric acid, in line with literature and linked to its smaller depletion rate. Ethanol was associated with a fast degradation that is however
not shown in the graphs. Acetic acid evolution also occurred in a bell curve in line with [27], courtesy of the acetogenesis-methanogenesis reactions. CW and DW cases provided exceptions, linked to small acetogenesis rates. Methane, carbon dioxide, and hydrogen all exhibited increasing trends, with hydrogen reaching a plateau first, because it is only produced through acidogenesis and acetogenesis. The early and continuous production of methane and carbon dioxide indicates that methanogenesis took place since the start. Moreover, hydrogenotrophic production is only depicted at the curve’s end, because it occurs in the separate equilibrium reactor. Nonetheless, the trend remains in line with literature.

A test simulation was then conducted for a semi-continuous case deduced from [28]. A continuous feed stream was inputted to the R-batch reactor along with a modified batch stream. The production rate was like that found in literature, with results stabilizing after twenty days. This further proves the model potential to handle industrial systems.

3.3. Sensitivity analysis and process optimization

This section considers the evolution of measured outcomes, such as biogas production, biogas composition and aceticlastic/hydrogenotrophic methane production, as a function of process conditions. For the studied cases, the biogas molar content varied, for methane, between 46% in the ethanol case and 93% in the PW case; for CO₂, between 0% in the ethanol case and 38% in the BWW case; for H₂S between 0% in the ethanol case and 5% in the PM case. Hydrogen composition was null for all cases except for the ethanol case where it equaled 50%. Water vapor composition equaled 3% for all cases. The share of aceticlastic methane production from total (aceticlastic + hydrogenotrophic) production varied between 31% for PM to 78% for UCW.

To better understand the relationship between input conditions and parameter results, multiple one-run simulations were performed. These simulations were based on the untreated Citric Waste (UCW) case as reference.

Considered changes were as follows: pretreatment, higher values for pH, TS, carbohydrate, lipid and protein contents in the input stream, along with mesophilic operation, shorter reactor time, stream, partial digestate recycling and hydrogen gas injection. Fig. 4 highlights changes in biogas content and specific methane production for the different cases.

In comparison to the no pretreatment case, the inclusion of pretreatment increases biogas production by 51% but reduces methane production at the expense of CO₂, linked to greater biomass hydrolysis. Moreover, the adjustment to a neutral pH of 7 further increases methane production by 220%, highlighting the importance of adequate pH. Methane content also rises at the expense of lower CO₂.

Considering pretreated input and neutral pH, mesophilic operation and lower residence time showed a small influence on measured parameters. This differed from the analysis of [18] which highlighted the potential adverse effect of a higher residence time on methane production. The all-carbohydrate case showcased a 35% and 14% drop in methane production and content respectively with a 23% increase in carbon dioxide content. This is linked to increased VFA inhibition on the methanogenesis step. The majority protein and majority lipid cases highlighted a 21% and a 53% higher SMP ratio, with increased methane and decreased carbon dioxide content. These results align with [6] which indicated that carbohydrates have high reaction rate but low yield, proteins have a faster reaction rate and a slightly higher yield with the opposite for lipids. This differs from [18] which were more critical of protein digestion and associated ammonia inhibition. In addition, the positive results were reversed if lipid or protein content decreased, courtesy of hydrogen inhibition on the methanogenesis of the acetic acid. High TS (total solids) content had limited effect on the system, whereas solid recycling and hydrogen injection both had positive effects.

Two optimization runs were performed. The set objective was to maximize Specific Methane Production (l methane/kg VS) for MSW and BWW respectively. pH, temperature, reaction time and molar flow rate of injected hydrogen were varied within specified ranges. An optimal value of 735 l CH₄/kg was obtained for MSW with a pH of 8, a temperature of 50 °C, a reaction time of 35 d and a hydrogen mole flow rate 85 times smaller than the input molar flow rate. An optimal yield of 550 l CH₄/kg was obtained for MSW with a pH of 7.7, a temperature of 49 °C, a reaction time of 40 d and a 265 times smaller input hydrogen flow rate. The lower yield is related to the lower lipid content in the MSW case, whereas the smaller hydrogen flow rate is related to the smaller carbohydrate fraction which yields a smaller CO₂ content. High
pH, high residence time and high reaction temperature remain interesting for both cases. This section presents thus the potential of the model to optimize AD processes.

4. Perspectives

This work presents a contribution to the ongoing field of robust Anaerobic Digestion modeling. Nevertheless, key improvements remain to be developed. First, for the kinetic model, reducing the residence time of the UCW case from 40 to 21 days yielded a methane rate of 72 \( I_{CH_4}/kgVS \) contrary to 96 \( I_{CH_4}/kgVS \) obtained in the experiment. Conversely, 519 \( I_{CH_4}/kgVS \) were obtained for a residence time of 17 days versus 488 \( I_{CH_4}/kgVS \) in literature. This may be circumvented by a rigorous train/test method where iterations are realized between the train and test method. This will ultimately reduce the fit with the training model to a mean between the two sets.

Alternatively, the inclusion of additional parameters such as pressure, solids recycling, and hydrogen injection may be included. Moreover, the study of high solids content Anaerobic Digestion may seem interesting as an alternative to low TS digestion. In fact, this alternative reduces capital costs, but may bring inhibition problems that need to be circumvented. This goes hand in hand with subsequent economic and environmental analyses which further reinforce the model.

5. Conclusion

This study highlights the strength of process flowsheet simulation for the design of anaerobic digestion reactors. Aspen Plus simulation enabled a modular and robust process modeling. The inclusion of multiple case studies better represented biochemical phenomena. VFA inhibition on methanogenesis was included, to emphasize high TS cases. Parameter optimization enabled a 0.994 R² fit with literature results and a parity plot of slope 0.981. Fitting results penalized operations under pH values of 5-6 and recommended operating under a pH of 7-8. Inhibition factors limited the impact of \( H_2 \) and stressed that of LCFA and \( NH_3 \). Sensitivity analysis indicated that a higher pH along with protein and lipid contents along with pretreatment favored the specific methane yield. Model optimization indicated the difference in optimal conditions for various input compositions. This model provides a steppingstone for future works that deal with either the design or the experimental exploration of the AD process.

Declarations

Author contribution statement

Rami Bechara, PhD: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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The authors declare no conflict of interest.
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