# Chapter 14
# Mathematical Modeling Challenges Associated with Waste Anaerobic Biodegradability


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**Abstract** Anaerobic digestion (AD) is a biological process, which, due to the multiple stages and microorganisms it involves, is complex to model. The feasibility of AD is highly dependent on the organic matter content, as well as physical and chemical factors that regulate the microbiological activity. Mathematical models are a constant challenge for the simulation and prediction of organic matter degradation and biogas production. This chapter is an overview of part of the great diversity of AD mathematical models from the stoichiometric and kinetic perspectives as well as microbiological and physicochemical points of view. The effect of waste composition and the changes in operational parameters on the AD modeling is analyzed. Stoichiometric, kinetic, and dynamic models are discussed. According to the review, it was confirmed that a wide number of researchers prefer the Buswell model, the first-order model, the modified Gompertz model, and the anaerobic digestion model (ADM) depending on available data and lab infrastructure. The literature related to AD modeling does not present a consensus regarding the use of statistical criteria, being a key factor to reflect the goodness of fit of the models. It was observed that there are still gaps in the co-digestion modeling due to the mixing effects on the kinetics of the anaerobic digestion. Current co-digestion models are derived from the experimental design to prove synergy or antagonism. Nevertheless, there is a need to predict the co-substrate synergy or antagonism with the kinetics, an aspect that is not solved at present using current models. To fill this scientific gap, an additive model is proposed.

**Keywords** Anaerobic digestion · Co-digestion · First-order model · Gompertz model · Statistical criteria

## 14.1 Introduction

Anaerobic digestion (AD) is a complex process where facultative and anaerobic bacteria and methanogenic archaea interact to convert organic molecules (e.g., carbohydrates, lipids, proteins) into useful products. The product of greatest interest is a gaseous mixture of methane ($CH_4$) and carbon dioxide ($CO_2$), commonly known as biogas. The possibility of efficiently degrading organic matter while simultaneously producing biogas as an energy carrier makes AD suitable for the treatment of solid and liquid organic-rich waste. Today, AD is considered a mature technology (Wang et al. 2020; Zitomer et al. 2008).

The feasibility of AD to degrade organic matter into biogas is highly dependent on the characteristics of the organic matter, as well as physical and chemical factors that regulate the microbiological activity. Among the different factors that influence AD performance, temperature, pH, the presence of inhibitory compounds, and the

lack of micronutrients appear particularly relevant on process performance (González-Suárez et al. 2018; Nguyen et al. 2019).

Mathematical models are tools capable of modeling and predicting variations in process behavior as a result of operational and environmental changes, which allow the prediction of organic matter degradation and biogas production. Additionally, mathematical models are an alternative to lab-based research to improve the understanding of AD, as well as to develop strategies to improve process performance, e.g., act against the presence of inhibitions in the system.

Biomethane potential ($B_0$) is a critical parameter in anaerobic digestion application since it determines the maximum amount of methane that can be recovered from a substrate (Hafner et al. 2020). Numerous methodologies have been used to quantify the biomethane potential of sole or combined substrates, since this is a necessary step for any AD industrial application (Nguyen et al. 2019). The accuracy of these methodologies is generally high, but they are time-consuming (Amodeo et al. 2020).

There is a great diversity of mathematical models, which approach the AD process from different combinations of stoichiometric and kinetic perspectives as well as microbiological and physicochemical aspects (Echiegu 2015; Pavlostathis and Giraldo-Gomez 1991; Pererva et al. 2020b). Most of the mathematical equations used in the literature provide an explanation of the process by means of kinetic parameters. Finally, another important aspect to take into consideration is the mathematical complexity of the models. Two large groups of models can be distinguished, named as "simple" and "complex" models. Simple models prioritize identifying methane production, using linear and nonlinear algebraic equations. Complex models explain the simultaneous variations of microorganisms, substrates, and methane, generally by means of a set of ordinary differential equations.

## 14.2 Overview of Waste Biodegradation Under Anaerobic Conditions

### *14.2.1 Steps of Anaerobic Digestion Process*

In early stages, anaerobic digestion was simplified to a two-step process: fermentation (acid formation) and methanization (gas formation), each mediated by communities of bacteria and archaea that are physiologically different. The fermentation step was carried out by microorganisms able to convert carbohydrates, lipids, and proteins into fatty acids through hydrolysis and fermentation, to be later transformed into carbon dioxide and methane, by means of methanogenic archaea (Toerien and Hattingh 1969).

McCarty and Smith (1986) described the AD process using a stoichiometric model that involved three additional steps for the transformation of ethanol, propionate, and butyrate into methane. Each step transformed the organic molecule into

acetate with the release of a hydrogen molecule and a hydrogen cation. Methane was produced from two distinct pathways. On the one hand, the molecular hydrogen reacts with carbon dioxide to form part of the methane produced in the process. On the other hand, acetate ions react to form methane.

Today, the most common AD approach includes four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. Each step is mediated by a specific group of microorganisms (Batstone et al. 2006; Calusinska et al. 2018; Nakasaki et al. 2019). In hydrolysis, complex particulate biomolecules are degraded to monosaccharides, long-chain fatty acids (LCFA), and amino acids. Hydrolysis is exogenous and occurs from enzymes excreted by hydrolytic-fermentative bacteria. Subsequently, in the acidogenic step, monosaccharides and amino acids are transformed into propionic, butyric, and valeric acids and, to a lesser extent, into glycerol, ethanol, and methanol. In the acetogenic step, monosaccharides, amino acids, LCFA, and volatile fatty acids (VFA) are transformed into acetic acid, carbon dioxide, and hydrogen. In the methane-producing steps, acetic acid is transformed to methane by a group of methanogenic archaea called acetoclastic methanogens, while hydrogenotrophic methanogens produce methane from carbon dioxide and hydrogen (Batstone et al. 2006; Silva and De Bortoli 2020).

### *14.2.2 Effect of Waste Composition on the Anaerobic Process*

Several substrates are used as organic matter source for the anaerobic process. Most of them are waste streams from different anthropogenic activities. Table 14.1 summarizes the main characteristics of different substrates in order to illustrate their diversity. The classification of these wastes depends on their origin and composition. On the one hand, according to Chen et al. (2008), waste can be classified according to their origin, including:

1. Municipal wastes: These are generated in the urban sector from domestic, commercial, and service activities. Anaerobic treatment of these residuals usually includes stages of separation of the inorganic and organic fraction. Two major groups are distinguished: municipal wastewater and organic fraction of municipal solid waste (OFMSW).
2. Agricultural wastes: These are generated in rural sectors; in some cases, the generation points are far from each other, so the most common practices are on-site treatment. They are divided into animal waste and crop residues.
3. Industrial wastes: This group includes waste from agro-industries and chemical industries. Food industry wastes receive the most attention.

On the other hand, the amount and rate of methane production are influenced by the substrate empirical formula (i.e., content of carbon, hydrogen, oxygen, and nitrogen) and the molecular structure of the organic matter. Rasapoor et al. (2020) proposed a classification based on the waste composition:

**Table 14.1** Summary of different characterizations of wastes

| Waste | COD | TS | VS | Carb. | Lignin | Prot. | Lip. | C/N | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Mango leaves | n.d. | 89.85[b] | 80.15[d] | n.d. | n.d. | n.d. | n.d. | 29.70 | Abudi et al. (2020) |
| Pig manure | n.d. | 28.29[b] | 19.5[d] | n.d. | n.d. | n.d. | n.d. | 12.47 | |
| Paunch | 106[a] | 117[a] | 90.60[b] | 55.5[a] | n.d. | 10.2[a] | 4.5[a] | n.d. | Astals et al. (2014) |
| Blood | 178[a] | 187[a] | 95.19[b] | 3.7[a] | n.d. | 129.5[a] | 1.5[a] | n.d. | |
| DAF sludge | 353[a] | 360[a] | 98.06[b] | 0.6[a] | n.d. | 11.8[a] | 265[a] | n.d. | |
| Zucchini leaves | n.d. | 15.31[b] | 11.50[d] | 5.69[a] | 1.76[d] | 0.05[a] | n.d. | 8.48 | Cai et al. (2019) |
| Snow pea leaves | n.d. | 18.01[b] | 14.36[d] | 7.52[a] | 0.74[d] | 0.05[a] | n.d. | 12.72 | |
| Potato leaves | n.d. | 10.50[b] | 8.36[d] | 3.50[a] | 0.82[d] | 0.15[a] | n.d. | 7.01 | |
| Potato stem | n.d. | 5.28[b] | 3.68[d] | 1.46[a] | 0.16[d] | 0.03[a] | n.d. | 5.05 | |
| Pepper leaves | n.d. | 17.55[b] | 12.36[d] | 5.56[a] | 1.18[d] | 0.04[a] | n.d. | 7.94 | |
| Pepper stem | n.d. | 16.39[b] | 13.67[d] | 11.05[a] | 2.56[d] | 0.01[a] | n.d. | 12.96 | |
| Bell pepper leaves | n.d. | 16.59[b] | 13.02[d] | 5.80[a] | 0.84[d] | 0.15[a] | n.d. | 6.74 | |
| Bell pepper stem | n.d. | 12.52[b] | 10.07[d] | 5.78[a] | 0.85[d] | 0.05[a] | n.d. | 8.58 | |
| Eggplant leaves | n.d. | 18.74[b] | 14.00[d] | 6.89[a] | 1.03[d] | 0.09[a] | n.d. | 8.53 | |
| Eggplant stem | n.d. | 14.79[b] | 12.46[d] | 8.35[a] | 1.19[d] | 0.15[a] | n.d. | 16.23 | |
| Lettuce | n.d. | 4.87[b] | 3.77[d] | 2.07[a] | 0.74[d] | 0.05[a] | n.d. | 8.38 | |
| Spinach | n.d. | 8.89[b] | 6.81[d] | 2.9[a] | 0.66[d] | 0.05[a] | n.d. | 8.04 | |
| Bok choy | n.d. | 3.93[b] | 2.56[d] | 1.22[a] | 0.19[d] | 0.02[a] | n.d. | 5.26 | |
| Chinese cabbage | n.d. | 5.67[b] | 3.94[d] | 1.9[a] | 0.37[d] | 0.01[a] | n.d. | 5.83 | |
| Crown daisy | n.d. | 6.40[b] | 4.77[d] | 2.22[a] | 0.78[d] | 0.05[a] | n.d. | 7.41 | |
| Celery leaves | n.d. | 11.41[b] | 8.21[d] | 3.47[a] | 0.64[d] | 0.06[a] | n.d. | 11.08 | |
| Celery stem | n.d. | 3.95[b] | 2.71[d] | 2.42[a] | 0.48[d] | 0.04[a] | n.d. | 16.46 | |
| Rice husk | n.d. | 89.2[b] | 77.8[d] | n.d. | 18.9[d] | n.d. | n.d. | 99 | Contreras et al. (2012) |
| Rice straw | n.d. | 87.8[b] | 79.6[d] | n.d. | 8.6[d] | n.d. | n.d. | 43 | |
| Drying process rice | n.d. | 89.3[b] | 77.5[d] | n.d. | 10.4[d] | n.d. | n.d. | 33 | |

(continued)

**Table 14.1** (continued)

| Waste | COD | TS | VS | Carb. | Lignin | Prot. | Lip. | C/N | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Domestic food | 511.5[a] | 399.4[a] | 73.73[d] | n.d. | n.d. | n.d. | n.d. | n.d. | Dennehy et al. (2016) |
| Pig manure | 80.9[c] | 78.1[c] | 56.1[c] | n.d. | n.d. | n.d. | n.d. | n.d. | |
| Sewage sludge | n.d. | 6.7[b] | 73.9[d] | n.d. | n.d. | n.d. | n.d. | 8.54 | Güngören Madenoğlu et al. (2019) |
| Vinasse | 299.25[c] | 27.87[b] | 284.66[c] | 268.65[c] | n.d. | 9.12[c] | 6.89[c] | n.d. | Iqbal Syaichurrozi and Sumardiono (2014) |
| Glycerol | 1056[c] | 829[c] | 746[c] | n.d. | n.d. | n.d. | n.d. | n.d. | Jensen et al. (2014) |
| Glycerol | 912[c] | 933[c] | 844[c] | n.d. | n.d. | n.d. | n.d. | n.d. | |
| Chicken manure | 10.74[c] | 6.43[c] | 6.76[c] | n.d. | n.d. | n.d. | n.d. | 12.40 | Jijai and Siripatana (2017) |
| Dairy manure | n.d. | 16.91[b] | 10.25[d] | 7.93[a] | 1.58[d] | 1.45[a] | 0.43[a] | 25 | Kafle and Chen (2016) |
| Horse manure | n.d. | 24.97[b] | 18.61[d] | 14.92[a] | 4.53[d] | 3.03[a] | 0.87[a] | 23 | |
| Goat manure | n.d. | 81.63[b] | 64.23[d] | 50.19[a] | 11.17[d] | 12.00[a] | 2.72[a] | 20 | |
| Chicken manure | n.d. | 67.84[b] | 47.50[d] | 29.30[a] | 3.44[d] | 18.32[a] | 0.69[a] | 10 | |
| Swine manure | n.d. | 31.02[b] | 26.93[d] | 15.87[a] | 1.18[d] | 8.31[a] | 2.92[a] | 12 | |
| Raw dairy manure | 128.9[a] | 124[a] | 82.34[b] | 74.02[a] | 14.09[a] | 5.82[a] | 16.44[a] | n.d. | Labatut et al. (2011) |
| Cheese whey | 64.9[a] | 128.3[a] | 55.65[b] | 57.76[a] | 0[a] | 9.57[a] | 4.07[a] | n.d. | |
| Plain pasta | 934.3[a] | 442.6[a] | 96.47[b] | 342.01[a] | 0[a] | 70.45[a] | 14.52[a] | n.d. | |
| Meat pasta | 562.8[a] | 381.8[a] | 89.21[b] | 227.18[a] | 0[a] | 65.74[a] | 47.68[a] | n.d. | |
| Used vegetable oil | 2880[a] | 991[a] | 99.78[b] | 0[a] | 0[a] | 0[a] | 988.82[a] | n.d. | |
| Ice cream | 266.8[a] | 113.8[a] | 109.1[b] | 65.93[a] | 0[a] | 10.3[a] | 47.92[a] | n.d. | |
| Snap bean | n.d. | 21.08[b] | 18.30[c] | 15.45[a] | 1.08[d] | 4.48[a] | 0.72[a] | 11.65 | Li et al. (2018b) |
| Capsicum | n.d. | 20.35[b] | 16.41[c] | 15.29[a] | 1.69[d] | 3.08[a] | 0.34[a] | 15.45 | |
| Cucumber | n.d. | 21.87[b] | 16.56[c] | 16.33[a] | 2.46[d] | 1.93[a] | 0.44[a] | 22.76 | |
| Eggplant | n.d. | 19.40[b] | 16.66[c] | 15.13[a] | 2.04[d] | 2.90[a] | 0.69[a] | 16.10 | |
| Tomato | n.d. | 17.52[b] | 14.53[c] | 12.66[a] | 1.33[d] | 3.25[a] | 0.43[a] | 11.99 | |
| Food waste | n.d. | 19.10[b] | 93.20[d] | 11.80[b] | n.d. | 2.50[b] | 3.50[b] | 14.4 | Li et al. (2018a) |
| | n.d. | 12.70[b] | 95.40[d] | 36.00[b] | n.d. | 41.50[b] | 18.5[b] | 9.71 | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Borås-Sweden OFMSW | n.d. | 84[b] | 4[d] | 77[a] | n.d. | 26[a] | 12[a] | n.d. | Pagés-Díaz et al. (2014) |
| Mixed manure | n.d. | 35[b] | 40[d] | 180[a] | n.d. | 26[a] | 180[a] | n.d. | |
| Slaughterhouse | n.d. | 26[b] | 95[d] | 1[a] | n.d. | 130[a] | 175[a] | n.d. | |
| Mixed crop wastes | n.d. | 24[b] | 90[d] | 287[a] | n.d. | 21[a] | 2[a] | n.d. | |
| Mixed crop wastes | 55[a] | 54.0[a] | 83[d] | 50.1[e] | 15.6[e] | 12.6[e] | 10.0[e] | n.d. | Pagliaccia et al. (2019) |
| Kitchen waste | 325[a] | 236[a] | 95[d] | 79.8[e] | n.q. | 13.3[e] | 6.0[e] | n.d. | |
| Treviso-Italy OFMSW | 395[a] | 334[a] | 91[d] | 53.2[e] | 20[e] | 5.2[e] | 11.0[e] | n.d. | |

*Carb* carbohydrates, *Prot* proteins, *Lip* lipids
[a][g $kg^{-1}$ww]
[b][%]
[c][g $L^{-1}$]
[d][%TS]
[e][%COD]

1. Protein-rich residues include meat, bones, blood waste from slaughterhouse, food industry (Astals et al. 2014; Pagés-Díaz et al. 2014), swine and chicken manure (Kafle and Chen 2016). In anaerobic degradation of proteins, $NH_3$ is obtained as an intermediate product. Ammonia is used for cell growth, but high concentration can lead to process inhibition (Rasapoor et al. 2020).
2. Carbohydrate-rich wastes such as fruits, vegetables (Cai et al. 2019; Labatut et al. 2011; Pagés-Díaz et al. 2014), food waste (Labatut et al. 2011; Pagés-Díaz et al. 2014; Pagliaccia et al. 2019), and mixed rumen and paunch from slaughterhouse waste (Astals et al. 2014; Pagés-Díaz et al. 2014). Cai et al. (2019) characterized the carbohydrates from residue samples in correspondence of their nature: structural (lignin, cellulose, and hemicellulose) and nonstructural (soluble sugars). Structural carbohydrates are found in cell walls in leaves, stems, some vegetables, and fruits, as well as in manure fibers.
3. Lipid-rich organic matter includes waste from the oil processing industry, food waste (Labatut et al. 2011), dissolved air flotation fat sludge (Astals et al. 2014), and municipal wastewaters Nakasaki et al. (2019). Nakasaki et al. (2019) indicated that microorganisms and their enzymes can actively degrade the water-soluble fraction, but the low solubility of fats limits their degradation. Lipid-rich wastes during the hydrolysis step produce long-chain fatty acids (LCFA) which are inhibitory to AD at different degrees. The principal stages affected by the presence of LCFA are acetogenesis and methanogenesis. LCFA disrupt membrane functionality as they are adsorbed into the cell (Ohemeng-Ntiamoah and Datta 2018). Rodriguez-Mendez et al. (2017) proposed two indicators to prevent inhibition: LCFA dynamics and LCFA/$VS_{biomass}$ ratio. Those control parameters were useful to predict and estimate the process inhibition degree.

It is common to find lipid-rich waste with high content of protein. Microbial behavior is similar due to the complexity of the hydrolysis stage due to the transformation of both components. Nakasaki et al. (2019) found *Methanosaeta* as the most dominant archaea in lipid-rich substrate, while Ning et al. (2018) found *Methanospirillum* as the predominant methanogenic archaea. Studies developed by Zhu et al. (2019) demonstrated that LCFA strongly inhibit acetoclastic methanogens promoting methane formation from the hydrogenotrophic pathway.

Substrate chemical characterization is necessary to evaluate the performance in anaerobic digestion processes. Some basic parameters for substrate characterization are chemical oxygen demand (COD), total solids (TS), and volatile solids (VS), which are used to estimate substrate degradability. More detailed research analyzed the content of carbohydrates, proteins, and lipids to estimate the amount of methane to be produced and elemental analyses to identify imbalances in the supply of carbon and nitrogen in the medium. Some common practices are to present the characterizations based on COD, total solids, or, in the case of liquid residues, the mass concentration.

Factors such as temperature, pH, and acclimatization of the inoculum to the substrate can influence the behavior of the microbial community involved (Chen et al. 2008). According to Astals et al. (2015), in an AD reactor, failures occur due to

(1) inhibitions (reversible effects, cause the decrease in microbiological function) and (2) toxicity (biocidal effect in microbiological communities, generally irreversible but not necessarily fatal). These effects are the product of the accumulation of substances: (1) generated in the biological pathway (LCFA, ammonia, and sulfide), (2) specific to the composition of the substrate (light metals, heavy metals, chlorophenols, halogenated aliphatics, and lignin), and (3) contaminants added to the substrate (nanoparticles, pharmaceuticals and personal care products, surfactants, microplastics, coagulants, and flocculants).

In terms of the process, the substrate composition is crucial for biogas production and rate. Both response variables depend on the relative richness of lipids (yield related) and proteins (rate related) (Lee et al. 2020). In the case of carbohydrate-rich waste, *Firmicutes* and *Proteobacteria* are widely distributed due to the ability to transform macromolecules in acidic media as the findings reported by Satpathy et al. (2015), Zhao et al. (2017), and Li et al. (2019), among others. Mixing several wastes to compensate substrate deficiencies (a process known as anaerobic co-digestion) stands as a feasible option to reach higher methane yields (Pagés-Díaz et al. 2014). The literature mentions that mixtures of substrates can have synergistic or antagonistic effects on methane production (Abudi et al. 2020; Astals et al. 2014; Li et al. 2018a, b; Pagés-Díaz et al. 2014). On the other hand, stimulation from different sources has increased both methane yield and rate in more than 20% as proven by González-Suárez et al. (2018) and Xu et al. (2020). As far as we know, the better environmental conditions might be created to control and optimize the bioprocess. This reinforces the complexity of modeling AD in which minor changes in operational parameters or substrate composition swift the microbial community with relative important changes in response variables.

## 14.3 Modeling the Anaerobic Biodegradation of Residues

### *14.3.1 Stoichiometric Models*

The literature reflects a great diversity of mathematical models for predicting AD behavior. Symons and Buswell (1933) proposed an empirical oxide-reduction reaction for the DA of carbohydrates in the presence of water, which were transformed to carbon dioxide and methane:

$$C_aH_bO_c + \left(\mathrm{a} - \frac{b}{4} - \frac{c}{2}\right)H_2O \rightarrow \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4}\right)CO_2 + \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4}\right)CH_4 \quad (14.1)$$

This model was an approach to the estimation of methane production with an estimation uncertainty of close to 5% in substrates such as dextrose, lactose, maltose, and sucrose, among others (Buswell and Mueller 1952; Symons and Buswell 1933).

This stoichiometric model involved a two-step reaction, the first to transform organic molecules to organic acids and the second to form methane.

The model did not consider factors such as growth of microorganisms, time, temperature, or inhibitory conditions. Buswell and Mueller (1952) reaffirmed the model (Eq. (14.1)) and defined that the estimates made were valid for the mesophilic and thermophilic regimes, in addition to ensuring that the variations in the experimental and theoretical results were due to causes such as (1) $H_2$ gas production, (2) the presence of structural carbohydrates such as cellulose and lignocellulose, (3) the variation of pH in the reactors, and (4) concentrations of inhibitory agents. Equation (14.1) adopted the name of Buswell's formula; it was the beginning of the development of other models. From this point on, the mathematical modeling of anaerobic digestion has pursued three objectives: (1) characterizing the steps of AD, (2) evaluating the kinetics of the process, and (3) describing the interactions between the biochemical, chemical, and physical processes.

Labatut et al. (2011) used the Buswell formula to predict the theoretical methane yield ($B_{0\text{-}Theo}$) of food residues, manure, invasive aquatic plants, switchgrass, and various liquid residues, in addition to testing mixtures of excreta with part of the evaluated residuals. Experimental methane yields were estimated as the total volume of methane produced during digestion divided by the amount of volatile solids in the substrate initially added. The results of the comparison showed that the Buswell formula overestimates the methane yield, since the model does not consider the substrate biodegradable fraction. To fit the Buswell's formula, Labatut et al. (2011) defined the biodegradable fraction ($f_D$) as:

$$f_D = \frac{COD_D}{COD_T} \tag{14.2}$$

This expression considers the degradable chemical oxygen demand ($COD_D$) from the experimental methane yield and the proposed ratio of 1 g of chemical oxygen demand for each 350 mL of $CH_4$ produced under standard conditions of pressure and temperature (1 atm and 0 °C). The term $COD_T$ refers to the total chemical oxygen demand of the substrate, which can be determined analytically, or can also be calculated by means of the elemental composition or the macromolecular composition. From the correction of the theoretical yields, the behavior of the results reflected that the Buswell formula reports theoretical performance values of methane close to the theoretical ones, with an error of close to 10%.

The Buswell's formula is widely used in determining the theoretical methane yield. To simplify the stoichiometric model, the expression used is:

$$B_{0Theo}\left[NmL\ CH_4\ gVS^{-1}\right] = \frac{(4a + b - 2c)22400}{(12a + b + 16c)8} \tag{14.3}$$

Achinas and Euverink (2016), Adghim et al. (2020), Contreras et al. (2012), Pagés-Díaz et al. (2014), and Raposo et al. (2011) implemented the Buswell's formula to evaluate the biodegradability of various substrates as starch, cellulose,

gelatin, agricultural residuals, livestock waste, poultry, and piggery. In addition to the modification proposed by Labatut et al. (2011), the literature reports other modifications such as:

1. Modified Buswell's formula: This modification allows the prediction of the methane yield from substrates that contain proteins. The expressions representing the stoichiometric equation and the methane yield are (Contreras et al. 2012; Lubken et al. 2010):

$$C_aH_bO_cN_d + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4}\right)H_2O \rightarrow \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8}\right)CO_2 + \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{4}\right)CH_4 + dNH_3 \quad (14.4)$$

$$B_{0Theo}\left[NmL\ CH_4\ gVS^{-1}\right] = \frac{(4a + b - 2c - 3d)22400}{(12a + b + 16c + 14d)8} \quad (14.5)$$

2. Boyle's equation: This modification includes the estimation of $H_2S$ from the stoichiometric reaction (Deublein and Steinhauser 2008) and the theoretical methane yield (Frigon and Guiot 2010; Raposo et al. 2011):

$$C_aH_bO_cN_dS_e + \frac{(4a - b - 2c + 3d + 2e)}{4}H_2O \rightarrow \frac{(4a + b - 2c - 3d - 2e)}{8}CH_4 + \left[a - \frac{(4a + b - 2c - 3d - 2e)}{8}\right]CO_2 + dNH_3 + eH_2S \quad (14.6)$$

$$B_{0Theo}\left[NmL\ CH_4\ gVS^{-1}\right] = \frac{(4a + b - 2c - 3d - 2e)22400}{(12a + b + 16c + 14d + 32e)\ 8} \quad (14.7)$$

3. Pererva's modification: This modification includes phosphorus and metals in the composition of organic matter. Stoichiometric reaction and performance are (Pererva et al. 2020a):

$$C_aH_bO_cN_dS_eP_fMe_g + \left(\frac{4a - b - 2c + 3d + 2e + 11f + 3g\ v}{4}\right)H_2O \rightarrow \left(\frac{4a + b - 2c - 3d - 2e + 5f + g\ v}{8}\right)CH_4 + \left(\frac{4a - b + 2c + 3d + 2e - 5f - g\ v}{8}\right)CO_2 + dNH_3 + eH_2S + fH_3PO_4 + g\ Me(OH)_v \tag{14.8}$$

$$B_{0_{Theo}}\left[NmL\ CH_4\ gVS^{-1}\right] = \frac{(4a + b - 2c - 3d - 2e + 5f + g\ v)\ 22400}{(12a + b + 16c + 14d + 32e + 30.9f + M(Me)\ g)\ 8} \tag{14.9}$$

### *14.3.2 Kinetic Models*

Kinetic models are characterized by representing DA by means of nonlinear expressions as a function of time. According to Echiegu (2015), the kinetic models can be classified as microbial growth and kinetic models of methane production or cumulative reduction of the organic fraction.

#### 14.3.2.1 Microbial Growth Models

Contois (1959) identified how the specific growth rate of microorganisms in a DA reactor is related to the concentration of nutrients as well as population density. The relationship between the consumption of the limiting nutrient and the population density was represented by means of a linear expression:

$$c(S_0 - S) = (P - P_0) \tag{14.10}$$

The coefficient $c$ is the yield of the process [organisms $mL^{-1}$ $mM^{-1}$]; $S$ is the concentration of the limiting substrate [mM]; $P$ is the population density; finally, the subscript *0* designates the initial values. For the estimation of the specific growth rate ($R$) [$h^{-1}$], Contois used a non-steady-state mass balance of population density:

$$\frac{dP}{dt} = RP - DP \tag{14.11}$$

where $D$ is the dilution factor in the medium [$h^{-1}$]. Contois (1959) evaluated expression Eq. (14.11) for a continuous reactor under steady-state conditions and

deduced from the Monod equation a relationship between the growth rate and the concentration of the limiting nutrient:

$$D = R = \frac{R_m S_e}{A + S_e} \tag{14.12}$$

where $R_m$ [$h^{-1}$], $A$ [mM], and $S_e$ [mM] are the maximum growth rate, the concentration of the limiting nutrient when $R$ is ½ $R_m$, and the concentration of the limiting nutrient in equilibrium, respectively. McCarty and Mosey (1991) present the Contois model as:

$$-\frac{dS}{dt} = \frac{kXS}{(aS_0 + S)} = \frac{kXS}{(K_s + S)} \tag{14.13}$$

As observed in Eq. (14.13), $aS_0$ is related to the Monod kinetic constant ($K_s$) [mM], $k$ is the growth rate [$h^{-1}$], and $X$ is the concentration of the microorganism [organisms $mL^{-1}$]. In addition, the Monod performance equation is implemented in two ways. The first is for the growth of microorganisms, in which the maintenance constant ($m$) [$h^{-1}$] is presented:

$$\frac{dX}{dt} = Y\frac{dS}{dt} - mX \tag{14.14}$$

where $Y$ is the growth yield coefficient [mM $mM^{-1}$]. The second is for the cell decay stage, with its respective constant ($b$) [$h^{-1}$]:

$$\frac{dX}{dt} = Y\frac{dS}{dt} - bX \tag{14.15}$$

Both cases present equations with similar structures; these differ in the interpretation of $b$ and $m$. These constants in high-load reactors are ignored, as well as for methanogens, which have low maintenance and decay coefficients. Lawrence and McCarty (1969) implemented the model for steady-state reactors and concluded that the reciprocal of biological solids retention time ($\theta_c$) [h] relates to the specific net rate of growth ($\mu$) [$h^{-1}$]:

$$\frac{1}{\theta_c} = \frac{1}{X}\frac{dX}{dt} = \mu = \frac{akS}{K_s + S} - b \tag{14.16}$$

The behaviors of microbial communities in anaerobic reactors are diverse, for which other models have been developed to describe the system. Some models have been presented to evaluate the microbial growth rate ($\mu$), the substrate variation $\left(\frac{dS}{dt}\right)$, and the concentration of the substrate ($S$). Echiegu (2015), Öktem (2019), and Pavlostathis and Giraldo-Gomez (1991) summarize some models of microbial growth kinetics and substrate consumption:

1. First-order model:

$$\mu = \frac{kS}{S_0 - S} - b \tag{14.17}$$

$$-\frac{dS}{dt} = kS \tag{14.18}$$

$$S = \frac{S_0}{1 + k\theta_c} \tag{14.19}$$

2. Monod model:

$$\mu = \frac{\mu_{max} S}{K_s + S} - b \tag{14.20}$$

$$-\frac{dS}{dt} = \frac{\mu_{max} XS}{Y(K_s + S)} \tag{14.21}$$

$$S = \frac{K_s(1 + b\theta_c)}{\theta_c(\mu_{max} - b) - 1} \tag{14.22}$$

where $\mu_{max}$ is the maximum rate of microbial growth [$h^{-1}$].

3. Contois model:

$$\mu = \frac{\mu_m S}{BX + S} - b \tag{14.23}$$

$$-\frac{dS}{dt} = \frac{\mu_m XS}{Y(BX + S)} \tag{14.24}$$

$$S = \frac{B\ Y\ S_0(1 + b\theta_c)}{B\ Y\ (1 + b\theta_c) + \theta_c(\mu_m - b) - 1} \tag{14.25}$$

4. Grau model:

$$\mu = \frac{\mu_{max} S}{S_0} - b \tag{14.26}$$

$$-\frac{dS}{dt} = \frac{\mu_{max} XS}{YS_0} \tag{14.27}$$

$$S = \frac{S_0(1 + b\theta_c)}{\mu_{max}\theta_c} \tag{14.28}$$

5. Chen and Hashimoto model:

$$\mu = \frac{\mu_{max} S}{K S_0 + (1 - K) S} - b \tag{14.29}$$

$$-\frac{dS}{dt} = \frac{\mu_{max} XS}{KX + YS} \tag{14.30}$$

$$S = \frac{K\, S_0 (1 + b\theta_c)}{(K - 1)(1 + b\theta_c) + \mu_{max}\theta_c} \tag{14.31}$$

Microbial activity can be affected; in this sense, models have been developed to study factors such as temperature as well as inhibitions. Lawrence and McCarty (1969) related *Ks* to the fermentation temperature, with an expression similar to the Arrhenius equation:

$$\log \frac{(K_s)_2}{(K_s)_1} = 6980 \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \tag{14.32}$$

Echiegu (2015) indicated that a more accepted alternative to estimate the effect of temperature on reaction speed is the van't Hoff relationship:

$$r_T = r_o\, T_a^{(T - T_0)} \tag{14.33}$$

where $r_T$ can be either $\mu$ or $k$, at an operating temperature ($T$); $r_0$ is defined at a reference temperature ($T_0$), usually of 20 °C; and $T_a$ is the temperature activity coefficient.

McCarty and Mosey (1991) studied the influence of pH on AD and proposed an inhibition factor ($K_i$) and a pH inhibition function ($i_{pH}$):

$$-\frac{dS}{dt} = \frac{k\, K_i\, XS}{(aS_0 + S)} \tag{14.34}$$

$$\frac{dX}{dt} = Y \frac{dS}{dt} - i_{pH} bX \tag{14.35}$$

The inhibition factor ($K_i$) has been implemented in various expressions to estimate the microbial growth rate in the presence of recalcitrant agents. One of the most recurrent expressions is the Haldane equation, which is a direct modification of the Monod equation. Haldane equation and other modifications are presented by (Kul and Nuhoğlu 2020; Li et al. 2020; Pishgar 2011; Priya et al. 2018):

1. Haldane equation:

$$\mu = \frac{\mu_{max}\, S}{K_s + S + \left(\frac{S^2}{K_i}\right)} \tag{14.36}$$

2. Aiba equation:

$$\mu = \frac{\mu_{max}\, S \exp\left(-\frac{S}{K_i}\right)}{K_s + S} \tag{14.37}$$

3. Yano and Koga equation:

$$\mu = \left(\frac{\mu_{max}\, S}{K_s + S + \frac{S^2}{K_i}}\right) - \left(\frac{S^3}{K_i\, K_{YK}}\right) \tag{14.38}$$

4. Tseng equation:

$$\mu = \left(\mu_{max}\left(\frac{S}{K_s} + S\right)\right) - (K_i(S - S_m)) \tag{14.39}$$

where $S_m$ is the concentration of the recalcitrant agent for which the system has no inhibition [mg $L^{-1}$] and $K_{YK}$ is an adjustment positive constant of the Yano and Koga equation. Table 14.2 presents expressions for pH inhibition ($i_{pH}$) (Astals et al. 2014; Batstone et al. 2002; Rosén and Jeppsson 2006):

**Table 14.2** Inhibition expressions

| | |
|---|---|
| Noncompetitive inhibition | Hydrogen, free ammonia, propionate, butyrate, valerate, LCFA |
| $i = \frac{1}{1+\frac{S_I}{K_I}}$ (14.40) | |
| Empirical | Any pH range<br>Low pH range |
| $i_{pH} = \frac{1 + 2x10^{0.5(pH_{LL} - pH_{UL})}}{1 + 10^{(pH - pH_{UL})} + 10^{(pH_{LL} - pH)}}$<br>$i_{pH} = e^{\left(-3\left(\frac{pH - pH_{UL}}{pH_{UL} - pH_{LL}}\right)^2\right)}$ (14.41) | |
| Hill inhibition function | Amino acids, acetic acid, hydrogen |
| $i = \frac{K_{pH}^{n_i}}{S_{H^+}^{n_i} + K_{pH}^{n_i}}$<br>$K^n = 10^{-\frac{pH_{LL} + pH_{UL}}{2}}$ (14.42)<br>$n_i = \frac{3}{pH_{UL,i} - pH_{LL,i}}$ | |

#### 14.3.2.2 Production, Yield, and Cumulative Reduction Kinetics of the Organic Fraction

According to Husain (1998), the complete mathematical treatment of the DA process requires the simultaneous solution of material balance equations for each individual substrate and microbiological population. Due to the complexity of microbiological processes, part of the efforts has focused on the study of methane production as well as the reduction of organic components. Brulé et al. (2014) describe the organic matter consumption by means of a first-order reaction model:

$$\left(\frac{dS_t}{dt}\right) = -k\, S_t \tag{14.43}$$

where k is the first-order kinetic constant [$d^{-1}$] and $S_t$ is the organic substrate concentration over the time [g $L^{-1}$]. The negative sign stands for the consumption of organic matter. When applying the separation of variables, the integral expression is:

$$\int_{S_0}^{S_t} \frac{dS_t}{S_t} = -k \int_{t_0=0}^{t_f=t} dt \tag{14.44}$$

The solution of the definite integral is:

$$S_t = S\, e^{-kt} \tag{14.45}$$

Brulé et al. (2014) explain that by rearranging terms Eq. (14.45) can be expressed in relation to the products formed ($B$):

$$B = B_0 \left(1 - e^{-kt}\right) \tag{14.46}$$

where $B$ represents the variable on which the system is evaluated; this can be (1) methane yield [NmL $gVS^{-1}$] or [NmL $gCOD^{-1}$]; (2) methane production [mL] or [L]; or cumulative reduction of organic compounds (e.g., volatile solids, lipid, carbohydrates, and protein reduction) over the time [d]; $B_0$ is the maximum value of $B$. The literature reports the use of the first-order kinetic model and other expressions such as modified Gompertz model, Cone model, Fitzhugh model, and transfer function. Table 14.3 presents these models of great relevance in the kinetic study.where $k$ is the first-order kinetic constant of the process [$d^{-1}$], $\lambda$ is the lag time phase [$d^{-1}$], and $n$ is a shape factor. The literature explores other models that are used much less frequently. Some models are based on the mathematical structure of microbial growth rate models such as Monod as well as Chen and Hashimoto. Another part of these models are empirical modifications to the first-order model.

**Table 14.3** Most frequently used models to describe methane yield kinetics

| | |
|---|---|
| Modified Gompertz model $B = B_0\, e(-e^{-\frac{e\ \mu_m(t-\lambda)}{B_0}+1})$ (14.47) | Abudi et al. (2020), Andriamanohiarisoamanana et al. (2017), Astals et al. (2014), Bedoić et al. (2020), Benabdallah El Hadj et al. (2009), Bohutskyi et al. (2018), Buendía et al. (2009), Cai et al. (2019), Chatterjee et al. (2017), Das Ghatak and Mahanta (2017), Dennehy et al. (2016), Dumitrel et al. (2017), Gallipoli et al. (2020), Güngören Madenoğlu et al. (2019), Iqbal Syaichurrozi and Sumardiono (2014), Jijai and Siripatana (2017), Kafle and Chen (2016), Koch et al. (2019), Li et al. (2018a, b), Maamri and Amrani (2019), and Zhen et al. (2016) |
| Cone model $B = \frac{B_0}{1+(kt)^{-n}}$ (14.48) | Abudi et al. (2020), Achinas and Euverink (2019), Bedoić et al. (2020), Cai et al. (2019), Güngören Madenoğlu et al. (2019), Li et al. (2018a), and Zhen et al. (2016) |
| Fitzhugh model $B = B_0(1 - e^{-kt})^n$ (14.49) | Cai et al. (2019), Contreras et al. (2012), and Li et al. (2018a) |
| Transfer function $B = B_0(1 - e^{-\frac{\mu_m(t-\lambda)}{Y_{max}}})$ (14.50) | Abudi et al. (2020), Bohutskyi et al. (2018), Gallipoli et al. (2020), and Li et al. (2018a) |

Pererva et al. (2020b), who reviewed existing empirical kinetic models, identified 19 kinetic models (including the models in Table 14.3).

The kinetic study of an AD system allows predicting the behavior of an anaerobic digester against variations in the concentration of substrates, organic loads, variations in pH, temperature, and other operating conditions. Therefore, the proper selection of the model is a rigorous task. The various investigations report statisticians for the selection of a model, among which are coefficient of determination ($R^2$), model efficiency (ME), sum of absolute errors (SAE), sum of squared errors (SSE), root-mean-square error (RMSE), average relative error (ARE), hybrid fractional error function (HYBRID), Marquardt's percentage standard deviation (MPSD), Akaike's information criterion (AIC), and corrected Akaike's information criterion (AICc). These error function can be classified in four groups: (1) percentual or fractional indicators of approach to the trends of the experimental data, (2) model errors, (3) error deviation, and (4) model comparison criteria. Table 14.4 shows the relationship between the groups of statisticians and the objectives pursued by the optimization of each statistician.where $B_{model,\ i}$ is the model evaluated in the *i*th point, $B_{exp}$ is the *i*th experimental value, *N* is the number of data points, and p is the number of adjusted parameters in the model. Table 14.4 shows that the objective to which each model is oriented is different. $R^2$ and ME present values between 0 and 1. A value close to 1 is an indicator of the best fit of the model. SAE, SSE, and ARE explain the differences between models by quantifying the absolute distance between each point of the model and the experimental data. The values of these error functions are positive, and their proximity to zero is the indicator of a smaller error and, therefore, a better fit of the model. SAE, SSE, and ARE explain the differences between models by quantifying the absolute distance between each point of the model and the experimental data. The values of these statisticians are positive,

**Table 14.4** Goodness of fit parameters

| Group | Expression | Objective |
|---|---|---|
| (i) | $R^2 = \frac{\sum_{i=1}^{N}(B_{model,i}-B_{\exp,i})^2}{\sum_{i=1}^{N}[(B_{exp,i}-\bar{B_{exp}})^2+(B_{model,i}-\bar{B_{exp}})^2]}$ (14.51) | $R^2 \approx 1$ |
| | $ME = \frac{\sum_{i=1}^{N}(B_{\exp,i}-\bar{B_{exp}})^2-\sum_{i=1}^{N}(B_{\mathrm{mod},i}-B_{\exp,i})^2}{\sum_{i=1}^{N}(B_{\exp,i}-\bar{B_{exp}})^2}$ (14.52) | ME ≈ 1 |
| (ii) | $SAE = \sum_{i=1}^{N}\left\lvert B_{model}-B_{exp}\right\rvert_i$ (14.53) | SAE ≈ 0 |
| | $SSE = \sum_{i=1}^{N}\left(B_{model}-B_{exp}\right)_i^2$ (14.54) | SSE ≈ 0 |
| | $ARE = \frac{100}{N}\sum_{i=1}^{N}\lvert\frac{(B_{model,i}-B_{exp,i})^2}{B_{exp,i}}\rvert$ (14.55) | ARE ≈ 0 |
| (iii) | $RMSE = \sqrt{\frac{\sum_{i=1}^{N}\left(B_{model,i}-B_{exp,i}\right)^2}{N}}$ (14.56) | RMSE ≈ 0 |
| | $MPSD = 100\sqrt{\frac{1}{N-p}\sum_{i=1}^{N}\left[\frac{(B_{model,i}-B_{exp,i})}{B_{exp,i}}\right]^2}$ (14.57) | MPSD ≈ 0 |
| | $HYBRID = \frac{100}{N-p}\sum_{i=1}^{N}\left[\frac{(B_{model,i}-B_{exp,i})^2}{B_{exp,i}}\right]$ (14.58) | HYBRID ≈ 0 |
| (iv) | $AIC = N\ln\left(\frac{\sum_{i=1}^{N}(B_{model,i}-B_{exp,i})^2}{N}\right)+2(p+1)$ (14.59) | Minimization |
| | $AIC_c = N\ln\left(\frac{\sum_{i=1}^{N}(B_{model,i}-B_{\exp,i})^2}{N}\right)+2(p+1)+\frac{2(p+1)(p+2)}{N-p}$ (14.60) | Minimization |

and their proximity to zero is the indicator of a smaller error and therefore a better fit of the model. RMSE, MPSD, and HYBRID quantify the dispersion of the errors and, as in the previous case, values close to zero indicate a good fit. Finally, AIC and AICc are alternative methods used for model comparison, in which the change of goodness of fit of the model is balanced by the number of model parameters, in addition to comparing nested and non-nested models. According to Donoso-Bravo et al. (2011), model selection is a delicate task due to the parameter identification dependence on experimental information. The literature related to AD does not present a consensus regarding the use of statistical criteria. Table 14.5 identifies the expressions used in various investigations, relates the applied models, and identifies the statistics used.

Table 14.5 indicates that the first-order kinetic model and the modified Gompertz model are the most used expressions to describe these processes. The first-order kinetic model is the simplest model to interpret, adjust, and apply to any chemical, biological, or physical process. On the other hand, the modified Gompertz model is

**Table 14.5** Statistical criteria used in model evaluation. First-order kinetic (FO), modified Gompertz (MG), Cone (CM), Fitzhugh (FM), transfer function (TF)

| Reference | FO | MG | CM | FM | TF | Statistical criteria |
|---|---|---|---|---|---|---|
| Abudi et al. (2020) | x | x | x | | x | RMSE; $R^2$; AIC |
| Achinas and Euverink (2019) | x | | x | | | RMSE; $R^2$ |
| Astals et al. (2014) | x | | | | | SSE |
| Andriamanohiarisoamanana et al. (2017) | x | x | | | | $R^2$ |
| Bedoić et al. (2020) | x | x | x | | | RMSE |
| Bohutskyi et al. (2018) | x | x | | | x | RMSE; $R^2$ |
| Buendía et al. (2009) | | x | | | | $R^2$ |
| Cai et al. (2019) | x | x | x | x | | $R^2$ |
| Contreras et al. (2012) | x | | | x | | $R^2$ |
| Chatterjee et al. (2017) | x | x | | | | SSE; SAE; ARE; HYBRID; MPSD; $R^2$ |
| Da Silva et al. (2018) | x | | | | | $R^2$ |
| Das Ghatak and Mahanta (2017) | | x | | | | $R^2$ |
| Dennehy et al. (2016) | x | x | | | | RMSE; $R^2$ |
| Du et al. (2019) | x | | | | | $R^2$ |
| Dumitrel et al. (2017) | | x | | | | RMSE; $R^2$ |
| Gallipoli et al. (2020) | x | x | | | x | $R^2$ |
| Güngören Madenoğlu et al. (2019) | | x | x | | | $R^2$ |
| Iqbal Syaichurrozi and Sumardiono (2014) | x | x | | | | $R^2$ |
| Jijai and Siripatana (2017) | | x | | | | $R^2$ |
| Kafle and Chen (2016) | x | x | | | | RMSE; $R^2$ |
| Koch et al. (2019) | x | x | | | | ME |
| Li et al. (2018b) | x | x | | | | RMSE; $R^2$ |
| Li et al. (2018a) | x | x | x | x | x | RMSE; $R^2$; AICc |
| Maamri and Amrani (2019) | | x | | | | SE; $R^2$ |
| Pagés Diaz et al. (2011) | x | | | | | $R^2$ |
| Zhen et al. (2016) | x | x | x | | | RSS; RMSE; $R^2$; AIC |

used in conditions for which the inoculum supplied to the medium presents a delay due to substrate adaptation.

It is also observed that $R^2$ is commonly used to describe goodness of fit in the kinetic models. Spiess and Neumeyer (2010) indicate that $R^2$ is the measure in which the variance of the data is explained by a linear fit, so its use as a measure of the goodness of fit in nonlinear models is a common error.

Nash and Sutcliffe (1970) developed the ME error function, which is a derivation from $R^2$, but the interval in which is bigger ($-\infty$ to 1). In addition, the interpretation is different: (1) a value of 1 indicates the best fit and (2) a value of zero indicates that the model is as good as using the mean of the observations. Values above 0.8 ensure the fit of the models.

The SAE, SEE, ARE, and RMSE criteria do not evaluate the number of parameters in the models, so two or more models could coincide; in this case, the selection will depend on the variability of the errors. HYBRID and MPSD consider in the denominators a term for the *i*th observation, so in the case of measurements at the initial time for which the values are zero, the model is indeterminate.

Akaike (1974) indicates that the AIC logarithmic probability term decreases the gaps between the experimental data and the models. Abudi et al. (2020) and Pererva et al. (2020b) consider the use of AIC pertinent, given that the probability that the selected model is the best increases as the AIC values are lower.

A common practice in fitting kinetic models is the use of only one or two statisticians in the analysis. To increase reliability in model assessment is necessary to implement combined goodness of fit criteria. Within the model selection strategy, the graphic analysis of the residuals must be considered since this allows us to easily identify if the model generates random errors or if, on the contrary, they describe trends.

### *14.3.3 Dynamic Models*

A dynamic model considers changes in one or more dependent variables in relation to time. The general formulation of these models considers macroscopic mass balance:

$$\frac{dm_i}{dt} = -\Delta(\rho vs) + W_i^m + r_i V_{tot} \tag{14.61}$$

where $dm_i/dt$ is the accumulation of an i component, in a defined control volume; $-\Delta(\rho\ v\ s)$ is the mass flow differential between control volume limits; $W_i^m$ represents mass transfer processes; $r_i$ is the kinetic law; and $V_{tot}$ is the reactant system volume. These models can represent processes in steady or non-steady states, in which the boundary limits correspond to the inputs and outputs of the reacting system. The terms for reactive processes in Eq. (14.61) are supported by the expressions of kinetic models.

In these models, the interactions between various components and processes are related. One of the dynamic models that stands out the most is the anaerobic digestion model 1 (ADM1) created by Batstone et al. (2000), which served as a baseline for other dynamic models. The ADM1 is a macroscopic mass balance model, which takes into account biochemical conversion processes (kinetics of microbial growth and digestion), as well as physicochemical conversion of mass transfer processes. According to Batstone et al. (2000), for the creation of ADM1, kinetic models were taken into account for the degradation of substrates that consider the substrate and biomass concentrations, as well as including inhibitions by hydrogen and pH. Enzymatic conversion processes are considered, which are carried out by means of soluble enzymes produced by the bacterial group that directly uses the

**Table 14.6** Biological, physical, and chemical processes in ADM1

| Process (number of species involved) | Kinetic model |
|---|---|
| Disintegration of complex material and hydrolysis (4) | $r_i = k_{dis,\ i}\ X_i$ (14.62) |
| Acidogenesis (3) | $r_i = k_{m,i} \frac{S_i}{K_{S,i}+S_i}\ X_i\ I_i$ (14.63) |
| Acetogenesis (2) | $r_i = k_{m,product} \frac{S_i}{K_{S,product}+S_i}\ X_{product} \frac{S_i}{S_j+S_i+1e-6}\ I_i$ (14.64) |
| Methanogenesis (3) | $r_i = k_{m,i} \frac{S_i}{K_{S,i}+S_i}\ X_i\ I_i$ (14.65) |
| Cell decay (7) | $r_i = k_{dec,X_i}\ X_i$ (14.66) |
| Acid base dissociation (6) | $r_{A,\ i} = k_{AB,\ i}(S_{i-}(K_{a,\ i} + S_{H+}) - K_{a,\ i}S_i)$ (14.67) |
| Gas transfer (3) | $r_{T,\ i} = k_L a(S_i - K_{H,\ i}P_{gas,\ i})$ (14.68) |

associated substrate. Enzyme production is directly related to the growth rate of the specific bacterial group and can be inhibited by the concentration of soluble substrate. The kinetic equations implemented in ADM1 are divided according to the process. Table 14.6 presents the general expressions for biological, physical, and chemical processes.

ADM1 has been widely implemented for the prediction of AD substrate, product, and by-product concentrations. Jeong et al. (2005) implemented genetic algorithms to estimate the model parameters. Thus demonstrating that the results of methane concentration by simulation fit the experimental data, although the concentrations of acetic and propionic acid presented deviations between the calculated and experimental data. Rosén and Jeppsson (2006) implemented the ADM1 model, with 110 equations and complex characterization of inocula and substrates required to model the digesters' start-up. Modifications have been made to the kinetic equations of ADM1 for simulation with various types of substrates including municipal, agricultural, and excreta solid waste (Zhao et al. 2018).

Batstone et al. (2006) indicated that ADM1 is a model that can be adapted to the study conditions of anaerobic digestion reactors. Some modifications have been made to ADM1, among which are:

1. Trace elements: Frunzo et al. (2019) evaluated the addition of trace elements in the AD. They considered dissolution processes for metal ions, sulfur, and phosphorus that influence biological processes due to consumption and the inhibition or stimulation effects of the process. Other physical and chemical processes considered were precipitation, complexation, metal sorption, and hydrogen sulfide mass transfer.
2. Phosphorus, sulfur, and iron: Flores-Alsina et al. (2016) modeled three extensions that considered processes related to phosphorus, sulfur, and iron. In the first extension, they added terms related to phosphorus consumption and its impact on the production of valerate, butyrate, propionate, and acetate. In the second extension, they evaluated the reduction of sulfate to sulfide from two pathways. The first pathway considered a single group of reducing sulfate microorganisms with $H_2$ consumption as electron donor. In the second pathway, multiple electron

donors were considered ($H_2$, valerate, butyrate, propionate, and acetate). The third extension evaluated the transformation of Fe(III) to Fe(II), using $H_2$ and sulfide as electron donors; this also estimates the precipitation rate of iron sulfide (FeS) as well as phosphates of iron ($FePO_4$ and $Fe_3(PO_4)_2$).

3. Propionate degradation pathway: Uhlenhut et al. (2018) used ADM1 as a basis for comparison against a previously established extension ($ADM1_{xp}$). This modification considered the fraction of inert decay products, through the evaluation of a cell death factor. From this comparison, the authors proposed an original extension called ADM1xpro. In this extension, the term referring to the propionate-oxidizing microorganisms was divided into three terms for a tri-culture media. Also, the researchers tested two propionate bioconversion paths. The first path considered the transformation of propionate into butyrate, and later into $H_2$ and acetate. The second path proposed the direct reaction of propionate into $H_2$, acetate, $CH_4$, and $CO_2$.
4. Free ammonia inhibition: Bai et al. (2017) implemented ADM1 and compared three free ammonia inhibition models: simple inhibition, Monod, and non-inhibition forms as established in Table 14.2.

According to Li et al. (2014), the most common parameters for the characterization of DA processes are pH, volatile fatty acids, alkalinity, biogas production, as well as the variation of total and volatile solids. Another modifications to ADM1 that allow working the model with kinetic parameters related to conventional characterizations in total, volatile, and suspended solids, in addition to carbohydrates, lipids, proteins, inerts, and elemental analysis (Zhao et al. 2018). The results obtained in this modification are adjusted to the experimental data ($R^2$ between 0.991 and 0.993), despite the fact that they only adjusted 5 of the 18 kinetic parameters proposed by Batstone et al. (2000).

Kythreotou et al. (2014) and Aceves-Lara et al. (2005) agree that the predictive capabilities of a model, such as ADM1, will be reduced due to parameters that have not been correctly estimated, even when the model's structure is relevant. Wichern et al. (2008) indicate that the results obtained using ADM1 may vary due to the fact that there are parameters such as the fractions of particulate materials and carbohydrates that have a strong impact on model outputs.

## 14.4 Co-digestion

Estimating methane production in anaerobic co-digestion represents a challenge due to the synergistic and antagonistic effects from substrate interaction. The usual practices reported in the literature for the evaluation of co-digestion mixtures include:

1. Comparison of the experimental methane yields of the co-substrates against the substrates individually

**Table 14.7** Substrate mixture experiment designs

| *No.* | *ML* | | *PM* | | *Experimental methane yield (mL $gVS^{-1}$)* | Abudi et al. (2020) |
|---|---|---|---|---|---|---|
| 1 | 75 | | 25 | | 340 | |
| 2 | 50 | | 50 | | 375 | |
| 3 | 25 | | 75 | | 465 | |
| *No.* | *SW* | *MM* | *CR* | *OFMSW* | *Experimental methane yield (mL $gVS^{-1}$)* | Pagés-Díaz et al. (2014) |
| 4 | 50 | 50 | 0 | 0 | 613 | |
| 5 | 0 | 50 | 50 | 0 | 432 | |
| 6 | 0 | 0 | 50 | 50 | 470 | |
| 7 | 50 | 0 | 50 | 0 | 461 | |
| 8 | 0 | 50 | 0 | 50 | 461 | |
| 9 | 50 | 0 | 0 | 50 | 647 | |
| 10 | 33.33 | 33.33 | 33.33 | 0 | 622 | |
| 11 | 0 | 33.33 | 33.33 | 33.33 | 535 | |
| 12 | 33.33 | 0 | 33.33 | 33.33 | 621 | |
| 13 | 33.33 | 33.33 | 0 | 33.33 | 617 | |
| 14 | 25 | 25 | 25 | 25 | 641 | |
| *No.* | *M* | *PP* | | *CW* | *Experimental methane yield (mL $gVS^{-1}$)* | Labatut et al. (2011) |
| 15 | 75 | 25 | | 0 | 353,5 | |
| 16 | 90 | 10 | | 0 | 285,6 | |
| 17 | 75 | 0 | | 25 | 252,4 | |
| 18 | 90 | 0 | | 10 | 237,6 | |

2. Analysis of the variation of the kinetic constants of the co-substrates with respect to the mono-substrates

To evaluate co-substrate methane yield, it is necessary to apply a mixture design of experiments. The complexity of the design of experiments depends on the objective of the study and the complexity of the substrate. To estimate whether or not the co-substrates have synergistic or antagonistic effects, a single mixture would suffice. However, a larger number is typically required to build up evidence. In the case of optimization, efforts should be made to identify every possible interaction between the substrates.

Below are the experimental designs from three experiences reported in the literature. Abudi et al. (2020) evaluated the anaerobic digestion of mango leaves and pig manure, which reported yields of 157 and 281 mL $gVS^{-1}$, respectively, subsequently performed binary mixtures in volatile solids ratios of 75:25, 50:50, 25:75. Pagés-Díaz et al. (2014) report methane yield from slaughterhouse waste (SW) (609 mL $gVS^{-1}$), mixed manure (MM) (384 mL $gVS^{-1}$), mixed crop residues (CR) (422 mL $gVS^{-1}$), and OFMSW (533 mL $gVS^{-1}$), from which they consider the TS and make binary mixtures (50:50), ternary (33.33:33.33:33.33), and

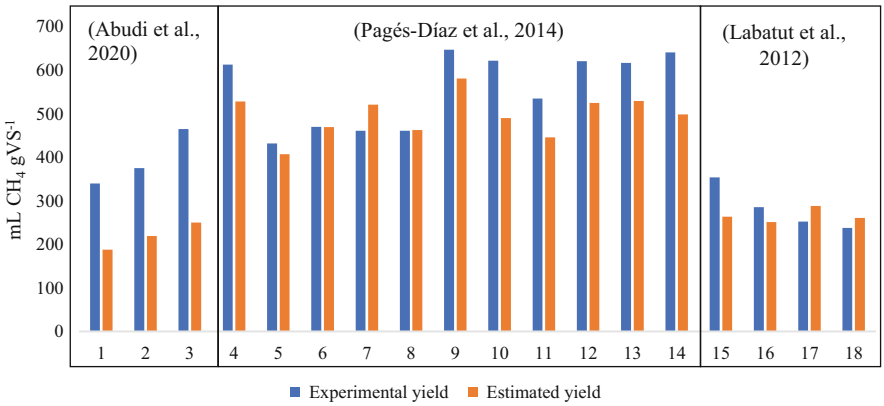


**Fig. 14.1** Comparison between experimental and estimated methane yields

quaternary (25:25:25:25). Labatut et al. (2011) evaluated the effects of binary mixtures of manure (242.7 mL $gVS^{-1}$) with various substrates like cheese whey (423.6 mL $gVS^{-1}$) and plain pasta (326.1 mL $gVS^{-1}$) in VS ratios of 75:25 and 90:10 with respect to manure. Table 14.7 presents the mixtures made in the different investigations as well as experimental methane yields.

The literature evaluates the results of anaerobic co-digestion by means of statistical analysis. Pagés-Díaz et al. (2014) evaluated co-substrate effects by means of the polynomial:

$$B = \sum_i \beta_i X_i + \sum_i \sum_j \beta_{i,j} X_i X_j + \sum_i \sum_j \sum_k \beta_{i,j,k} X_i X_j X_k \tag{14.69}$$

where $X_i$, $X_j$, and $Xk$ are the fractions of each substrate, $\beta_i$ refers to the maximum mono-substrate yield, and $\beta_{i,j}$ and $\beta_{i,j,k}$ are related to the synergistic and antagonistic effects of binary and ternary mixtures, respectively.

Labatut et al. (2011) applied Buswell's formula to identify substrate and co-substrate theoretical methane yields. They established the biodegradability of substrates and co-substrates from expression (14.2) and used it as a measure of synergistic and antagonistic effects.

Abudi et al. (2020) applied a simpler approach to evaluate methane yield based on the VS mixture proportion. The expression by which they estimate the methane yield of a mixture that does not present synergistic or antagonistic effects is:

$$B_0 = \sum_i VS_i B_{0,i} \tag{14.70}$$

Expression Eq. (14.70) refers to the *i* component of a mixture. For its simplicity, this expression will be used to analyze the synergistic and antagonistic effects of the

**Table 14.8** Kinetic data of selected cases

| *Mango leaves to pig manure ratio* | | *100:0* | *75:25* | *50:50* | *25:75* | *0:100* | Abudi et al. (2020) |
|---|---|---|---|---|---|---|---|
| $B_0$ | mL $CH_4$ $gVS^{-1}$ | 155.1 | 336 | 368 | 454 | 278 | |
| $k$ | $day^{-1}$ | 0.1645 | 0.0694 | 0.0707 | 0.2245 | 0.1505 | |
| $n$ | – | 1.2669 | 0.776 | 0.6954 | 1.1409 | 0.9957 | |
| *Microalgae to food waste ratio* | | *100:0* | *38.15:61.85* | *14.9:85.1* | *5.98:94.02* | *0:100* | Du et al. (2019) |
| $B_0$ | mL $CH_4$ $gVS^{-1}$ | 292 | 329.8 | 385.4 | 415 | 383.9 | |
| $k$ | $day^{-1}$ | 0.16 | 0.46 | 0.35 | 0.32 | 0.31 | |
| *Microalgae to sewage sludge* | | *100:0* | *66.83:33.17* | *50.01:49.99* | *33.34:66.66* | *0:100* | |
| $B_0$ | mL $CH_4$ $gVS^{-1}$ | 292 | 324 | 314 | 295 | 278.7 | |
| $k$ | $day^{-1}$ | 0.16 | 0.16 | 0.16 | 0.16 | 0.15 | |

mixtures reported in Table 14.7. In the case of Pagés-Díaz et al. (2014), VS data reported in Table 14.1 were used. Figure 14.1 presents the comparison between the experimental and estimated results.

Figure 14.1 shows that the estimates are, in some cases, less than the experimental results. The increased methane yield is an indication of the synergistic effects experienced in co-substrate. Mixtures 1–4 and 9–15 exhibit synergistic effects during co-digestion. Mixtures 6 and 8 do not present effects. Mixtures 5 and 16 cannot be defined as synergistic due to minimal differences between experimental and estimated values. This approach can be applied to the treatment of kinetic data, for which expression Eq. (14.70) is set as:

$$B = \sum_i VS_i B_i \tag{14.71}$$

The difference between Eqs. (14.70) and (14.71) is that the first one only evaluates the maximum methane yield and the second one evaluates the kinetic behavior of the methane yield of each experimental run. Table 14.8 presents the adjusted kinetic for mono- and co-substrate presented by Abudi et al. (2020) and Du et al. (2019) that used Cone and first-order models, respectively.

From the information presented in Table 14.8, Eq. (14.71) was evaluated. Figure 14.2 presents the kinetics from the experimental data and from Eq. (14.71).

According to Abudi et al. (2020), Du et al. (2019), Labatut et al. (2011), and Pagés-Díaz et al. (2014), mixing waste tends to improve methane yield. With both expressions, the results obtained differ from what was experimentally proposed. It should be noted that both expressions only consider the additive contribution of each mono-substrate component to the co-digestion methane yield.

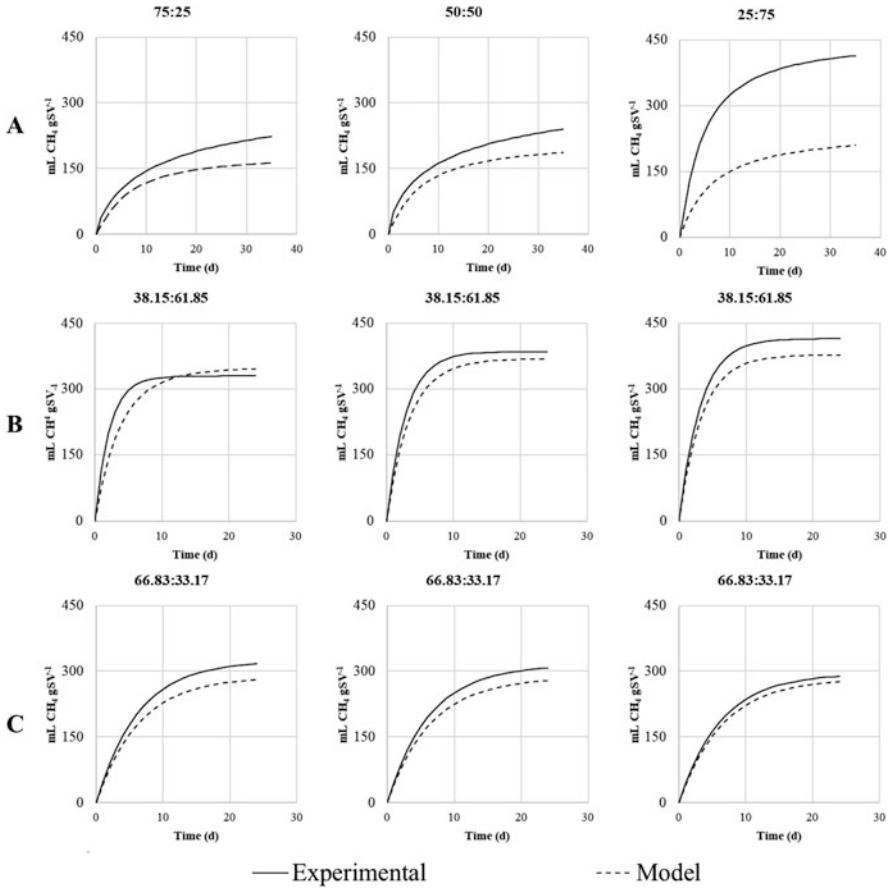


**Fig. 14.2** Comparison between experimental kinetics and modeled kinetics in co-digestion. (**a**) Mango leaves—pig manure. (**b**) Microalgae—food waste. (**c**) Microalgae—sewage sludge

The importance of Eq. (14.71) lies in the possibility of establishing the extent to which the methane yield of the substrates varies, which is of interest to establish a mixture optimization route. On the other hand, it should be noted that the conventional analysis of the mixture effects is based on mono-substrate kinetics (first-order, modified Gompertz, Cone models, and others), which is convenient in terms of making a comparison, but does not allow to estimate the performance of methane or kinetic constants without having an experimental design. Astals et al. (2014) indicate that mixture effects, both synergies and antagonisms, affect the kinetics of the process. Therefore, a mathematical expression can be established to consider the mixture effect on methane yield as well as on the kinetic constants of the process.

## 14.5 To Model or Not to Model: Where Is Really the Opportunity?

### *14.5.1 Trends in Anaerobic Digestion Modeling*

To identify research trends, an analysis of titles, keywords, and abstracts of the publications made in Scopus between 2010 and 2020 was carried out. The search terms focused on:

1. First-order kinetic model to describe methane performance
2. Modified Gompertz kinetic model to describe methane performance
3. Cone kinetic model to describe methane performance
4. Fitzhugh kinetic model to describe methane performance
5. Transfer function to describe methane performance
6. Anaerobic digestion model 1

In total, 853 journal articles between 2010 and 2020s first semester refer to terms related to kinetic models to describe methane performance. Figure 14.3 shows the proportion of the research items that evaluate the proposed models. The analysis of Fig. 14.3 did not rule out publications using more than two models.

It is observed that the first-order model is the most widely used expression to describe the methane yield kinetics. This analysis is in accordance with what is proposed in Tables 14.3 and 14.5, which highlights the wide application of the first-order model.

In addition, the comparison of the application of the first-order model and the ADM1 was made; this was done from two perspectives:

1. Countries with the highest number of publications (Fig. 14.4)
2. Number of publications from 2010 to 2020 (Fig. 14.5)

It is observed that the country with the highest contribution in terms of methane yield modeling is China, with just over 100 publications in the period evaluated, followed by the USA with around 60 publications. Regarding ADM1, a total of

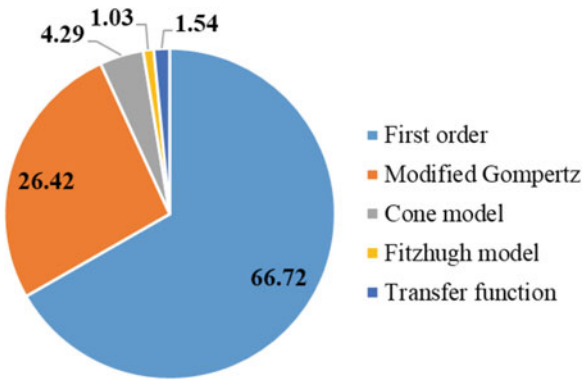


**Fig. 14.3** Percentage of publications between 2010 and 2020 related to the methane yield kinetics

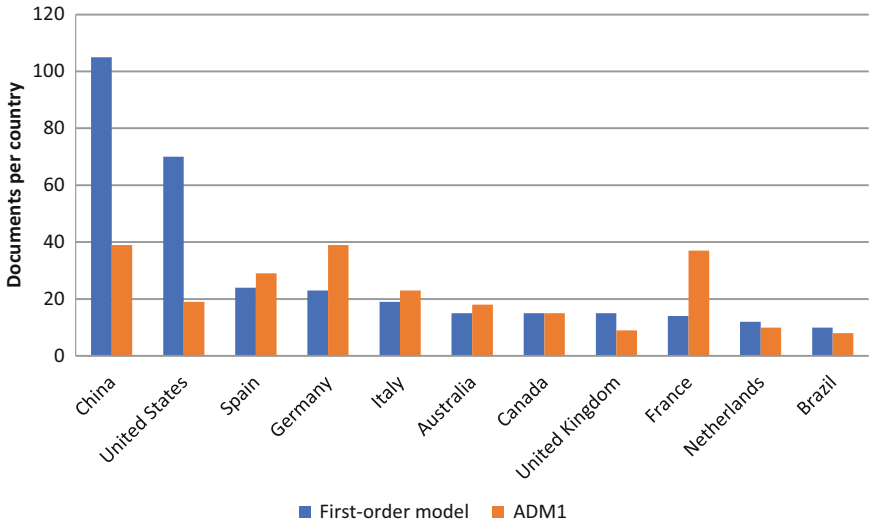


**Fig. 14.4** Number of publications per year in the period 2010–2020

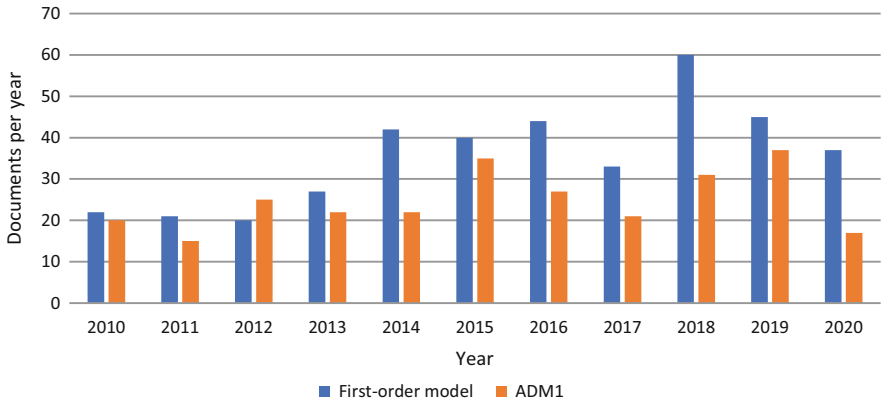


**Fig. 14.5** Number of publications in the last 10 years

381 publications were registered at the date of the analysis (until June 2020). Figure 14.4 shows that the countries that concentrate more than 30% of the publications are Germany, China, and France. In Fig. 14.5, it is notable how the publications referring to ADM1 increase but still do not exceed those related to the first-order model.

### *14.5.2 Feasibility of Applying the Models*

Mathematical modeling is a tool to broaden the understanding of processes in general. In the field of anaerobic degradation of residues, mathematical modeling allows estimating:

1. Methane production (methane yields, accumulated volume)
2. Composition of sludge and gas streams (TS, VS, particulate and soluble material)
3. Interactions between substrates in co-digestion (synergies and antagonisms)
4. Effects on the system (temperature, pH, toxic substances)

Different approaches to mathematical modeling allow its application in industrial and agricultural sectors. To this is added that the models that have been developed present different mathematical structures (algebraic equations and ordinary differentials) developed from the study of the phenomenon.

Models in algebraic equations are characterized by their relative simplicity for studying the degradation of a substrate; they allow to identify constants of production and consumption. These can be implemented from complete characterizations of the substrates (C, H, O, N, metals, carbohydrates, lipids, proteins, and others) or from basic parameters (TS and VS), as well as measurements of volumes of the methane generated. The resolution of these models is relatively simple; the software used does not require high performance and can even be solved without the need for processors. This facilitates the evaluation of proposals for the application of AD in areas where economic resources are limited.

Dynamic models stand out due to the application of these in the design, control, and optimization of processes. In addition, they allow the study of the degradation of organic residues, variation of microbial populations and interactions between substrates, as well as the effect of factors such as temperature and pH. These models require specialized software for the simultaneous resolution of differential equations. The implementation of control systems requires the collection of data from monitoring systems and the sending of analog or digital signals to control systems.

## 14.6 Remarks

1. Anaerobic digestion is a biological process, which due to the multiple stages and microorganisms it involves is complex to model. Other factors that influence the modeling of the process are related to the sensitivity of microorganisms to variations in environmental conditions such as temperature, pH, and concentration of inhibitory substances. Furthermore, the model is subject to the complexity of the composition of the substrate.
2. For the determination of reaction kinetics, a discontinuous study is recommended. For this task, the most widely accepted models are first order and Gompertz modified. The goodness of fit of the models must be performed by

comparing statisticians that reflect the least error as well as the least variability of these.
3. The selection of the model is linked to the possibilities of characterizing the reacting system (substrates, inocula, sludge, biogas, among others), according to the available economic and technological resources.
4. There are still gaps in the modeling of mixing effects on the methane yield kinetics. From the mono-substrate kinetics, the aim is to study the co-substrate kinetics, which cannot be done using current models.

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