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Simulation of two-dimensional attainable regions and its application to model digester structures for maximum stability of anaerobic treatment process

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ABSTRACT

Unlike high-rate anaerobic digesters that employ some mechanism to retain microbial sludge mass, low-rate systems use sufficiently long hydraulic retention times to ensure process stability, which becomes economically unattractive for treating large quantities of waste. This study presents the use of attainable region to develop a new strategy to enhance the stability of low-rate digesters. By considering three digestion cases, diary manure only (batch 1) or diary manure with granular (batch 2) or lagoon (batch) sludge as innoculum, the following findings were obtained. (1) For a given concentration of volatile acids in an anaerobic digester, higher concentrations of methanogenic archae can be attained using a digester structure (combination of different digesters) as opposed to single digester. (2) For a given digested substrate, a change in the source of inoculum results in a change in the limits of achievability by the system (attainable limits for batches 1, 2 and 3 were 46.486$(g/L)^2$, 5.562$(g/L)^2$ and 0.551$(g/L)^2$, which resulted in performance improvements of 118.604%,175.627% and 200.436% respectively), and hence optimal digester structure. The evidence from this study suggests that the technique can be used to simultaneously improve process stability, define performance targets and propose digester structures required to achieve a given target.

1. Introduction

The anaerobic digestion process for waste treatment and biogas generation has received considerable attention from the scientific community due to rising demand for renewable energy and environmental sanitation. As with any other bioprocess, central to the operation of the anaerobic treatment process is the anaerobic digester in which microorganisms grow, breakdown organic pollutants and produce methane-rich biogas (Alford, 2006). Unlike aerobic treatment systems in which the loading rate is limited by the supply of a reagent (such as O_2), the loading rate of anaerobic reactors is limited by the processing capacity of the microorganisms (Mes et al., 2003). These microorganisms generally include two groups: Acid-forming and methane producing microorganisms (Demirel and Yenigun, 2002), with the latter having a growth rate five times relatively higher than the former (Henze et al., 2008). Therefore the stability of anaerobic digesters is highly dependent on the viability and mass of methanogenic archae retained in the digester with respect to a given substrate concentration. The specific growth rate of methanogenic archae increases with concentration of volatile fatty acids until a maximum specific growth rate is reached above which volatile acids turn to inhibit growth rate (Henze et al., 2008; Chen et al., 2008, 2014). Hence an optimal archae to acid ratio (generally referred to as inoculum to substrate (I/S) ratio) is necessary to ensure an optimal efficiency of biogas production from anaerobic digesters. This explains why biodigester designs that

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maximize retention of microbial biomass are crucial to the stability of the anaerobic treatment process and hence its industrial efficiency compared to other biological treatment processes. One of the major causes of failure in the anaerobic treatment process is inhibition, which depends on the components of the digester, byproducts of microbial metabolism as well as a combination of loading rate and retention time, which can result in microbial wash out or inhibition from chemical species. Of the two main type of anaerobic digester systems, 'high rate' systems (e.g. Contact Process, Anaerobic Filter, Fluidized Bed, UASB, EGSB) enhance process stability by employing some mechanism either to retain microbial sludge mass in the digester or to separate the sludge from the effluent and return it to the digester (Mes et al., 2003; Henze et al., 2008). On the other hand, 'low rate' systems (e.g. CSTR or PFR), use sufficiently long hydraulic retention times to ensure process stability, which becomes economically unattractive for treating large quantities of waste or requiring large digester volumes if a given quantity of waste must be treated (Mes et al., 2003). Hence alternative techniques that maximize process stability in low-rate anaerobic digesters will be a major breakthrough in the application of anaerobic treatment process. The use of digester networks, in which multiple digesters are designed to operate as a single unit is such technology (EPA, 2006). It is well known that each type of anaerobic digester has specific characteristics often making them more appropriate under specific substrate or digester conditions. In addition, the anaerobic digestion (AD) process involves multiple reactions (each catalyzed by different groups of microorganisms) and when operated in a single digester, the process conditions are only suitable for all the reactions but not optimal for any particular reaction. Hence a combination of digesters allows for the flexibility and possibility of improving overall process performance. Previous experimental studies confirming the efficacy of digester networks have only been limited to series combinations (Zhang et al., 2017; Akobi et al., 2016; Nasr et al., 2012) with a lot of empiricism in the design process. In particular, some of the plants that use the series digester combinations cannot prove whether there exist (or not) other network configurations that produce better performance. In other words, there exist the problem of local optimum or multiple solutions (existence of other digester combinations that achieve same or improved results). In our recent publication, Abunde et al. (Abunde Neba et al., 2019) we solved this challenge by developing a novel theoretical framework for optimal synthesis of digester networks based on the concept of attainable regions. The attainable region is a collection of all possible output for all possible digester designs by interpreting the anaerobic digestion process as a geometric object that define a region of achievability without having to explicitly enumerate all possible design combinations (Ming et al., 2016). In the previous study, we concluded that a change in the type of digested substrate results in a change in the limits of ahievability (as well as the optimal combination of digesters), while considering the volumetric methane productivity and waste stabilization as design objectives. In the current study we aim to illustrate how the attinainable region concept can be used to solve instability problems in low rate anaerobic digesters. Unlike the previous study that considered different organic substrates, this study considers same substrate for different sources of inoculum and uses I/S ratio and instantaneous methanogenic yield as design objectives. In other words, we lay down a theoretical framework to design an optimal digester combination that gives the desired stability parameters (I/S ratio or instantaneous methanogenic yield) based on the concept of attainable regions.

It is important for readers to note that the attainable region is unique for given reaction kinetics (model structure and/or parameter values), and anaerobic biodegradation kinetics depends on the inhibitory conditions or type of organic substrate in the digester. All inhibitory conditions in anaerobic digesters will often upset the balance between acid-forming and methane-producing microorganisms resulting in accumulation of volatile acids (Chen et al., 2014). Different inhibitory conditions and/or substrates will result in different kinetic behaviour of volatile acids on methanogenic archae, and some of the published inhibitory patterns include: competitive, non-competitive, uncompetitive, linear or exponential kinetic behaviors (Kythreotou et al., 2014). Hence by using attainable regions, we can understand how the performance of the digester (concentration of methanogens) can be enhanced (under higher concentration of volatile acids) using digester structures as opposed to single digesters.

The determination of performance targets for anaerobic digestion of different organic substrates has been investigated extensively in the past using either experimental methods (such as the biomethane potential test and spectroscopy) or theoretical methods (based on chemical composition, chemical oxygen demand or elemental composition) (Jingura and Kamusoko, 2017). However these approaches are limited to only methane yield and gives no information about the other states and hence cannot predict exact cause of process failure or inhibition. In addition, it provides no information with respect to the digester design required to achieve a defined target. This paper discusses how the attainable region concept can be used as a technique to define performance targets under different inhibitory conditions as well as model anaerobic digester configurations to optimize process stability.

2. Process modeling and model identification

2.1. State dynamic model of anaerobic treatment process

For synthesis of low rate anaerobic digesters using attainable regions, simplified models are considered most appropriate as the geometric and hydrodynamic analysis are relatively more complex. The attainable region (AR) technique is suitable for use because it can solve problems not because of multiple reactors but because of multiple reactions, such as the biological reactions in anaerobic digestion involving complex metabolic pathways. However, for practicality, the authors have applied 2-stage lumped reaction models focusing on acid producing bacteria and methanogenic archae to make the problem more tractable. Our subsequent studies will seek to consider more complex (parallel and series) reaction set to align more closely with the biochemical pathways, i.e. series of rate equations for hydrolysis, acidogenesis, acetogenesis and parallel reactions for acetoclastic and hydrogenotrophic methanogenesis. The modified Hill model (Finn et al., 2013), which was developed for anaerobic digestion of animal manure (diary, poultry, beef and swine wastes) has been selected for this study. The model presents a compromise between the overly simplistic models capable of predicting only gas production and sometimes substrate consumption and simplistic models (such as the AM2) (Bernard et al., 2001) that include a hydrolysis step, alkalinity, cation concentration, dissolved carbon dioxide and ammonia. These effects are 'lumped' into and become part of the biodegradability constant (Bo) and acidity factor (AF) present in the modified Hill model (Finn et al., 2013). The species conservation equations for the modified Hills model are presented as follows:

a) Total biodegradable volatile solids (S_1) in the liquid phase of the bioreactor

$$\frac{dS_1}{dt} = (S_{1_{in}} - S_1)D - k_1\mu_1X_1 \tag{1}$$

b) Volatile fatty acids (S_2) in the liquid phase of the bioreactor

$$\frac{dS_2}{dt} = (S_{2_{in}} - S_2)D + k_2\mu_1 X_1 - k_3\mu_2 X_2 \tag{2}$$

c) Acidogens (X_1) in the liquid phase of the bioreactor

$$\frac{dX_1}{dt} = (\mu_1 - K_{d_1} - D)X_1 \tag{3}$$

d) Methanogens (X_2) in the liquid phase of the bioreactor

$$\frac{dX_2}{dt} = (\mu_2 - K_{d_2} - D)X_2 \tag{4}$$

e) Methane gas flow rate

$$Q_{CH_4} = V\mu_2 k_4 X_2 \tag{5}$$

The organic waste is characterized by using the two parameters, which are biodegradability (B_o), Eq. (6) and acidity (A_f), Eq. (7). B_o measures the ease with which the organic substrate can be broken down and stabilized by anaerobic bacteria while A_f of a substrate can be defined as the amount of volatile fatty acids contained in the substrate per unit mass of biodegradable volatile solids

$$S_{1_{in}} = B_0 S_{in} \tag{6}$$

$$S_{2_{in}} = A_f S_{1_{in}} \tag{7}$$

The anaerobic biodegradability can be computed via Eq. (8) while the acidity factor is computed using Eq. (19).

$$B_0 = \frac{g\ VS_{destroyed}}{g\ VS_{added}} \quad as\ HRT \rightarrow \infty \tag{8}$$

$$A_f = \frac{VFA_{in}}{B_0 \times VSL} \tag{9}$$

The modified Hill's model considers temperature dependence of the anaerobic treatment process through an empirical model, Eq. (10) and since the death rates are set to one tenth of the maximum reaction rates, Eq. (11) they are also show temperature dependent.

$$\mu_{1m}(T) = \mu_{2m}(T) = 0.012T - 0.086 \tag{10}$$

$$K_{d1} = K_{d2} = 0.1\mu_{1m} \tag{11}$$

$$10^\circ C < T < 60^\circ C$$

For the purpose of our study, the model is adapted as follows: The Monod function used to describe the growth rates of acidogenic and methanogenic microorganisms in the original model will be used only for acidogenic bacteria, Eq. (12). The growth model for methanogenic archae will vary depending on the cases presented in Table 1.

$$\mu_1 = \mu_{m1}\frac{S_1}{K_{s1} + S_1} \tag{12}$$

In addition, a new parameter, known as the acidogenic fraction in inoculum (ϑ) is however included to characterize the inoculum. The value of this parameter is lies in the range $0 \leq \vartheta \leq 1$ and is selected to give the best fit between model and experimental predictions.

2.2. Kinetic patterns of volatile acid inhibition

Anaerobic digestion involves the complex interaction of different groups of microorganisms but the methanogenic archae are known to be the most sensitive to inhibition (Chen et al., 2008). As the volatile acid concentration is increased, a maximum specific growth rate of methanogenic archae will be reached at a certain concentration. A further increase of the substrate concentration results in a decrease of the specific growth rate. The kinetic patterns for volatile acid inhibition have been based on modification of the Monod model, Eq. (13) for growth of methanogenic archae to include inhibition term.

$$\mu_2 = \mu_{m2}\frac{S_2}{K_{s2} + S_2} \tag{13}$$

The effect of volatile acid on microbial inhibition in anaerobic digestion has generally been modeled through two main approaches: The empirical approach, which include a linear or, exponential inhibition patterns and the enzyme kinetic approach, which include a competitive, non-competitive and uncompetitive inhibition patterns. Both approaches are lumped into Eq. (14) by multiplying the Monod model with a factor that describe the different inhibition patterns.

$$\mu_2 = \frac{\mu_{m2}S_2(1 - K_i S_2)^a}{K_{s2}\left(1 + \frac{S_2}{K_i}\right)^e + S_2\left(1 + \frac{S_2}{K_i}\right)^d}\left(1 + \frac{S_2}{K_i}\right)^c\left(e^{-K_i S_2}\right)^b \tag{14}$$

Eq. (14) presents a generalized modified Monod model to describe volatile acid inhibition on methanogenic archae from which the different inhibition cases can be derived as shown in Table 1.

It should be noted that even though there exist other product inhibition models that have been used to model growth of anaerobic microorganisms, we consider the most common ones to illustrate the effect of anaerobic digester conditions on the type of kinetic pattern used to describe the effect of volatile acids on methanogenic archae. Instead of predefining an inhibition pattern as practiced by modelers of anaerobic digestion, the authors of this study present a framework for determining the inhibition patterns before using the model for digester synthesis. Since it is not feasible to measure the specific growth rate of both microbial populations during the anaerobic treatment process, the strategy consist of using the kinetic models in a full dynamic model so that the kinetic constants can be estimated from easily measurable parameters such as volumetric biogas and total volatile fatty acid concentration.

2.3. Model identification

In order to better illustrate the different kinetic patterns and how the patterns will change with characteristics of digestion substrate, AD experiment, using diary manure (1.7% TS) mixed inoculum from different sources was selected for model identification (Zaher et al., 2009). The experiments were conducted in continuously mixed batch reactors at 35 °C. Further details on the experimental study can be obtained from the cited literature.

In order to identify the model parameters for the different kinetic cases, the adjoint-based gradient algorithm defined in Fig. 1 is implemented. First, the gradient algorithm fits the whole set of model parameters and assesses the variability of the fit using marginal and joint confidence regions of the model parameters. Second, for parameters that show a high correlation, one of them is kept constant and a readjustment of the uncorrelated set of

Table 1
Structural patterns of volatile acid inhibition.

Empirical constant					Kinetic Pattern	Model
a	*b*	*c*	*d*	*e*		
1	0	0	0	0	Linear inhibition	Dagley and Hinshelwood
0	1	0	0	0	Exponential inhibition	Aiba et al. model
0	0	0	0	1	Competitive inhibition	Anonymous
0	0	−1	0	0	Non-competitive inhibition	Haldane model
0	0	0	1	0	Uncompetitive inhibition	Andrews model

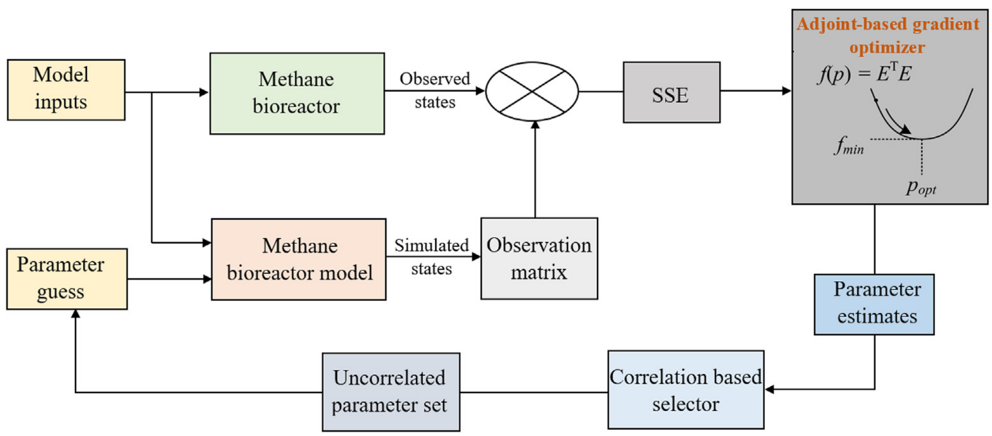

Fig. 1. Model identification framework using the adjoint-based gradient optimizer.

parameters is performed using the algorithm. This allows a more accurate adjustment of the whole set of model parameters to experimental data, as illustrated in subsequent sections.

The advantage of this procedure is that parameter estimation and variability assessment is performed simultaneously, which allows the user to better understand the model's sensitivity to different influences and obtain reliable estimates. It is not the intention of this article to go into the mathematical formulations leading to a full description of the adjoint-based gradient method for parameter estimation. Interested readers can find a detailed description of the procedure in the following literature (Benítez et al., 2017).

3. Attainable region analysis

3.1. Brief theoretical overview

The AR theory is a technique for process synthesis and optimization, which incorporates elements of geometry to understand how networks of chemical reactors can be designed and improved (Hildebrandt and Glasser, 1990; Hildebrandt et al., 1990). The attainable region is defined as the set of all possible output for all possible reactor designs that can be achieved by using the fundamental processes occurring within the system and that satisfies all the constraints placed by the system. Geometrically, the attainable region represents the region bounded by the convex hull for the set of points achievable by the fundamental processes occurring in the system. Once the AR has been determined, the limits of achievability by the system for the given kinetics and feed point is known and the boundary of the AR can then be used to answer different design or optimization questions related to the system (Ming et al., 2016). The theory provides guidelines for construction of attainable regions as well as some necessary conditions to test the results.

The following requirements are necessary before an AR analysis can be performed (Glasser et al., 1987, 1993).

Choose the fundamental processes occurring in the system.

- ➢ Choose the state variables
- ➢ Define the reaction scheme and process kinetics
- ➢ Determine the geometry of the process units.
- ➢ Define the process conditions
- ➢ Determine the objective of the optimization

Given a set of reactions and associated kinetics, the following five key steps need to be performed in order to complete an attainable region analysis.

- ➢ Define the reaction dimension and feed set
- ➢ Generate the AR using combinations of the fundamental processes
- ➢ Interpret the AR boundary in terms of reactor equipment
- ➢ Define the objective function and overlay this onto the AR to determine point of intersection with the AR boundary
- ➢ Determine the specific reactor configuration required to achieve the intersection point

Some necessary conditions for AR can be summarized as follows:

- ➢ The AR includes all feed points to the system.
- ➢ The AR is convex.
- ➢ No rate vectors point out of the AR boundary.
- ➢ Backward extension of rate vectors in the complement region do not intersect the AR

The following section outlines the methodological flow for AR construction and application for process synthesis and optimization. The framework involves five main steps (Ming et al., 2016):

3.1.1. Step 1: Preparation

This involves definition of the reaction kinetics, AR dimension, state variables (those used to represent the AR) as well as the feed point used to generate the AR. The feed point defines the initial value or the concentration of states fed into the reactor.

3.1.2. Step 2: AR construction

This step generates the AR using a combination of PFR, CSTR and mixing for two-dimensional ARs or a combination of PFR, CSTR, DSR (Differential side-stream reactor) and mixing for higher dimensional constructions. This is the most difficult and time-consuming step but also provides the most valuable information about the operating limits of the system. AR construction typically begins by determining the PFR trajectory and CSTR locus from the feed. The PFR trajectory is the set of points generated by solving the steady state model of a PFR reactor (a set of ordinary differential equations) while the CSTR locus is the set of points generated by solving the CSTR model (a set of nonlinear equations).

3.1.3. Step 3: Boundary interpretation

This step involves interpretation of the AR boundary into reactor structures, based on the fundamental characteristics of the AR boundary. The boundary of the AR is composed of reaction and mixing surfaces only. Reaction surfaces are always convex and the points that form convex sections of the AR boundary arise from effluent concentrations specifically from PFR trajectories. For a two-dimensional system, points on the AR boundary that initiate these convex PFR trajectories arise from specialized CSTRs while for a three dimensional system, they arise from DSRs. The convex hull of the set of points generated by all possible combinations of fundamental reactor types and mixing defines the attainable region.

3.1.4. Step 4: Overlay objective function

The objective function is modeled in terms of the variables used to represent the AR and then overlaid onto the AR. The points of intersection between the objective function and the AR boundary represent the optimal points of operation.

3.1.5. Step 5: Optimize

Since the entire boundary of the AR has been interpreted in terms of reactor structures (step 3), the particular reactor structure required to achieve the optimal operating points (point of intersection) is known.

Summarily, starting from the feed point, the procedure entails finding all possible achievable outputs for the system under consideration, from the trajectory of the states of interest describing the system operation. These trajectories are convexified to obtain candidate attainable regions, which are tested against the necessary conditions and recursively updated so that any violated necessary conditions is eliminated. The process continues until no other necessary conditions are violated otherwise, a candidate AR (subset of the true AR) is obtained, which can still provide better understanding of the achievable limits of the system. It is not the intention of this article to present a detailed explanation of the AR theory. Interested readers can consult the above sited literature for a more in-depth understanding.

3.2. Application of AR approach to maximize methanogenic activity

3.2.1. Reaction scheme and process kinetics

Using the estimated kinetic constants, a stoichiometric scheme of the bioreaction occurring in the anaerobic digester consist of two main reactions catalyzed by acid-forming bacteria, Eq. (15) and methane-forming bacteria Eq. (16)

$$k_1S_1 \xrightarrow{r_{X_1}} X_1 + k_2S_2 \tag{15}$$

$$k_3S_2 \xrightarrow{r_{X_2}} X_2 + k_4CH_4 \tag{16}$$

If we assume the specific death rate to be negligible compared to the specific growth rate of both microbial populations, the rate expressions for the different reaction species is defined by Eqs. (17) − (20)

$$r_{X_1} = \mu_1 X_1 \tag{17}$$

$$r_{X_2} = \mu_2 X_2 \tag{18}$$

$$r_{S_1} = -k_1\mu_1 X_1 \tag{19}$$

$$r_{S_2} = k_2\mu_1 X_1 - k_3\mu_2 X_2 \tag{20}$$

3.3. Fundamental processes

Various fundamental processes can occur within a system, which for bioreactors may include: mass transfer, mixing, bioreaction (biodegradation, bioconversion), adsorption, heat transfer, etc. The AR approach requires the fundamental processes taking place in the system be identified. The following two main fundamental processes are identified to be associated with the anaerobic treatment process: Biodegradation and mixing. The attainable region (AR) for the anaerobic treatment process therefore represents the set of all possible states that can be achieved by a combination the two fundamental processes, biodegradation and mixing. In AR theory, mixing is performed by a continuous stirred tank reactor (CSTR) while reaction (biodegradation) is achieved in a plug flow reactor (PFR), since the operation of both reactors respectively mimic the two fundamental processes. At steady state operation, the general mathematical representation of a CSTR and PFR are given by Eqs. (21) and (22) respectively.

$$C = C_f + \tau r(C) \tag{21}$$

$$\frac{dC}{d\tau} = r(C) \tag{22}$$

C is the state vector while $r(C)$ is the reaction rate vector as shown by Eqs. (23) and (24) respectively.

$$\mathbf{C} = [X_1 \quad X_2 \quad S_1 \quad S_2\,]^T \tag{23}$$

$$\boldsymbol{r}(\boldsymbol{C}) = \left[r_{X_1} \quad r_{X_2} \quad r_{S_1} \quad r_{S_2}\,\right]^T \tag{24}$$

Solving the CSTR system to obtain the roots at a given feed point (C_f) and for different residence times (τ_i *for* $i = 1$ *to* n) results in a set of points referred to as a CSTR locus. In the same way, integrating the PFR system for a given feed point and residence time results in a set of points referred to as PFR trajectory.

3.3.1. Dimensionality analysis and model reduction

The reaction stoichiometry of the system can be used to determine the dimension of the system. The dimension of the AR is determined from the number of independent reactions occurring in the reactor system, which defines the dimension of the stoichiometric subspace (the rank of the stoichiometric coefficient matrix A), in which the AR must reside. Since there are two independent reactions occurring in the system, the set of points generated by the anaerobic treatment process must reside in a two-dimensional subspace in $\mathbb{R}^5$ (Ming et al., 2016).

Before constructing the AR, the space wherein the AR must reside (by choosing unique species components in the reactions that will represent the AR) must first be determined. Methanogenesis has been known to be the most sensitive step of the anaerobic treatment process and since the volatile fatty acids and methanogenic microorganisms, are the key player in this stage, it is sensible to generate the candidate AR in $(S_2 - X_2)$ space, which provides information required to maximize gas production as well as process stability. However, even if only a subset of the states is used to construct the AR (candidate AR), it can still be transformed in terms of the other variables if required (Ming et al., 2016). The reduced state and reaction rate vectors are therefore presented by Eqs. (25) and (26).

$$\boldsymbol{C} = [S_2 \ \ X_2 \,]^T \tag{25}$$

$$\boldsymbol{r}(\boldsymbol{C}) = [\, r_{S_2} \ \ r_{X_2}]^T \tag{26}$$

This reduction in the dimensions of the state and rate vectors is possible because the reaction rate of biodegradable volatile solids (r_{S_1}) can be expressed in terms the reaction rate of acidogenic bacteria (r_{X_1}), which can in turn be expressed as functions of reaction rates of volatile acids (r_{S_2}) and methanogenic archae (r_{X_2}) as shown by Eqs. (27) and (28):

$$r_{S_1} = -k_1 r_{X_1} \tag{27}$$

$$r_{X_1} = \frac{1}{k_2}\left(r_{S_2} + k_3 r_{X_2}\right) \tag{28}$$

This implies that S_1 can be expressed in terms of X_1, which can in turn be expressed as a function of S_2 and X_2, illustrated by Eqs. (29) and (30). Notice the presence of two new terms in Eqs. (29) and (30), $X_{1_{in}}$and $X_{2_{in}}$, which represent the respective feed concentrations of acidogenic bacteria and methanogenic archea. These terms are absent in Eqs (1)–(5) because the material balance assumes that the concentration of anaerobic microbes in the feed is negligible compared to that inside the digester (Finn et al., 2013; Hill, 1983). So in Eqs (29) and (30), $X_1 - X_{1in} \cong X_1$ and $X_2 - X_{2in} \cong X_2$.

$$S_1 = S_{1_{in}} - k_1\left(X_1 - X_{1_{in}}\right) \tag{29}$$

$$X_1 = X_{1_{in}} + \frac{1}{k_2}\left[S_2 - S_{2_{in}} + k_3\left(X_2 - X_{2_{in}}\right)\right] \tag{30}$$

The model reduction assumes that the specific death rates of acidogens and methanogens is negligible compared to their respective specific growth rates.

3.3.2. AR construction

After stating the process kinetics, the AR construction process is initiated by defining feed point and process conditions that influence the system. In this study, three anaerobic digestion batches: diary manure, diary manure + granular sludge and diary manure + lagoon inoculum were considered each with respective feed concentrations, $C_f = [S_{2f}, X_{2f}]^T$ of $[1.89, 0.84]^T$, $[1.89, 0.84]^T$ and $[1.62, 1.53]^T$. The controlled process condition was mainly temperature, which was maintained at a constant value of $35°C$ throughout retention time. Using the specified feed, kinetics and temperature conditions, the set of points generated by solving the PFR equation are called the PFR trajectory and those generated by solving the CSTR equation are called the CSTR locus. The convex hull for the set of points generated by all possible combinations of CSTR, PFR and mixing defines the AR. The attainable region is unique for a given kinetics and feed point and process conditions. A change in any of these may result in a change in the AR and hence the operating limits of the system.

3.4. Objective function for optimizing microbial activity

Since the methanogens are most susceptible to process instabilities, we are interested in determining the optimal operating point that ensures stability of methanogenic microorganisms. For doing this, we define two objective functions, which translate the stability of methanogenic archae: The inoculum to substrate (I/S) ratio and the instantaneous yield of methanogens from volatile acids.

The inoculum to substrate ratio describes the concentration of volatile acids that should be maintained in the digester for optimal activity methanogenic archae. Studies have reported the optimal tolerance range of volatile acids, above which the methanogens experience inhibition or toxicity (Chen et al., 2008). The Instantaneous yield is defined as the rate of formation of the desired product (methanogens), divided by the rate of consumtption of the reactant (volatile acids). The inoculum to substrate ratio (I/S) was modeled using Eq. (31) while the instantaneous yield of methanogenic archae (Υ_{X_2}) from volatile acids was modeled by Eq. (32).

$$IS = \frac{X_2}{S_2} \tag{31}$$

$$\Upsilon_{X_2} = \frac{r_{X_2}}{-r_{S_2}} = \frac{\mu_2 X_2}{-k_2\mu_1 X_1 + k_3\mu_2 X_2} \tag{32}$$

Eqs. (31) and (32) can be rearranged to express X_2 as a function of S_2, presented by Eqs. (33) and (34) respectively. It should be noted that the term $\mu_1 X_1$ in Eq. (34) contains X_2 and the numerical computations additionally made use of Eqs. (29) and (30).

$$X_2(S_2) = IS \times S_2 \tag{33}$$

$$X_2(S_2) = \frac{\Upsilon_{X_2} k_2 \mu_1 X_1}{\mu_2(S_2) \times \left(\Upsilon_{X_2} k_3 - 1\right)} \tag{34}$$

Eqs. (33) and (34) can seperately be plotted over the AR boundary as contours to determine the intersection with the boundary. Sections of the objective function that intersect the AR are optimal points, relative to the I/S ratio or Υ_{X_2} specified. The points of intersection can be interpreted in terms of digester networks depending on the manner in which the AR is constructed (Ming et al., 2016), and the reactor structure corresponding to the I/S ratio or $\Upsilon_{X_2}$of interest is the optimal reactor structure.

4. Results and discussion

4.1. Model fits and estimate of kinetic constants

We have explored the capabilities of the different biokinetic models to describe the degradation of organic substrate in the anaerobic digestion process. Experimental results for three anaerobic-digestion batches of diary manure, each under different process conditions were considered (Zaher et al., 2009). In Batch 1, no external inoculum was added during start-up of the digester. In Batch 2, granular sludge is added into the digester as inoculum while in Batch 3, sludge from a lagoon was used as the inoculum. Fig. 2 presents the fitting results for all the 5 biokinetic models with experimental measurements of volatile fatty acids and methane flow rate obtained from batch 1. From the fitting results, it can be concluded that the models give a good prediction of the experimental data. However, the competitive model shows the smallest SSE (see Table 2) and can thus be considered to more closely represent the experimental data. Hence anaerobic digestion of diary manure with no external inoculum leads to methanogenic inhibition described as being competitive. Similar fittings were performed for Batches 2 and 3, which was observed that the linear model more closely represented the experimental data for both cases. Figs. 3 and 4 present the fitting for the linear model with experimental measurements of volatile acid and methane flow rate obtained from batches 2 and 3. Table 2 presents the parameter estimates for all the fitting cases. Even though batches 1 and two fit well with the linear model, the kinetic constants are different and we can thus conclude that inhibition characteristics exerted by volatile acids on methanogenic archae differs based on the conditions in the anaerobic digester. This kinetic behaviour of methanogenic archae might be explained in this way. The growth kinectis of microorganisms widely depends on nutritional availability as well as operational and environmental conditions, which in turn vary for different digester worts. The different sources of inoculum results in different wort characteristics, which can be measured in terms of nutritional differences, presence of different toxicants or other competitive microorganisms in the digester, thereby varying the kinetic behaviour of the methanogens.

The findings of the current study are consistent with those of Yang et al. (Ref) who studied the effect of temperature and substrate characteristics on kinetic behaviour of anaerobic digestion process. The authors considered four different substrates (swine wastewater, palm oil mill wastewater, protein production wastewater, synthetic wastewater and pharmaceutical wastewater), five temperature regimes ($10°C$, $15°C$, $20°C$, $25°C$, $30°C$) and four kinetic models (modified Stover-Kincannon, Chen and Hashimoto, Deng and modified Deng) were tested. It was observed that changes in substrate and temperature as well as a combination of thereof resulted in different fitting characteristics of the different kinetic models. This effect of substrate and operating conditions on the kinetic behaviour of the anaerobic treatment process has very important implications in the concept of attainable regions. This is because the attainable region is unique for a given kinetics (Ming et al., 2016) and a change in kinetics therefore results in a change in the limits of achievability by the system. What this implies practically is that the reactor structures required to achieve the optimal operating point will differ for each digested substrate, which paves the way to use the concept of attainable regions to solve operational challenges for different types of wastewaters. In addition, the study uses the adjoint method for computing gradient of the parameter estimation objective function before using the conjugate gradient method for model calibration. Gradient-based methods are widely used for calibration of anaerobic digestion models (Donoso-Bravo et al., 2011) with gradients mostly computed using the finite difference method. The adjoint method presents an alternative approach for computing gradients. Other model calibration methods that have been applied to anaerobic digestion models include the asymptotic state observers (López and Borzacconi, 2009), Simplex algorithm (Zaher et al., 2009), genetic algorithm combined with the gradient descent method (Martinez et al., 2012), etc. Even though we have presented the kinetic analysis of anaerobic digestion process using the adjoint-based gradient method, the emphasis of this paper is not necessarily on the fitting performance of the different biokinetic models, but on how we use the models to develop new policies for operation of anaerobic digesters to ensure stability of methanogenic archae.

4.2. Effects of process kinetics on optimal reactor configuration

4.2.1. Attainable regions: limits of achievability by the system

Fig. 5 presents the PFR trajectory and CSTR locus (dubed base trajectories) for the anaerobic digestion process in batch 1 while Fig. 6 presents the two-dimensional candidate AR obained from the based trajectories, using the specified feed and kinetics. Employing a CSTR gives a maximum attainable methanogenic concentration of 5.01gme/L (Fig. 5). A PFR however improves upon this concentration to an attainable value of 24.09gme/L. At this point, the reader can already notice that by using an anaerobic PFR as opposed to a CSTR, the concentration of methangoneic archae in the biodigester increases by approximately 5 times. It can be observed from Fig. 6 that constructing the attainable region further extends the concentration of methanogenic archae to 37.51 gme/L. This increase in the concentration of methanogenic archae for the same feed and kinetics is attributed to the fact that a systematic manipulation of the fundamental processs (mixing and reaction in this case) occurring in a system serves to expand the states that can be achieved by a system, which is one of the key strengths of the attainable region theory. If more fundamental processes are considered (e.g seperation), the limits of achievabtily by the states of the system can be further improved. Fig. 7 presents the base trajectories for the anaerobic digestion process in batch 2 while Fig. 8 presents the candidate AR. Recall that the AR is specific for a given kinetics, which explains why the nature of AR for batch 2 is different from that in batch 1. We oberve from the base trajectories that using a CSTR will result in higher concentrations of volatile fatty acids in the digester (an indication of process instability), while a PFR presents a maximum limit of volatile acid concentration that can be attained. Unlike the case of batch 1, constructing the AR doesn't serve to increase the maximum concentration of methanogenic archae attained (compared to the that attained with the base trajectories). However, in this case, the AR analysis shows that higher concentrations of methanogenic arhae can be attained at higher concentrations of volatile fatty acids by running a PFR from a CSTR and a bypass valve from feed (see mixing line AB on Fig. 8). Practically, this implies that using a digester network as opposed to a single digester results in an increased stability of the methananogenic archae. Fig. 9 presents the base trajectories for the anaerobic digestion process in batch 3 while Fig. 10 presents the candidate AR. Similar to the case of batch 2, constructing the AR doesn't serve to increase the maximum concentration of methanogenic archae attained but concentrations of methanogenic archae origninally not attainable at higher concentrations of volatile acids now become attainable by using a digester structure indicated by line BC of Fig. 10.

Even though we have observed a change in the nature of attainable region for the different kinetics, the boundary of ARs however have a simple fundamental structure irrespective of the kinetics used. This boundary is composed entirely of mixing surfaces (straight lines) and manifolds convex reaction surfaces (Ming et al., 2016). The points that form the convex reaction surfaces arise from effluent concentrations of the PFR trajectories, which are initiated by points from specialized CSTRs. We will now illustrate how interpret the AR boundary into anaerobic digester strucures by using the fundamental characteristics of the AR boundary. The illustration will be done by using the AR for batch 1 presented in Fig. 6. In Fig. 6, the point B is the feed point, while the region defined by ABC is the AR. The convex segment BA are trajectories obtained by running PFR from points on CSTR locus. The point A is therefore obtained by running a CSTR from point B followed by a PFR from CSTR while the point C is obtained by running a CSTR from feed (point B). The lines AC and BC are the mixing surfaces while AB is the reaction surface. Concentrations along the line AC (C_{AC}) can

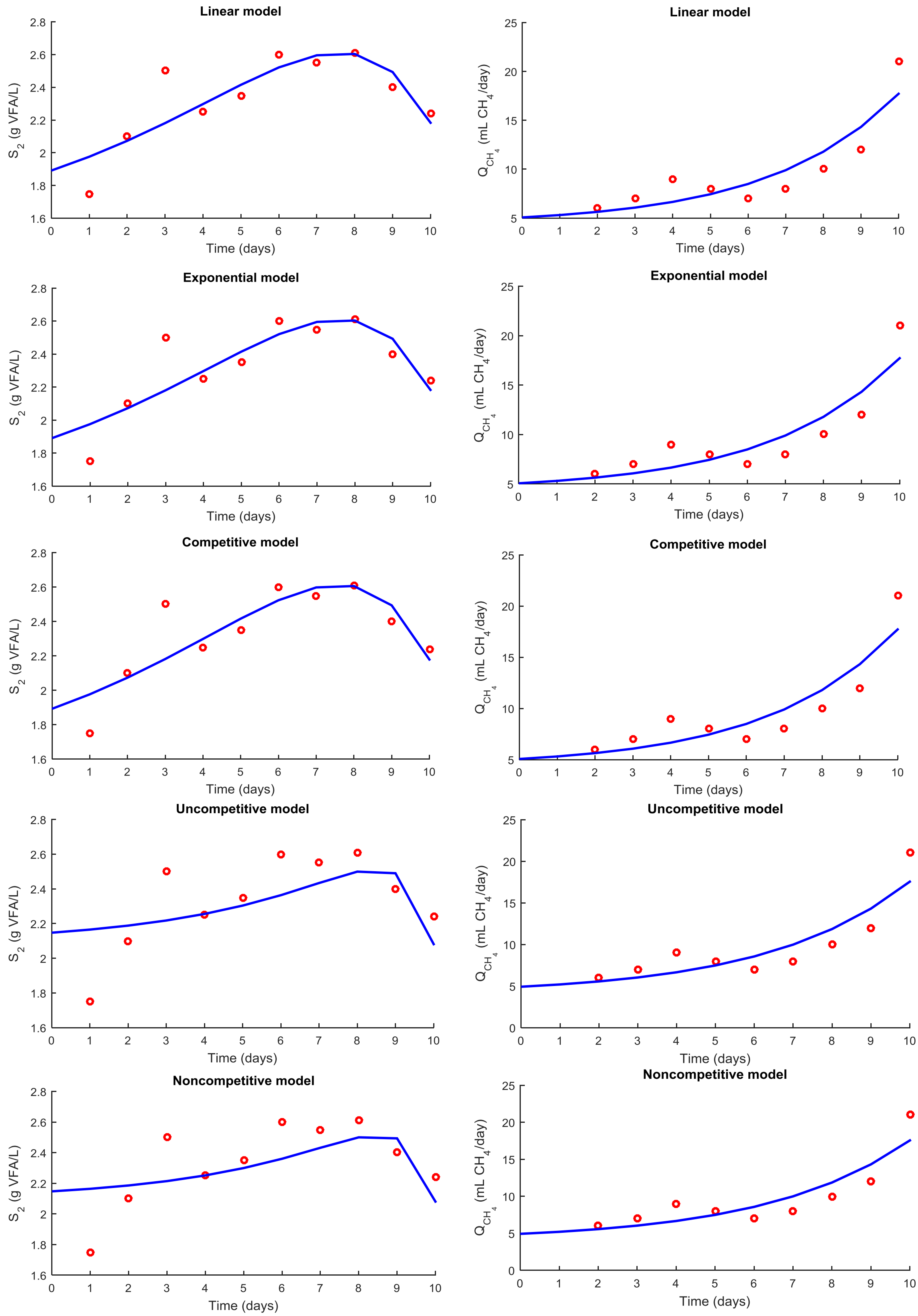

Fig. 2. Fitting of biokinetic models to experimental measurements from Batch 1. Columns one and two show the fitting of the volatile fatty acids, (S_2) and methane flow rate (Q_{CH_4}) with experimental measurements respectively while the rows show the performance of each biokinetic model (linear, exponential, competitive, non-competitve and uncompetitive).

Table 2
A generalized table for model parameters and fitting characteristics.

Model	Model parameters							SSE
	k_1	k_2	k_3	k_4	K_{s1}	K_{s2}	K_i	
Batch 1: Diary manure								
Linear	1.996e-04	3.515	4.915	1.117	0.779	0.278e-4	0.136e-04	5.67130
Exponential	1.999e-04	3.515	4.915	1.116	0.778	0.278e-4	0.135e-04	5.67129
Competitive	0.0011	9.376	13.712	1.118	0.278	0.056e-4	32.717	5.67124
Noncompetitive	0.421	7.754	11.581	1.3514	2.486	0.0215	45.338	5.86042
Uncompetitive	0.406	7.760	11.581	1.3499	2.487	0.0215	39.338	5.85868
Batch 2: Diary manure + granular sludge								
Linear	14.026	1.152	4.71e-7	112.995	0.061	28.432	61.065	14.1601
Exponential	7.294	0.742	14.501	97.558	1.498	31.401	45.438	43.3498
Competitive	9.1887	1.66e-6	56.367	53.318	26.965	1.1545	76.762	39.4748
Noncompetitive	1.1125	2.8272	60.143	2.73e-6	1.6375	6.8891	2.279	39.4221
Uncompetitive	4.1808	8.9413	23.552	7.66e-6	7.0412	0.8130	0.2758	39.4221
Batch 3: Diary manure + Lagoon innoculum								
Linear	9.3970	0.3433	0.5855	384.557	0.5103	2.3350	0.3960	10.7005
Exponential	12.0561	0.0004	0.8396	9.5819	4.9221	2.4868	0.0266	30.4303
Competitive	14.9995	1.0976	2.5811	15.3191	0.0024	0.0026	5.5585	30.2694
Noncompetitive	12.8286	2.9529	31.873	0.2078	271.81	32.576	0.0011	30.5584
Uncompetitive	12.869	4.465	13.474	56.4751	422.73	53.154	7.148e-8	30.5584

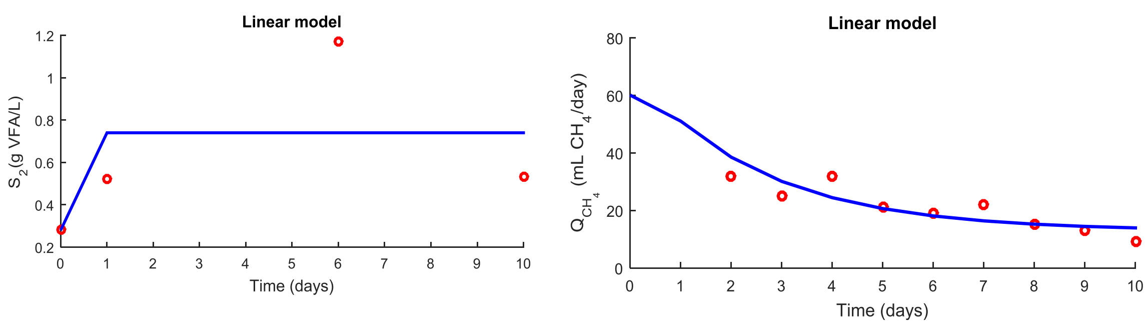

Fig. 3. Fitting of linear model to experimental measurements from Batch 2.

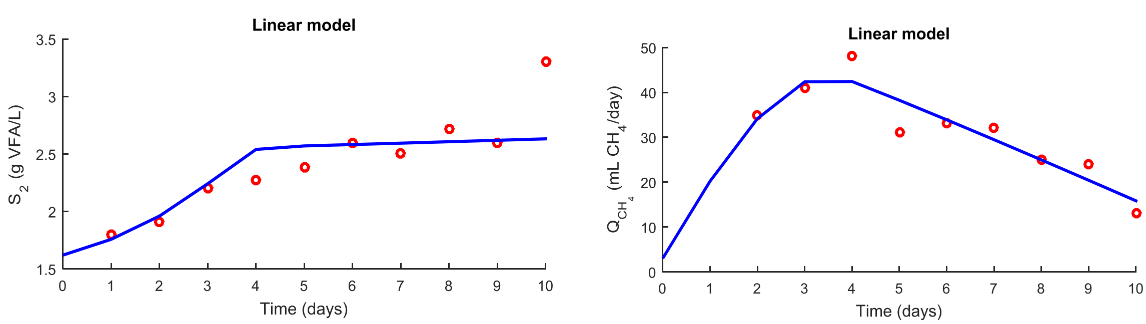

Fig. 4. Fitting of linear model to experimental measurements from Batch 3.

be obtained by mixing points A and C, Eq. (35) (the lever-arm rule) and the digester structure is therefore given by a CSTR + PFR (point A) run in parallel with a CSTR (point C) and both contents mixed at the end. Concentrations on the line BC (C_{BC}) can be obtained by mixing points B and C, Eq. (36) and the required digester structure is given by a CSTR (point C) with a bypass from feed (point B). Similar digester interpretations were made for batches 2 and 3 as displayed on Figs. 8 and 10.

$$C_{AC} = \alpha C_A + (1 - \alpha) C_C \,, \qquad 0 \le \alpha \le 1 \tag{35}$$

$$C_{BC} = \alpha C_B + (1 - \alpha) C_C, \qquad 0 \le \alpha \le 1 \tag{36}$$

Where α is known as the mixing ratio.

The results obtained imply practically that a systematic scheduling of the fundamental processes of mixing and reaction occurring in the anaerobic digester can result in an increased stability of methanogenic archae. It is interesting to note that for a two-dimensional attainable region, when mixing and reaction are the only fundamental processes occurring in a system, the AR may be constructed by a combination of reactors involving PFRs, CSTRs and mixing only (Ming et al., 2016). What this means is that there is no need to devise new or perhaps novel types of digesters with the aim of extending the limits of achievability by the system. Instead, it is required to focus attention on optiimally arranging combinations of these two fundamental digester types or researching more fundamental processes to the system.

Table 3 presents a summary of the performance characteristics

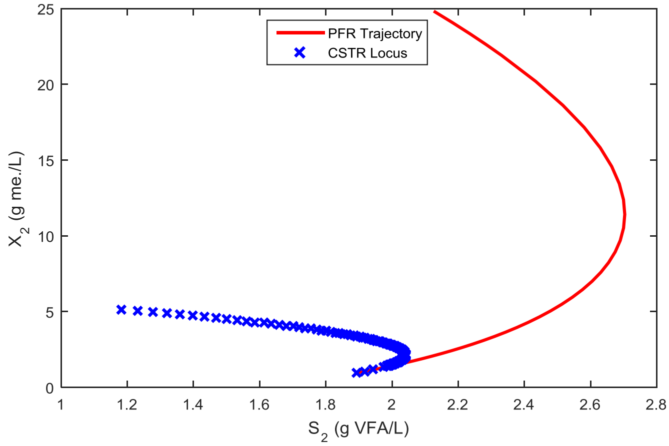

Fig. 5. Anaerobic base trajectories for digestion process in batch 1.

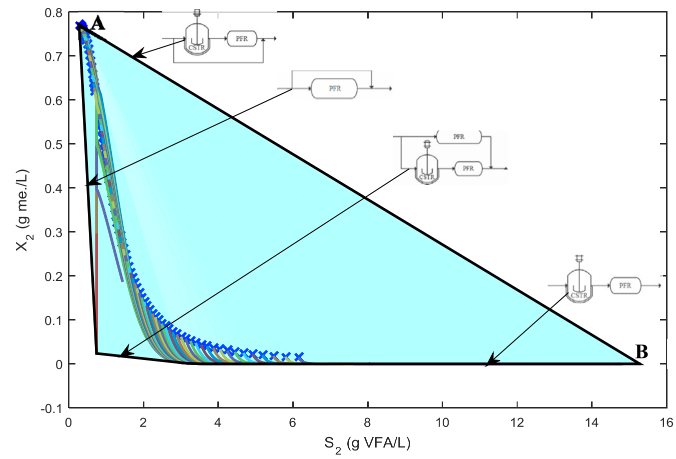

Fig. 8. Two-dimensional attainable region for anaerobic digestion process in batch 2.

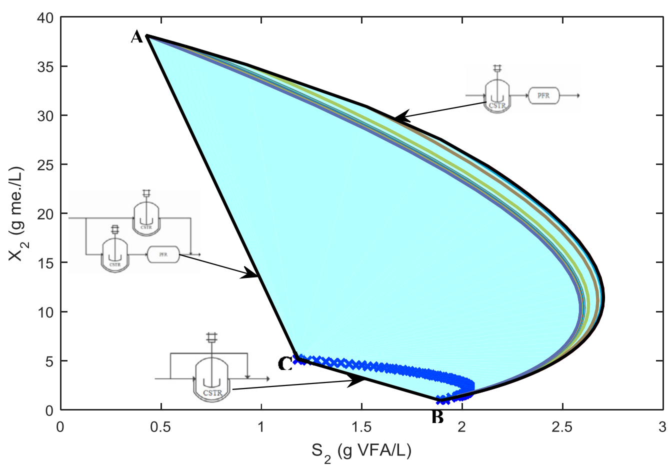

Fig. 6. Two-dimensional attainable region for anaerobic digestion process in batch 1.

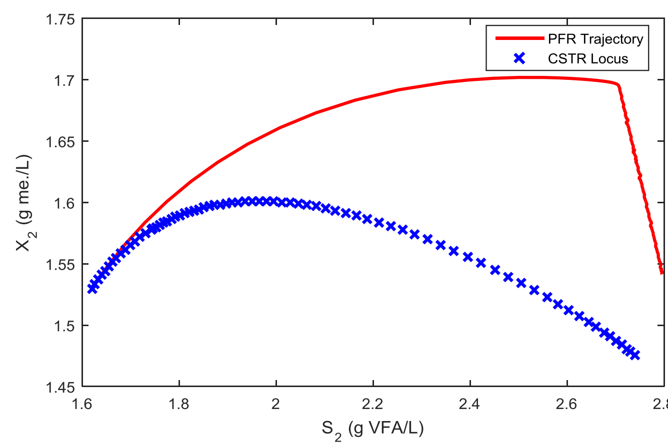

Fig. 9. Anaerobic base trajectories for digestion process in batch 3.

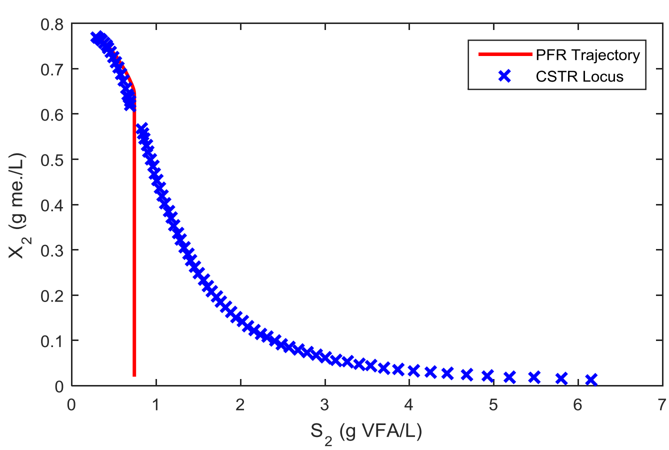

Fig. 7. Anaerobic base trajectories for digestion process in batch 2.

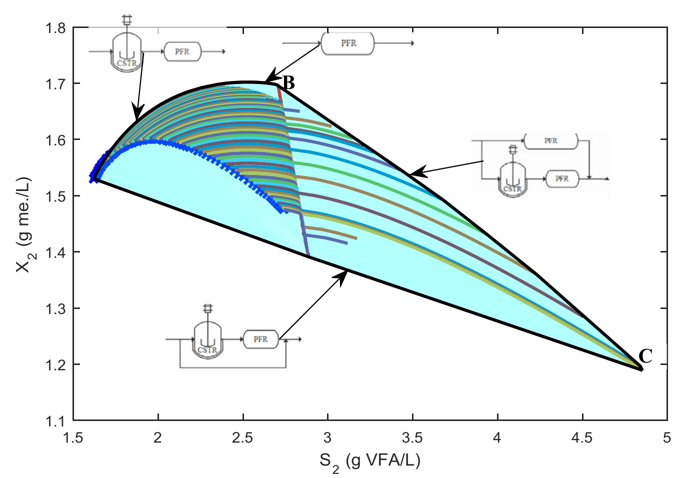

Fig. 10. Two-dimensional attainable region for anaerobic digestion process in batch 3.

of limits of achievability of the three batches of anaerobic digestion. The limits of achievability by the systems have been measured quantitatively in terms of the area of the convex hull. Note that the AR is defined by the convex hull of the set of points (states) generated by the fundamental processes occurring within the system. The convex hull represents the smallest subset of a set of points that can be used to generate all other points by reaction and mixing. Geometrically, a convex hull is a finite convex polytope enclosed by a finite number of hyperplanes, which is interpreted in a two-dimensional space as the smallest polygon enclosed by planar facets such that all of the elements lie on or in the interior of the polygon (Asiedu et al., 2015).

Table 3
Performance characteristics of the limits of achievability by the batches.

Batch	Digested condition	Area of convex hall $(g/L)^2$		Performance improvement
		Base trajectory	Attainable region	
1	Diary manure only	21.265	46.486	118.604%
2	Diary manure + granular sludge	2.018	5.562	175.627%
3	Diary manure + lagoon innoculum	0.183	0.551	200.436%

From the results in Table 3, The following two conclusions can be made. (1) The AR analysis serves to improve the peformance of the system (measured in thems of states attained by the concenertation of methanogenic archae) for all the three batches. (2) We observe that the % increase in peformance differs for each batch of anaerobic digestion. This is because a change in digester characterisitics (source of innoculum) results in a change in kinetics and the ability of the AR to improve the peformance of the system depends on the process kinetics. We can conclude that even if all the necessary conditions of the AR are not met, the candidate (otherwise true) AR still serves to improve the limits of achievabilitity by the system. In the next section, we will present how the AR has been used to answer few design questions on the anaerobic digesters.

4.2.2. Digester structures for optimal methanogenic activity

The optimal digester structures for the different batches of anaerobic digestion have been obtained from the point of intersection between the objective function and boundary of the AR. Fig. 11 shows a number of contour lines for I/S ratio and the instantaneous methanogenic yield for batch 1. Recall that in the case of batch one, the competitive inhibition model was selected for use in modeling the digester configuration using attainable regions. So for optimizing the instantaneous yield, we substitute $\mu_2(S_2)$ corresponding to competitive inhibition model (see Table 1) into Eq. (34) to obtain objective function for competitive model, Eq. (37). Since the term $\mu_1 X_1$ in Eq. (37) contains X_2, the numerical computations additionally made use of Eqs. (29) and (30) in order to overlay Eq. (37) onto the AR boundary constructed in the $(S_2 - X_2)$ space.

$$X_2 = \frac{Y_{X_2} k_2 \mu_1 X_1 \left[K_{s2}\left(1+\frac{S_2}{K_i}\right)+S_2\right]}{\mu_{m2} S_2 (Y_{X_2} k_3 - 1)} \tag{37}$$

Observe that the two objective functions intersect the AR boundary at several points. The I/S ratio becomes smaller while the instantaneous methanogenic yield becomes larger as we move toward the horizontal line $X_2 = 0$. This suggests that for a given concentration of methanogens in the digester, higher I/S ratio corresponds to lower concentration of volatile acids while the instantaneous methanogenic yield corresponds to higher concentration of volatile acids.

Fig. 12 shows a number of contour lines for I/S ratio and instantaneous yield for batch 2. In the case of batch 2, the linear inhibition model was selected to describe the anaerobic digestion kinetics. So for optimizing the instantaneous yield, we substitute $\mu_2(S_2)$ corresponding to linear inhibition model (see Table 1) into Eq. (36) to obtain Objective function for the linear inhibition model (Eq. (38)) as in the case for batch 1.

$$X_2 = \frac{Y_{X_2} k_2 \mu_1 X_1 (K_{s2} + S_2)}{\mu_{m2} S_2 (1 - k_i S_2)(Y_{X_2} k_3 - 1)} \tag{38}$$

Similarly to the case of batch 1, the two objective functions intersect the AR boundary at several points and the I/S ratio becomes smaller w as we move toward the horizontal line $X_2 = 0$. However, contrarily to batch 1, the instantaneous methanogenic yield becomes smaller as we move toward the horizontal line $X_2 = 0$. This suggests that for a given concentration of methanogens in the digester, higher I/S ratio and higher instantaneous methanogenic yields corresponds to lower concentration of volatile acids. A possible explanation for the reversal of trend observed in instantaneous methanogenic yield can be attributed to the fact that the range of concentrations of volatile acids attained in batch 2 fall within the inhibitory range there by causing inhibition to the growth of methanogenic archae. Another possible explanation could be that the granular sludge used as inoculum for batch 2 is less adapted to higher concentrations of volatile acids and studies have confirmed that acclimation or adaptation of methanogens greatly influence their ability to withstand higher concentrations of inhibitory substances (Asiedu et al., 2015; Chen et al., 2008, 2014).

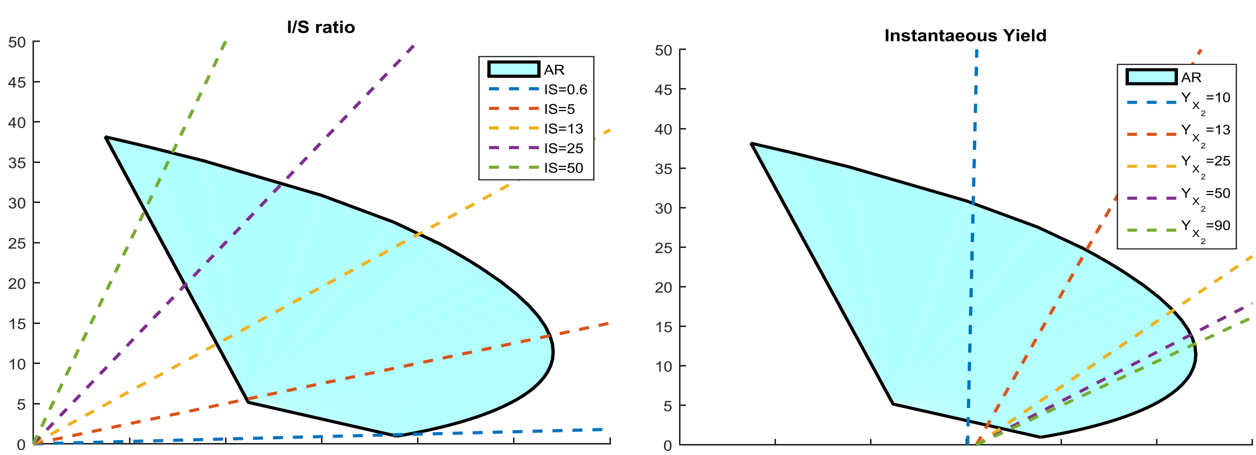

Fig. 11. Contour lines for I/S ratio and instantaneous methanogenic yield for batch 1.

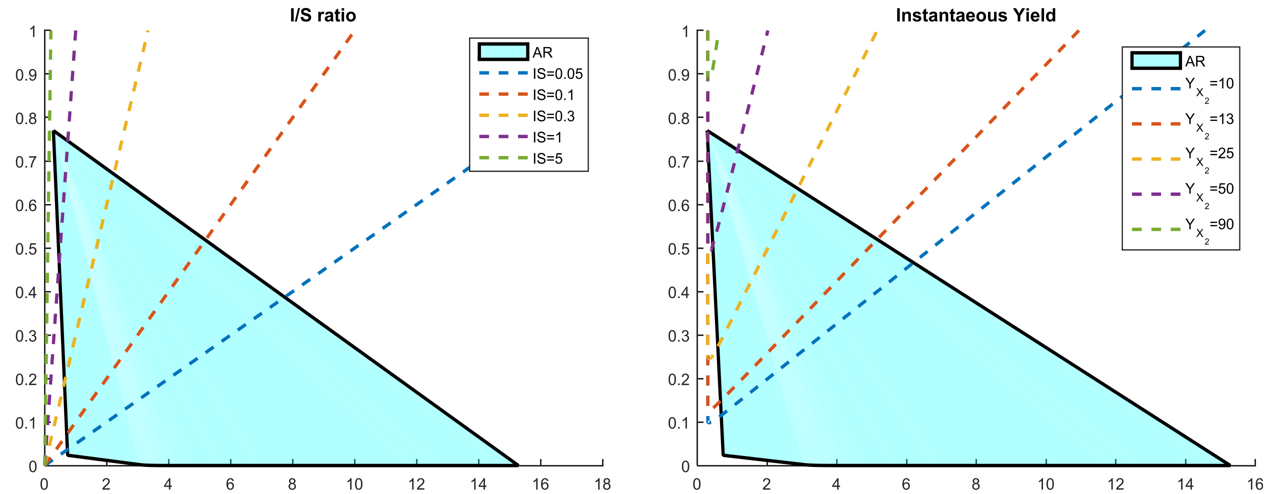

Fig. 12. Contour lines for I/S ratio and instantaneous methanogenic yield for batch 2.

Fig. 13 shows a number of contour lines for I/S ratio and instantaneous yield for batch 3. Contrarily to batches 1 and 2, for some concentrations of methanogenic archae in the digester, certain values of instantaneous methanogenic yield correspond to two different concentrations of volatile acids within the limits of achievability by the system.

Multiple points of intersection between objective functions and boundary of the attainable region is an indication of multiple operating points (multiple optima) for the system. If the only criteria for design is the I/S ratio and the instantaneous methanogenic yield, then the optimal digester structure to achieve a given I/S ratio or instantaneous methanogenic yield can be seelected from any of the intersection points. However, points corresponding to lower concentrations of methanogenic yield (points associated with the lower part of the AR) are preferable since the growth rate of these microbial population is about 5 times slower that of acidogens (Henze et al., 2008) hence making it difficult to maitain higher concentrations in the digester unless a seperation system is included.

It is interesting to compare the results of this study with that of Abunde et al. (Abunde Neba et al., 2019), who used attainable regions to compare the limits of achievability of five different digested substrates using volumetric methane productivity and waste stabilization as objective functions. The authors concluded that a change in the type of digested substrate results in a change in the limits of ahievability as well as the optimized AR parameter of an anaerobic digestion system. In this study, the results have demonstrated that for the same digested substrate (diary manure), different sourcess of inoculum will result in different limits of achievability by system and hence the optimal digester structure (using I/S ratio and instantaneous methanogenic yield as objective functions. The results have shown that using digester structues as opposed to single digesters can improve the viability of methanogenic archae at higher concentrations of volatile fatty and for an anaerobic digestion system, a change in digested subtrate and/or source of innoculum results in a change in the limits of achievabilty by the system. This study therefore lays down the theoretical framework for using attainable regions to define the anaerobic digetion performance targets for a given innoculum and/or substrate characteristics. Therefore, unlike the BMP assay and the Buxuells technique for defining performance targets (limits of achievability), the AR approach does not only provide information about the limits of achievabily, but it provides the optimal digester structures required to achieve a given target.

In our previous study (Abunde Neba et al., 2019), we considered measurable outputs from the digester (volumetric methane

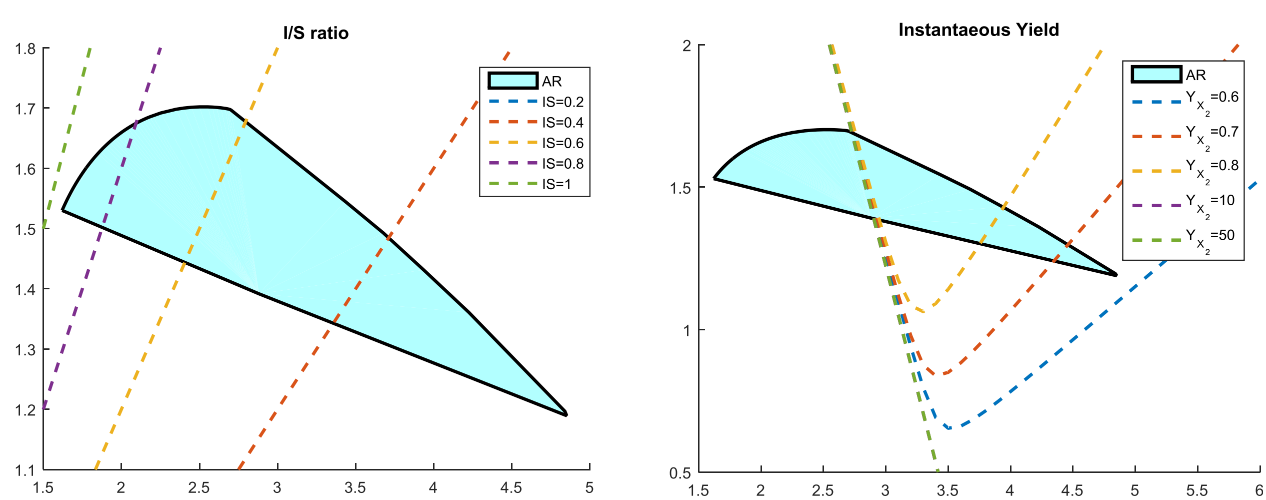

Fig. 13. Contour lines for I/S ratio and instantaneous methanogenic yield for batch 3.

productivity and waste stabilization) as objectives, while the current study we considered parameters directly linked to microbial stability (I/S ratio and instantaneous methanogenic yield) as objectives. The combination of results suggest that the AR can be used to answer any design and optimization questions. This is possible because for a defined kinetics (model structure and/or kinetic coefficients), the AR is fixed for a given feed point and multiple objective functions (and hence multiple optimizations) may be formed using a single AR. In other words, the attainable region represents the solution to several different optimization problems implying several optimization scenarios can be performed without any requirement to perform further optimizations (or reconstruct the attainable region) when the objective function is changed. Therefore the design approach presented in this study can be used to optimize any process and design parameter of the anaerobic treatment processes.

5. Conclusion

Returning to the problems posed at the beginning of this study, it is now possible to state that the use of digester structues as opposed to single digesters can improve process stability and performance. For a given concentration of volatile acids in an anaerobic digester, higher concentrations of methanogenic archae can be attained using a digester structure (network) as opposed to single digester. This study has shown that a for a given digested substrate, a change in the source of innoculum results in a change in the limits of achievabilty by the system and hence the optimal digester structures required to achieve a given objective. Another major finding was that the attainable region technique can be used as reliable alternatives to the BMP assay and the Buxuells technique for defining performance targets (limits of achievability), because the AR approach does not only provide information about the limits of achievabily, but it provides the optimal digester structures required to achieve a given target.

The design technique presented in this study can be used to answer any design and optimization questions regarding the anaerobic treatment process. This concept has been proven by formulating and solving two optimization problems to obtain optimal structures for anaerobic digesters to achieve a given inoculum to substrate ratio as well as instantaneous methanogenic yield. The evidence from this study suggests that the technique of using digester structures presents a break through in the application of low-rate anaerobic digesters as it can be used to improve upon the process dynamics. The current findings add to a growing body of literature on the application of attainable regions for solving operational challenges in processs engineering.

These findings enhance our understanding of that a systematic manipulation of the fundamental processes (mixing and reaction in this case) occurring in a system serves to expand the states that can be achieved by a system, which is one of the key strengths of the attainable region theory. It is highly interesting for readers to note the geometric optimization technique presented in this study can also be to optimize operation of other wastewater treatment processes (e.g., activated sludge treatment, coagulation, etc.). The technique is suitable not because of multiple reactors, but because of multiple reactions in a process.

In order to subject the operational technique to actual experimental verification, pilot scale studies are currently under design. In the mean time, interested researchers could consider using economic indicators such as net present value, internal rate of returns, benefit cost ratio or payback period as objective function for attainable region optimization, which would present a key motivation for investors.

Further theoretical study is needed to account for the effect of temperature regimes (pychrophillic, mesophillic and thermophillic) on the limits of avhievabilit by the system. In this study, the anaerobic digester networks have been staged two-stage biochemical kinetics in which acid-forming stage is physically separated from the methane gas-forming stage. Other studies could consider applying thermodynamic staging techniques where digester networks are designed based on different temperature regimes in order to take advantage of the higher stability of the mesophilic digestion as well as the higher digestion rate of thermophilic digestion.

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Nomenclature

Y_{X_2}	Instantaneous methanogenic yield
A_f	Acidity factor $(g\ VFA\ /L)/(g\ BVS/L)$
B_0	Biodegradability constant $(g\ BVS\ /L)/(g\ VS/L)$
K_{s_1}	Monod half-saturation constant for acidogenic bacteria $(g\ BVS\ /L)$
K_{s_2}	Monod half-saturation constant for acidogenic bacteria $(g\ VFA\ /L)$
K_{d1}	Specific death rate of acidogenic bacteria (d^{-1})
K_{d2}	Specific death rate of methanogenic archae (d^{-1})
K_i	VFA inhibition constant for methanogenic archae $(g\ VFA\ /L)$
Q_{CH_4}	Volumetric methane flowrate $(mL\ CH_4\ /d)$
$S_{1_{in}}$	Input concentration of biodegradable volatile solids $(g\ BVS\ /L)$
$S_{2_{in}}$	Initial concentration of volatile fatty acids $(g\ VFA\ /L)$
S_2	Concentration of biodegradable volatile solids $(g\ VFA\ /L)$
S_2	Concentration of volatile fatty acids in bioreactor $(g\ VFA\ /L)$
S_{in}	Input concentration of volatile solids $(g\ VS\ /L)$
VFA_{in}	Inlet concentration of volatile fatty acids $(g\ VFA\ /L)$
$X_{1_{in}}$	Initial concentration of acidogenic bacteria $(g\ ac.\ /L)$
$X_{2_{in}}$	Initial concentration of methanogenic archae $(g\ me.\ /L)$
X_1	Concentration of acidogenic bacteria in bioreactor $(g\ ac.\ /L)$
X_2	Concentration of methanogenic archae in bioreactor $(g\ me.\ /L)$
k_1	Yield constant $(g\ BVS\ /g\ ac./L)$
k_2	Yield constant $(g\ VFA\ /g\ ac./L)$
k_3	Yield constant $(g\ VFA\ /g\ me./L)$
r_{S_1}	Reaction rate for biodegradable volatile solids $(g\ BVS\ /L/d)$
r_{S_2}	Reaction rate for volatile fatty acids $(g\ VFA\ /L/d)$
r_{X_1}	Reaction rate for acidogenic bacteria $(g\ ac.\ /L/d)$
r_{X_2}	Reaction rate for methanogenic archae $(g\ me.\ /L/d)$
μ_{m_1}	Maximum specific growth rate of acidogenic bacteria (d^{-1})
μ_{m_2}	Maximum specific growth rate of methanogenic archae (d^{-1})
μ_1	Specific growth rate of acidogenic bacteria (d^{-1})
μ_2	Specific growth rate of methanogenic archae (d^{-1})
AD	Anaerobic digestion
AR	Attainable Regions
CSTR	Continuous Stirred Tank Reactor
DSR	Differential Side-stream reactor

I/S	Inoculum to substrate ratio
PFR	Plug Flow Reactor
T	Reactor temperature ($^{\circ}C$)
V	Volume of digester (L)
VSL	Volatile Solids Load ($g\ BVS\ /L$)
α	Mixing ratio
τ	Residence time (days)
ϑ	Acidogenic fraction

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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