



# **Decoding Anaerobic Digestion: A Holistic Analysis of Biomass Waste Technology, Process Kinetics, and Operational Variables**

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Abstract: The continual generation and discharge of waste are currently considered two of the main environmental problems worldwide. There are several waste management options that can be applied, though anaerobic digestion (AD) process technology seems to be one of the best, most reliable, and feasible technological options that have attracted remarkable attention due to its benefits, including the generation of renewable energy in the form of biogas and biomethane. There is a large amount of literature available on AD; however, with the continuous, progressive, and innovative technological development and implementation, as well as the inclusion of increasingly complex systems, it is necessary to update current knowledge on AD process technologies, process variables and their role on AD performance, and the kinetic models that are most commonly used to describe the process-reaction kinetics. This paper, therefore, reviewed the AD process technologies for treating or processing organic biomass waste with regard to its classification, the mechanisms involved in the process, process variables that affect the performance, and the process kinetics. Gazing into the future, research studies on reduced MS-AD operational cost, integrated or hybrid ADbiorefinery technology, integrated or hybrid AD-thermochemical process, novel thermochemical reactor development, nutrient recovery from integrated AD-thermochemical process, and solid and liquid residual disposal techniques are more likely to receive increased attention for AD process technology of biomass wastes.

Keywords: waste management; anaerobic digestion; biogas; biomethane; organic biomass

## 1. Introduction

A large amount of liquid and solid waste is globally produced on a daily basis, and these wastes result in the pollution or contamination of the environment (land or soil, water, and air). Inadequate management of these wastes, especially in developing countries, is a serious environmental and health problem. Rapid population growth, alongside urbanisation and industrialization, the standard of living, disposable income, and consumption of goods and services, have led to a continual increase in solid waste generation [1]. Furthermore, in developing countries such as Nigeria, this waste generation is on the increase due to poor storage systems.



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Most conventional solid waste management methods that have been widely used [2,3] reduce the amount of waste disposed of in uncontrolled dumping sites, which, if unmanaged, produce leachates and release pollutants into the air, water, and soil, as well as contribute to greenhouse gas (GHG) emissions that are harmful to the environment [4–8]. In addition, these methods incur high energy losses and are thus not economically feasible [2,3,9]. Therefore, the challenge of managing these solid wastes while ensuring the protection of the environment has instigated the need for developing suitable new and innovative treatment options that would allow the organic fraction of solid wastes (e.g., animal wastes and fruit wastes) based on the concept of a circular economy to be used for other purpose and help alleviate the waste problem. One such treatment option is the use of anaerobic digestion (AD).

AD is defined as the biodegradation of organic material by microorganisms in the absence of oxygen in which four sequential main reactions occur during the entire process [10,11]. AD of organic biodegradable wastes in a fermentation digester produces biogas [6]. Various consortia of microorganisms are involved in the anaerobic degradation process, producing energy-rich biogas and a nutritious digestate that serves as a biofertilizer [12]. Meanwhile, the main priority of most countries in the world is driving towards finding clean and renewable energy. AD of solid waste provides a unique technological approach and opportunity for obtaining this clean, renewable energy (biogas). All countries in the world throw away large volumes of solid organic waste, so all can benefit from the use of AD as an appropriate waste treatment technology option to generate biogas as a global growth energy of the future [13]. Thus, the AD process technology contributes to improved waste management practices and the achievement of sustainable energy management goals [5,14]. In addition, it also contributes to the production of renewable green energy and a circular economy, stimulates sustainable socioeconomic development, and simultaneously mitigates climate change [15]. Even though this technology is widely applied globally, its industry utilization is still limited [15]. One of the primary renewable energy sources is biomass wastes (e.g., agricultural biomass wastes); these are organic in nature and biodegradable [16]. Therefore, they can be degraded by a consortium of bacteria to generate bioenergy [17,18]. Using biowaste to produce biogas creates a carbon-neutral cycle, in which the carbon emitted from burning the gas is absorbed by new crops from which the waste residues can be used again as feedstock [13].

Biogas is considered one of the cheapest renewable resources of energy as well as the best alternative for fossil fuel (e.g., for the generation of heat and electricity) and also as vehicle fuel [11]. Biogas production from organic waste may play an essential part in both a circular economy and a bioeconomy [11,19]. Biogas is used not only for power generation but also for solid waste management, and the digestate from the biogas process can be used as fertilizer for farmers. This is especially useful in countries where soil quality has been degraded due to overintensive farming; it improves hygienic conditions by reducing pathogens in the environment, and it creates macroeconomic benefits by decentralizing energy generation [20–22]. The recovery of biogas from waste is an area of vital interest since it combines both alternative energy production and environmental impact reduction through methane and carbon dioxide, two of the main greenhouse gas emissions [4–6]. In developing countries, biogas/biomethane production and its utilization are still facing different problems, among which is the lack of capital or funds, the lack of adequate knowledge, and the lack of adequate policymaker or government support seem to be the most significant barriers to overcome. Although many pieces of review on the different segments of the AD process have been published [23–32], there has been no systematic and comprehensive review of the complete AD process technology.

Also, to better understand the AD process dynamics and optimize the process operating parameters or conditions, the availability of mathematical kinetic models is of great importance. These models have to be derived from prior knowledge and experimental kinetic data obtained from a real biodigester or reactor. Several reviews of kinetic models, from the simplest to the more complex models for the AD process, have been published in the literature in the last 10 years [25,33–37]. However, there is a need to know which models are most commonly applied in recent advances in the AD of organic wastes.

This paper, therefore, aims to provide a comprehensive review of the complete AD process technologies for organic biomass waste, together with its kinetic modeling. Each type is discussed based on its classification. Based on the existing literature, the process variables influencing the AD process technology performance are identified and discussed. Therefore, this review will serve as a comprehensive AD process technology design guideline.

## 2. Feedstock for Anaerobic Digestion

The feedstocks that can be utilized for AD include agricultural wastes or residues, municipal solid wastes, industrial wastes and wastewater, and aquatic biomass (e.g., algae) [27,38–41]. The survey of the various feedstocks from different sources is shown in Table 1. The extraction of biogas from various feedstocks relies on the physical and chemical compositions of the substrate that promote biodegradation. The composition of biogas from different types of feedstocks and substrates is shown in Table 2. These feedstocks encompass a range of substrate components, including carbohydrates (cellulose, hemicellulose, and lignin), lipids (fats, oils, and glycerols), and proteins, which are readily biodegradable. However, not all of these components are equally biodegradable. For instance, lignin is highly resistant to degradation. The breakdown of cellulose requires several weeks, whereas hemicelluloses, fats, and proteins can be biodegraded in a few days, and volatile fatty acids and alcohols can be broken down in several hours [27]. Hence, the selection of appropriate feedstock concerning reactor design, waste disposal, and the amount of energy production is essential.

Table 1. Survey of the Various Feedstocks from Different Sources.

Agriculture	Communities	Industry
Manure	OFMSW	Food/beverage processing
Energy crops	Municipal solid waste	Dairy
Algal biomass	Sewage sludge	Starch industry
Harvest remains	Grass clippings/garden waste	Sugar industry
	Food remains	Pharmaceutical industry
		Cosmetic industry
		Biochemical industry
		Pulp and paper
		Slaughterhouse/rendering
		plant

Table 2. Composition of Biogas from Different Types of Feedstock.

Component (%vol)	Household Waste	Wastewater Sludge	Agricultural Wastes	Food Industry Waste
$CH_4$	50-60	60-75	60–75	68
CO <sub>2</sub>	38–34	33-19	33–19	26
$N_2$	0–5	0–1	0–1	-
O <sub>2</sub>	0–1	0-0.5	0-0.5	-
H <sub>2</sub> O	6 (40 °C)	6 (40 °C)	6 (40 °C)	6 (40 °C)
Total	100	100	100	100

Protein-rich substrates and lipid-rich substrates (i.e., substrates that contain a high level of proteins and lipids), which, when utilized for AD, influence the development or production of high concentration levels of ammonia and sulfide. Elevated levels of ammonia can have detrimental effects on methanogens, resulting in process instability, imbalances, and inhibition of pH buffering. This, in turn, leads to reduced degradation rates, accumulation of fatty acids, lower yields of biogas or biomethane, and sometimes even process failure [42,43]. Despite these challenges, lipid-rich feedstocks offer significant

potential for enhanced methane production when codigested with other substrates [44,45]. Various methods have been suggested to overcome the problems associated with proteinrich and lipid-rich feedstocks, including reducing particle size [46], operating at mesophilic temperatures [47], increasing hydraulic retention time [47,48], lowering organic loading rates [48], stripping ammonia by adding sodium hydroxide, calcium hydroxide, or potassium hydroxide [49], and adjusting pH through the addition of acidic iron and acid [47,50].

Furthermore, carbohydrate-rich substrates, which include lignocellulosic biomass, have been used as a good source for biogas production. Lignocellulosic biomass such as grass, wheat, straw, and sorghum demonstrate relatively high theoretical biogas/biomethane potential [27]. However, due to their heterogeneous structure, recalcitrant nature, and low accessibility by enzymes, they are difficult to degrade [51,52], and hence oppose microbial hydrolysis [53] and are recalcitrant to anaerobic conversion [27]. Nevertheless, a number of research studies have suggested the pretreatment of these classes of feedstock to maximize their utilization [27,51,52].

## 2.1. Agricultural Wastes

Agricultural wastes include animal or livestock manure, slaughterhouse waste, food waste, fruit waste, energy crops, forest residues, and crop residues.

#### 2.1.1. Food Waste

Food waste (FW) can be generated from food processing industries, household or kitchen waste, restaurants, slaughterhouses, and marketplaces, and partly from municipal solid wastes [22,27]. FW possesses several characteristics such as high carbohydrate, protein, and fats (lipid) contents, various trace elements, low pH, high moisture content, and high volatile solid (VS), which makes it one of the best substrates for AD due to its biogas/methane production potential [25]. If the waste contains too much protein, problems can arise with ammonia inhibition [2,22].

## 2.1.2. Animal (Livestock) and Poultry Manure

Animal manure and poultry or chicken manure are common sources of biodegradable organic biomass utilized as feedstock for AD. The manure that has been mostly used as feedstock for AD is obtained from cattle/cow, sheep, goat, pig, and chicken [10,54–57]. However, in recent times, manure from animals, such as horses [58,59], donkeys [60], camel [61], lions, elephants, hippopotami, and orangutans [62] has been utilized as feedstock for AD processes in the generation of biogas/biomethane. Animal manures contain the presence of diverse microbial species, or microbial load, and moisture content (75–92%) [63], as well as high amounts of lignocelluloses, proteins, polysaccharides, and other biomaterials [64]. Nevertheless, the characteristics and composition (volatile solid, total solid, pH, and carbon to nitrogen ratio) of manure from different animals vary, as presented in Table 3, which could be due to their digestive system, diet, management system, and animal type [65].

Table 3. Physicochemical characteristics of different animal manure [65].

Animal Manure	pН	Total Solids (%)	Volatile Solids (%)	Carbon/Nitrogen Ratio
Cattle manure	7.1-8.6	14.5-22.7	11.9-72.0	14.6-18.9
Sheep manure	7.2-8.1	22.3-40.0	18.7-72.7	11.3-14.7
Goat manure	7.9	33.7-55.5	27.7-89.4	18.0
Pig manure	6.4-7.5	8.2-36.7	6.2-82.8	5.7-13.5
Chicken manure	6.9–7.4	20.0–92.6	18.3–84.1	7.5–9.8

Therefore, manures vary in their suitability as feedstock for biogas generation processes [66]. The pH of the different animal manure ranges from 6.4 to 8.6, which will effectively support the methanogenesis step in the AD process and enhance the hydrolytic enzymes' activities [65–67]. Manure can be classified into solid and liquid manures (or slurry), depending on the dry solids content. Solid manure typically has a higher carbon content and dry solids content (27–70%) than liquid manure since it includes straw and hay in addition to feces [68]. Liquid manure is more accessible for digestion, as it contains more nitrogen and has a dry solids content of 5% to 10%.

Manure provides a good buffering capacity for the degradation of substrates low in nitrogen, controls for volatile fatty acids levels and essential nutrients (micro and macro) for bacterial proliferation [27], as well as eliminates the step of digester inoculation during AD [63].

The biogas/biomethane potential of animal manure can vary widely depending on factors like animal species, amount and type of bedding, feed, breed, and growth stage [27]. In addition, it also depends on the variation in animal digestion, intestinal microbial community, the difference in the animal manure origin, mechanisms of manure storage prior to the AD process, and the management system [65,69]. Biogas production from manure is gradually increasing, but the rate of development is slow due to difficulties in profitability [43,70]. Manure from cows or cattle has high water and fiber content [43] as well as high lignin content [71]. The lignin contents in cattle manure, pig manure, sheep manure, and chicken manure are 11.5–14%, 8.5%, 8.6%, and 4.2%, respectively [71,72]. The use of this cattle manure results in low degradation efficiency and low yields of biogas/methane, which tends to hamper the increased utilization of biogas technology in agriculture [43,70]. In general, the manure from cattle yields less biogas/biomethane than that from pigs, sheep, goats, and chicken manures [65]. Goats' and pigs' manure generates higher biogas/biomethane yields than sheep and chicken manure [65]. The low biogas/biomethane yield displayed by cattle manure in comparison with other manures is due to its high lignin content, which inhibits or reduces biogas/biomethane production [65,72].

Typically, the biogas or biomethane potential of manure is decreased by its recalcitrant solid content, particularly when biofibers or bed contents (e.g., straw) are present [27]. However, to enhance the conversion of the recalcitrant fraction, pretreatment of the manure is often recommended prior to its use for biogas production [27]. Manure from pigs and chickens contains more protein than manure from cattle. It can lead to ammonia inhibition if these materials are digested in the digester without including materials containing more carbohydrates [73,74]. If the manure is digested along with other types of materials, such as food waste or forage crops, the gas yield can increase [75]. The manure from cattle can also have a stabilizing effect on an unstable biogas process since its addition results in the inoculation of more microorganisms as well as nutrients. In addition, a dilution may reduce the concentrations of inhibitory components such as ammonia or volatile fatty acids.

## 2.1.3. Slaughterhouse Waste

The major livestock slaughtered in an abattoir or slaughterhouse for the purpose of meat production includes cattle, sheep, goats, pigs, and poultry [1]. Slaughterhouse wastes can be categorized into two types: livestock slaughterhouse waste and poultry slaughterhouse waste. Abattoir or livestock slaughterhouse operations generally lead to the generation of a considerable quantity of organic waste which consists of blood, urine, animal trimmings, feces, paunch content, fat, horns, and bones [1,76,77], while poultry slaughterhouse operations result in the generation of blood, poultry droppings or manure, feathers, and intestinal wastes [78]. Slaughterhouse waste contains high contents of carbohydrates, lipids or fats, and proteins, which are very energy-rich [77] and possesses a high biogas/biomethane generation potential [79]. Slaughterhouse wastes due to higher nitrogen contents have a poor carbon/nitrogen (C/N) balance, or ratio that varies between 7 and 10, which makes it inhibitory for a stable AD process as this value is lower than the optimal C/N balance of 25–30 required for a stable AD process [80,81]. However, excessive fat and protein contents allow for increased concentrations of ammonia, volatile fatty acids, and long-chain fatty acids production during the AD process, which can then lead to process instability and breakdown [82,83]. It is, therefore, difficult to use slaughterhouse

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waste as the sole substrate, especially at a thermophilic temperature, because the proportion of ammonia in relation to ammonium can easily become too high [84]. Nevertheless, with the application of co-digestion with a carbon-rich substrate that is low in fat and protein, the likelihood of a stable process operation without inhibition is significantly improved [80,85].

## 2.1.4. Bioenergy Crops/Crop Residues

Many crops, such as cereal crops (e.g., corn or maize, grains), crop residues (like rice, cotton, and maize residues), and plant materials, which include perennial grasses and silages, can be used for biogas/biomethane production due to their high energy content [64,70,86,87]. One of the critical factors to consider is if bioenergy crops are to be utilized for biogas/biomethane production, their relatively high environmental impact, and production cost as compared to waste feedstock or substrate [70]. Bioenergy crops often have a relatively high content of dry solids (10–50%). Many bioenergy crops also have a high carbon/nitrogen ratio (C/N) [88]. The biomethane yield of energy crops is affected by the storage process, site properties, and time of harvest since these factors affect the chemical composition of the crop, and, hence, the ability of microorganisms to use them as substrates for their growth depends on the chemical composition [87]. With regard to the time of harvest, the maturity stage of the crop affects its energy value, and thus the biomethane potential decreases with increasing maturity of the crop [70]. Hence, for the use of bioenergy crops for biogas/biomethane production, there should be a balance between the time of harvest and yield [70,89]. In most bioenergy crops, the level of essential trace metals is low [70]. For its usage as biogas feedstock, these low trace metal concentrations can be complemented by co-digesting with the more nutrient-rich substrate [90]. This essential trace metal level differs for different types of crops based on the soil type and the fertilization used during cultivation [90].

## 2.2. Municipal Solid Waste

Municipal solid waste (MSW) is a major component of the solid waste generated in municipal cities. This waste is made up of different kinds of waste generated by households, industries, and commercial setups [65], such as commercial waste, household waste, institutional waste, construction and demolition waste, shop waste, retail waste, garden waste, and park waste [91]. Although the composition of MSW varies with time, globally, food and green waste constitute a significant portion of the MSW [92,93]. FW constitutes about 40–50% of the MSW weight [94], while according to Kaza et al. [93], food and green waste constitute about 44% of the MSW. This is followed by paper and cardboard (17%), plastics (12%), glass (5%), metal (4%), wood (2%), rubber and leather (2%), and others (14%) [93]. This indicates that the organic fraction (OGF) or organic wastes present in MSW is heterogeneous and consists of different wastes with varying biodegradability [95] and FW constituting a greater percentage of the organic wastes and having the highest biogas/biomethane potential compared to other biodegradable wastes [65]. According to Nwokolo et al. [65], the total solids and volatile solids content of the organic fraction of MSW ranges from 10.8 to 23.0% and 10.2 to 18.5 respectively, while the carbon/nitrogen ratio ranged from 13.6 to 32.5.

Sludge from various stages of sewage treatment can be utilized for biogas production. The use of this material has accounted for the largest single source of biogas production in Sweden [63]. Sludge could contain a relatively low content of organic matter (3% to 4%) and different chemical compounds, such as metals and organic pollutants, which are capable of inhibiting the microorganisms in the process [96]. Although a large amount of biogas is produced during the anaerobic digestion of sewage sludge, some of the organic matter may still remain in the residual sludge. This indicates that the digestion process has a relatively low efficiency [97]. This can be linked to several factors, such as the retention time may be too short for the microorganisms to degrade the material and the presence of inhibitory substances, as well as the organic matter in the sludge may be too complex for the microbes' hydrolyzing enzymes to effectively break up the organic matter [98].

## 2.3. Industrial Waste

Industrial wastes are wastes, residues, and byproducts that are generated from different industrial activities, such as from the food industry, textile industry, petrochemical industry, pulp, paper industry, etc. [65]. Aside from the food industry wastes, other industrial wastes have not been widely utilized as feedstock in AD as a result of their low biodegradability (about 30–50%) and recalcitrant chemical properties [99].

## 2.4. Aquatic Biomass

Aquatic biomass such as macro- and microalgae, water hyacinth, and seaweeds can be utilized as feedstock for the AD process [100–103]. This is because they possess relatively high polysaccharides, lipids, and proteins and low or no lignin contents [102], do not compete with arable land areas utilized for food cultivation as they can be cultivated on non-cultivable land areas or in lakes/ponds or ocean, and have faster growth with higher production rate than the terrestrial biomass [63]. The factors that affect its AD usage effectiveness and restrain its biogas/biomethane production mechanism include cell walls that are recalcitrant to anaerobic degradation due to the presence of cellulose/hemicellulose, the production of substances that are toxic to anaerobic bacteria, the presence of poor C/N ratio in the biomass, long chain fatty acid inhibition, and an increasing pH level in the case of algae species with a high C/N ratio and ammonia inhibition [100,103]. Some of these challenges can be overcome by utilizing the pretreatment method [101,104] and the codigestion method [27]. Among the aquatic biomass, microalgae and water hyacinth are the most utilized feedstock for AD since they demonstrate higher biogas yield efficiency [102].

## 3. Process and Mechanism of AD (Biomethanation)

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The process of producing biogas/biomethane through AD is termed biomethanation or biomethanisation [17]. AD describes the biodegradation of organic material in the absence of oxygen, in which four main reactions occur during the entire process [105]. These reactions are hydrolysis, acidogenesis, acetogenesis, and methanogenesis [17]. These four reaction stages occur simultaneously and are interdependent [39].

## Stage 1: Hydrolysis

It is the first stage of AD. This complex multiple-step process is mediated by extracellular enzymes in which the bacteria decompose or depolymerize or convert long chains of complex organic molecules (carbohydrates, proteins, and lipids) into small chains of soluble monomers [5]. For example, polysaccharides are converted into monosaccharides, and the proteins are split into peptides and amino acids [5,106]. The required hydrolytic enzymes, called hydrolase, which is present in microorganisms, can either be secreted to the medium or still remain attached to the microbial cells [27,107]. These hydrolases include glycosidase, esterase, and peptidases [31]. The hydrolysis reaction of the fraction of the wastes can be represented by Equation (1):

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{hydrolysis} nC_6H_{12}O_6 \tag{1}$$

There are different groups of hydrolytic microorganisms that are involved in the metabolic degradation of different substrate compositions, where bacterial species such as *Bacteriods, Clostridium, Micrococcus, Bacillus, Vibrio,* and *Staphyloccocus* are the significant drivers [27]. In the AD process, hydrolysis is considered to be the stage-limiting process, and this stage is influenced by [26]: (a) temperature, (b) pH, (c) substrate structure or nature, (d) particle size, and (e) organic load. The formation of total ammonium nitrogen during hydrolysis can result in high alkalinity, thereby leading to process disturbances or collapse [27].

#### Stage 2: Acidogenesis

This is the second stage of AD. In this stage, the products (sugars and amino acids) obtained from the hydrolysis stage are transformed or fermented by acidogenic bacteria (or acidogens) such as *Streptococcus*, *Lactobacillus*, and *Clostridium* species to produce volatile

fatty acids (propionic acid, butyric acid, and acetic acid) [26,27,108], organic acids (succinic acid, valeric acid, and lactic acid) [27], low alcohols [27,108], ammonia (NH<sub>3</sub>), carbon dioxide ( $CO_2$ ), hydrogen gas ( $H_2$ ), and hydrogen sulfide ( $H_2S$ ) [26,27]. The acidogens have the characteristics of strong and rapid growth with a minimum doubling time of 30 min [30,109]. The concentration of H<sub>2</sub> gas produced during digestion has an impact on the final product. As a result, the organic products generated, including volatile organic acids, are not appropriate for direct conversion to methane by methanogens [27]. Thus, the need for the third stage. The surrounding pH conditions of the bacteria significantly affect the volatile fatty acids products. If the pH falls below 4.0, the formation of volatile fatty acids is strongly inhibited [30,110], while stepwise pH perturbation from four to eight results in a change of the main products from acetic and butyric acids to propionic and acetic acids [30]. Therefore, a pH that is in the range of 5.5 to 6.5 has often been reported to be the optimal range for this stage [30,111]. If the VFAs produced during acidogenesis are not metabolized into products, it will significantly result in lowering or decreasing the pH (<3), which eventually will lead to process collapse [27]. The reaction that occurs during the acidogenesis stage is shown in Equations (2)–(5).

$$nC_6H_{12}O_6 \xrightarrow{acidogenesis} 3nCH_3COOH$$
 (2)

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2 \tag{3}$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$$
 (4)

$$C_6H_{12}O_6 \rightarrow 2CH_2CH_2OH + 2CO_2 \tag{5}$$

#### Stage 3: Acetogenesis

It is the third stage of AD. This stage comprises two reactions: fermentation and acetogenesis reactions. Involved in this stage are acetogenic bacteria, which are also known as acetogens or acid formers, or acid-producing bacteria. They are strict anaerobic microbes that can grow under acidic conditions [22] but cannot tolerate the presence of oxidants such as oxygen and nitrate [30,112]. These anaerobes perform better in a weak acid environment with a pH range of 6.0 to 6.2 [30,109]. In this stage, acetogenic bacteria convert the intermediates of fermentation (volatile fatty acids), especially acetic acids and butyric acids, into acetate, hydrogen, and carbon dioxide. Also, they reduce the compounds with low molecular weights into alcohols, organic acids, amino acids, carbon dioxide, hydrogen sulfide, and traces of methane [39]. This process is partially endergonic (i.e., only possible with energy input) since bacteria alone cannot sustain this type of reaction [22]. Among the volatile fatty acids, propionic acid primarily remains unconverted due to its degradation being thermodynamically less favorable in comparison to butyric acid, while about 65 to 95% of methane is directly produced from acetic acid [27,113]. The kinetics of acetogen's growth during acetogenesis is slower than that of the acidogens, having a minimal doubling time that lies in the range of 1.5–4 days [30,109]. Equations (6)–(9) show the reactions that occur during acetogenesis.

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2 \tag{6}$$

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2 \tag{7}$$

$$CH_3CH_2OH + H_2O \to CH_3COOH + 2H_2 \tag{8}$$

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O \tag{9}$$

## Stage 4: Methanogenesis

The fourth stage is methanogenesis, which is the final and most important stage involved in the generation of methane gas. In this final stage, acetogenesis products (hydrogen, carbon dioxide, and acetic acid) from the third stage are converted or transformed into methane and carbon dioxide by three groups of methanogens (methane-producing bacteria), namely acetotrophic, hydrogenotrophic, and methylotrophic methanogens [27,39,106]. Nevertheless, the majority of the methane has been produced by acetotrophic methanogens, which act on the acetate [27,114]. In this pathway, the principal reaction is given in Equation (10).

$$CH_3COOH \xrightarrow{acetotrophic methanogens} CH_4 + CO_2$$
(10)

The hydrogenotrophic methanogens convert hydrogen and carbon dioxide into methane, as depicted in Equations (11) and (12) [27] (25;156). About 30% of methane may be produced through this route.

$$CO_2 + 4H_2 \xrightarrow{hydrogenophic methanogens} CH_4 + 2H_2O$$
 (11)

$$4CO + 2H_2O \xrightarrow{hydrogenophic methanogens} CH_4 + 3CO_2$$
(12)

The growth kinetics of acetotrophic bacteria are much lower, with doubling times of two to three days, while the maximum growth rate of hydrogenotrophic bacteria is higher, with doubling times of range 4 to 12 h [30,109]. Apart from the above two methanogenic bacterial groups, some methane can be produced by the methylotrophic methanogens by transforming the methyl or trimethylamine component of a given feedstock, as provided in Equations (13) and (14) [27]. Figure 1 shows the schematic of the relationships between each group of bacteria in the anaerobic ecosystem.

$$3CH_3OH + 3H_2 \xrightarrow{\text{methylotrophic methanogens}} 3CH_4 + 3H_2O$$
 (13)

$$4(CH_3)_3N + 6H_2O \xrightarrow{\text{methylotrophic methanogens}} 9CH_4 + 3CO_2 + 4NH_3$$
(14)



Figure 1. Schematics of the relationships between each group of bacteria in the anaerobic ecosystem.

## 4. Anaerobic Digestion Technology

The AD process, an environmental protection technology through organic wastes and wastewater treatment, involves converting biodegradable organic waste into biogas and biofertilizer [115,116]. It is a biotechnological treatment process that recovers energy (biogas), value-added products, and nutrients (nitrogen, phosphorus, and potassium) from biodegradable organic waste in the absence of oxygen [117]. Nitrogen (N), phosphorus (P), and potassium (K) are recovered in biosolid form, which may be applied as biofertilizers on agricultural land if the level of the pathogen is very low. The biogas can as well be transformed into electricity and heat [118]. Despite the noncommercialization of this technology, it remains one of the promising technologies that convert wastes into biogas and odor-free residues that are rich in nutrients that can be used as fertilizers [119].

#### 4.1. Classification of the AD Process Technology

The AD process technology can typically be categorized or classified based on the following: (a) the nature of the total solid content, (b) the feeding mode, (c) the operating temperature, (d) the number of operational stages, and (e) the type of digester and reactor configuration (i.e., technical) [30]. The AD process can be categorized into different types based on various factors. The total solid content determines whether the process is dry or wet, while the feeding mode determines if it is a batch or continuous process. The operating temperature determines if the process is mesophilic or thermophilic. The number of stages involved in the process categorizes it as a single-stage or multistage process. Finally, the type of digester used classifies the AD process as a fixed dome, floating dome, balloon, or garage type.

#### 4.1.1. Dry and Wet AD Process Technology

The dry and wet AD process technologies are dependent on the amount of total solid content (TSC) in the system. The dry AD (D-AD) process technology which is also referred to as high-solid (HS-AD) or solid-state process technology, is the one that generally operates with a feedstock of 15–40% TSC [120] or 20–40% TSC [29]. That is, D-AD process technology works at a higher TSC than wet AD process technology [29]. This indicates that D-AD allows for treating or handling higher quantities of waste per digester volume [29]. It has been claimed that D-AD or HS-AD is more advantageous over wet AD process technology based on a number of reasons, such as reduced energy input for heating and stirring, higher volumetric loading capacity, greater ease in handling of the digestate, smaller reactor volume, and abrasion reduction in the reactor from sand and grit [29,94,121]. Despite the merits of D-AD or HS-AD process technology, it also has some demerits, which include low operational stability, long degradation times, lower biogas and biomethane production when compared to the wet AD process technology, liquid and gas diffusional problems, higher inoculation ratio and the accumulation of toxic and inhibitory components or compounds (volatile fatty acids, ammonia, and heavy metals), which still hinders their wide applications [29,120,122]. The reasons for these demerits have been attributed to the high TSC [122] and reduced water content which consequently reduces the availability of substrate to the microorganisms and thus affects their metabolism [123].

Wet AD (W-AD) process technology, also referred to as liquid AD (L-AD) process technology, is the one in which the feedstock is mixed with a large quantity of water to provide a dilute feed of 10 to 15% dry solids [124]. That is, the W-AD or L-AD systems typically operate with 0.5–15% TSC [102,124,125]. Consequently, dilution with water, liquid digestate fraction, or slurry is essential to acquire total solid contents of less than 15%. Some studies, as obtained from the literature, all revealed that an increase in the water content results in an increase in biogas and biomethane yields [126,127]. This increase in water content produces a better homogenization of the digester's contents in the AD, increasing the interaction between bacteria and nutrients, reducing the problems of diffusion problems, and diluting any potential inhibitors [29,127]. The advantages and disadvantages of W-AD have been well documented [121,124]. However, one of the main disadvantages of the wet process is that a large amount of water is required, and the biogas output is not proportional to the volume of water required; thus, when a large volume of biogas is required, a large reactor volume will be required to accommodate the large volume of water required [124].

## 4.1.2. Batch and Continuous AD Process Technology

The AD is classified on the basis of its feeding mode or operation mode, namely batch and continuous modes. In a batch AD process technology, the digester is fed with fresh raw materials, then tightly closed and sealed, and left for a fixed duration until the overall degradation or digestion is accomplished. The digester is emptied once the digestion is completed, and a new batch of organic feedstock is fed. The effluent or residues are then removed to allow the new process to take place [128]. Generally, it is essential to have a number of digesters in a batch process so that alternate loading and emptying can be done. A batch digester is technologically simple and straightforward, requires fewer moving parts, is cheap or inexpensive, has a low maintenance cost, and has limited energy losses [129].

In a continuous AD process technology, fresh raw materials are fed regularly and constantly into the digester to replace or maintain the same amount of digested waste as products are continuously withdrawn [120]. Typically, a pumping system is fixed for the transportation of the feed into the digester. Any interruption during pumping will affect biogas production. The advantages of using a continuous feeding mode in anaerobic digestion include (i) a constant biogas production rate by maintaining a steady feedstock input, (ii) a smaller land area requirement, (iii) lower operating costs, (iv) uninterrupted digestion, (v) a continuous cycle of input and removal of bio-waste, and (vi) the achievement of steady-state conditions [30]. However, there are also some disadvantages associated with this method, including (i) higher initial investment costs, (ii) technical difficulties associated with the pump used for loading, and (iii) a requirement for high internal fluidity to ensure a smooth feedstock intake and removal process.

## 4.1.3. Mesophilic and Thermophilic AD Process Technology

Based on the operating temperature, as earlier mentioned, AD process technology can be classified as mesophilic AD process technology and thermophilic AD process technology. Mesophilic AD process technology is the technology where the AD process is performed at a temperature range of 20–40 °C in which the mesophilic organisms that are involved in the degradation or digestion process grow and perform optimally. According to Gebreeyessus and Jenicek [130], the advantages of this technology are: (i) the microorganisms can tolerate greater environmental changes, (ii) it is more stable and easier to maintain, and (iii) it involves the use of smaller or minimal energy, while the disadvantages include longer retention time and lower biogas production. Several studies have been performed with the use of this technology for the biological treatment of sewage sludge [131], slaughterhouse waste [132], sugarbeet pulp [133], cattle manure [134], corn silage [135], and fruit and vegetable waste [136].

Thermophilic AD process technology is the technology in which the AD process is carried out at a temperature range of 50 °C–65 °C, where the thermophilic organisms involved in the digestion or degradation process grow and perform optimally. A review of the advantages and disadvantages of the use of this technology has been made by Gebreeyessus and Jenicek [130]. According to the review, the advantages of this technology include lower retention time, higher organic loading rate, increased biogas/biomethane generation, and higher pathogen destruction, while the disadvantages are responsive to toxins, the presence of less distinct microorganisms with an attendant less efficient mechanism, difficult maintenance of the system, and higher energy required for heating. Many studies have been conducted with the use of this technology for the biotreatment of organic wastes to produce biogas/biomethane, and such wastes include sewage sludge [137], sugar beet pulp [133], cattle manure [134], solid waste residues from palm oil mill (empty fruit bunches, oil palm fronds, and oil palm trunks) [138], and food waste [9].

## 4.1.4. Single and Multistage AD Process Technology

AD process technology is further classified based on the number of operational stages, namely, single-stage and multistage AD process technologies. A single-stage AD (SS-AD) process technology is that technology that involves the use of a single biodigester or reactor where all the four steps (i.e., hydrolysis, acidogenesis, acetogenesis, and methanogenesis) involved in microbial digestion simultaneously take place [139]. This implies that in SS-AD, acidogenic and methanogenic microbial species have to cohabit despite their marked differences with regard to nutritional needs, environmental factors such as temperature and pH, growth factors, and kinetics [139,140]. It is pertinent to note that most AD applications operate in single-stage systems [27]. This is because the SS-AD process has proven to possess many advantages, such as simplicity in design, low cost or low capital investment,

low maintenance cost, recirculation adaptability, less technical failure, lower volatile solid losses, and smaller reactors required [9,27,124]. Notwithstanding the advantage, the SS-AD process still has some disadvantages or limitations, such that it cannot alone handle organic waste with TSC under 20%, the possibility of dilution with water is low, restricted bioreactor heights, high fluctuations in biogas/biomethane production, and the loss of biogas during the emptying of the bioreactors [139]. So far, the SS-AD process technology has been utilized to biologically treat several arrays of feedstock, including food waste [3,9,124], manure [141], sewage sludge [142], vegetable waste [143], and municipal solid waste (MSW) [144], and process performance was optimized in the greatest number of cases by recirculating the process digestate back into the reactor [145].

The multistage AD (MS-AD) process technology currently includes two-stage, threestage, and four-stage systems. In the MS-AD process, there is the physical separation of the four biochemical reactions or digestion steps. A two-stage AD (TS-AD) process technology is a technology where the AD process is conducted in two biodigesters or bioreactors in which all the biochemical reactions sequentially occur [146]. That is, in a TS-AD process system, the first step entails introducing the feedstock into the first digester or bioreactor (acidogenic bioreactor), where hydrolysis, acidogenesis, and acetogenesis occur, and the partially digested feedstock is then removed and fed into the second bioreactor (methanogenic bioreactor), where the biogas/biomethane is finally produced [27]. This implies that in a TS-AD process, acid fermentation, and methanogenesis are separated into two different bioreactors in order to optimize operating conditions for the acidogenic and methanogenic microbial species. The first (acidogenic) stage is typically performed at a low hydraulic retention time range of two to three days and a pH range of five to six, while the second stage (methanogenic) is operated at a hydraulic retention time of 20 to 30 days and a pH range of six to eight [125]. Comparing the TS-AD process to the SS-AD process, the TS-AD process allows rapid and efficient biogas/biomethane generation in the second stage [147]. The multistage AD (MS-AD) process concept that involved a three-stage reactor was developed in the early part of the 1990s [27]. The distribution of the biochemical reactions or digestion steps in a three-stage AD is hydrolysis/acidogenesis, acidogenesis/acetogenesis, and acetogenesis/methanogenesis [30]. In this MS-AD (i.e., three-stage AD), the first stage involves the semianaerobic hydrolysis of feedstock at a low hydraulic retention time and the removal and transfer of undegraded waste to the secondary bioreactor for acidogenisis. From the secondary bioreactor, the liquid and solids output are removed and fed into a tertiary bioreactor where biogas/biomethane is finally produced [27]. The key benefits of the TS-AD,  $T_h$ S-AD, or MS-AD processes over the SS-AD process are higher biogas/biomethane yield or better energy recovery, increased volatile solid removal performance, enhanced process stability and reliability, better control of pathogens, reduced retention time, reduced reactor size [139,140,148]. Nevertheless, the disadvantages lie in the fact that the design is complex (i.e., they are complex systems), biogas/biomethane yield is low if solids are not digested and involve large or high cost of investment, operations, and maintenance. Voelklein et al. [149] reported that the biomethane production performance of TS-AD is 30% higher than that of SS-AD. TS-AD or MS-AD process technologies are suitable for processing a wide range of wastes. The TS-AD process technology has been applied for the processing of wastes in biogas/biomethane. Such wastes are swine manure and market biowaste [150], cheese whey and cattle manure [151], fruit and vegetable waste and food waste [152], vegetable oil residue and pig manure [153], and food waste and sewage sludge [98]. Also, the MS-AD (i.e., three stages) has been utilized to process organic wastes into biogas, and this includes wastes such as food waste [154], food waste, and horse manure [59].

## 4.2. Types of Anaerobic Digesters

The construction of a biodigester depends on some key factors, such as the type of feedstock, hydrological and geological conditions, and weather or climate conditions [155]. In the design of a biodigester, the two key parameters that must be chosen correctly

are the number of stages and the total solid content since these parameters significantly affect its performance and reliability as well as the overall cost [30]. Primarily, digester design is concerned with the rate, stability, and completion of biochemical reactions [156]. There are various types of anaerobic digesters. The variations in their designs are due to climate differences, feedstock types, feedstock amount, feedstock fluid dynamics, structural strength, material availability and cost, design complexity, and process duration [156]. Each designed digester has its advantages and disadvantages. In anaerobic digester technology, there are several types of digester configurations. The three major types of anaerobic digesters are (a) covered anaerobic-lagoons digesters, (b) plug-flow digesters, and (c) complete-mixed digesters [157]. The other types of digesters include fixed-dome digesters, floating-drum digesters, and balloon-type digesters [155].

## 4.2.1. Covered Anaerobic Lagoons

Anaerobic lagoons are ponds that are covered in which feedstock is fed at one end, and the residue is removed at another end (Figure 2) [157]. It is used primarily for liquid or diluted waste that contains <2% solids. Plastic with an impermeable cover is used to collect the produced biogas [156]. It is widely used in cold climate regions for swine or dairy operations and uses a flush system to transport the manure. However, its drawbacks include a low rate of reaction due to the low reaction temperature, no mixing due to a closed lagoon causing coagulation of solids at the bottom of the digester, which results in less contact between the bacteria and feed, and a higher energy requirement to screen out coagulated solids [158].



Figure 2. Covered Anaerobic Lagoon.

#### 4.2.2. Plug-Flow Digester

The plug-flow digester consists of a long tubular digester or tank with varying sizes (2.4–7.5 m<sup>3</sup>), which has a constant volume that produces biogas at variable pressures (Figure 3) [155]. It can be fixed either vertically or horizontally. The digester consists of an inlet and two outlet pipes, which are fixed at opposite ends above ground level. The outlet pipes are connected to the digestate extraction system unit. As the fresh feedstock is introduced into the digester through the inlet, the digestate moves towards the other end of the tank and comes out through the outlet pipes into the digestate extraction unit. It is best suited for feedstocks such as cattle manure with high total solid content in the range of 11% to 14% [155,158]. Plug-flow digesters may have fewer moving parts [157] or no moving parts [155], thus requiring less maintenance. Since the plug-flow digester is a growth-based system, cleaning the reactor is inexpensive [156]. The main advantages of plug-flow digesters are their ease of use, adaptability to extreme conditions, ease of installation, and low maintenance costs [155].



Figure 3. Plug-Flow Digester.

## 4.2.3. Total-Mixed Digester

In this type of digester, all the organic wastes are combined together into a single tank, and an agitation system is introduced to mix the content while it is being digested (Figure 4) [158]. Various agitators can be used, such as mechanical mixers or recirculation pumps. The most efficient type, in terms of power consumed per gallon mixed, is the mechanical mixer. This system is suitable for handling manures with 3% to 10% solids [157]. The advantage of the completely-mixed reactor is that it is a proven technology that achieves reasonable conversion of solids to gas [157]. This process is widely used in industries to convert waste into biogas [156].



Figure 4. Total-Mixed Digester.

4.2.4. Fixed-Dome Digester

The fixed-dome digester, also known as the hydraulic digester, is the most prevalent model developed for biogas production [155]. It is characterized by a simple construction

that does not include any movable components. The digester comprises a dome-shaped chamber equipped with inlet and outlet pipes, as well as a gas pipe attached at the top of the dome chamber. The substrates are loaded through the inlet pipe until they reach the bottom of the chamber, and the resulting biogas collects in the upper storage part of the digester. Modified versions of the fixed-dome digester have been created in many countries worldwide [155]. Generally, these digesters are constructed underground and require minimal space [159]. Thus, it is expected that this type of digester can be utilized for a long number of years. Fixed-dome digesters take a longer time to warm up. The digester's size depends on the amount of substrate available daily and the location and number of households that will make use of it [155]. In general, if well constructed, fixed-dome digesters have advantages, including lower manufacturing or investment cost, low maintenance costs, long life span, less variation in temperature (due to being built underground), and less space requirement [160]. Nevertheless, some disadvantages could be that a skilled technician will be required for the construction, it might be hard to repair since it is built underground, fluctuation in gas pressure depending on the stored gas volume, and difficulty in constructing it in bedrock.

## 4.2.5. Floating-Drum Digester

A floating-drum digester, also known as a Gober gas plant, comprises a cylindrical or dome-shaped chamber, an underground digester (either cylindrical or dome-shaped), and an inverted movable steel drum or gas holder [155]. The steel drum, positioned on the digester, serves as a gas storage tank that separates gas accumulation from the production process, thereby maintaining a constant gas pressure [161]. Floating-drum digesters generate biogas with a variable volume at a steady pressure [155]. The pressure required for gas flow through the pipeline for utilization is achieved by the weight of the steel drum [162]. The inverted steel drum moves up and down depending on the quantity of accumulated gas stored at the top of the digester, necessitating regular painting to prevent rusting [155]. The advantage of this type of biodigester is its simplicity, ease of construction, and operation. However, it has several drawbacks, such as high steel material costs, regular maintenance and repair expenses, and a relatively short lifespan [32].

## 4.2.6. Balloon Digester

The balloon biodigester consists of a polyethylene tubular film sealed at both ends along with inlet and outlet polyvinyl chloride (PVC) pipes with rubber straps of recycled tire tubes wound around them [32]. The digester also consists of an installed PVC pipe at the top of it to allow the generated biogas to be released into a reservoir collection bag. A hydraulic level is created within the digester between the inlet and outlet in such a way that the amount of digestate that leaves the outlet is equal to the quantity of organic matter (a mixture of feedstock and water) that is added. The advantages of this type of digester lie in the fact it is easy to construct with low cost for construction, it has a shallow installation depth that makes it suitable in areas with high groundwater tables, and not being complicated in digester emptying and maintenance [32]. Its demerits are that the digester is susceptible to mechanical damage, scum cannot be removed from it, and it relatively has a short life span [32].

## 5. The Physiochemical and Biological Variables Affecting AD Performance

In addition to maintaining an absolute anaerobic environment, AD's performance or efficiency depends on two major groups of variables or factors: environmental (physical, chemical, and biological) factors and operational factors [125]. The environmental factors are comprised of pH, temperature, pressure, and feedstock characteristics. The feedstock characteristics include feedstock particle size, total solid content (TSC), the amount of volatile solids (VS), nutrients, carbon/nitrogen (C/N) ratio, and inhibitory components (volatile fatty acids and ammonia). The operational factors are agitation (mixing or stirring), organic loading rate (OLR), solid retention time (SRT), and hydraulic retention

time (HRT) [17,31,163]. The OLR, pH, temperature, agitation, pressure, SRT, and HRT are greatly influenced by the reactor or digester type, while volatile fatty acids and ammonia are basically influenced by the biochemical reactions involved [27]. Any drastic changes in these variables can lead to a breakdown in the AD process, as this results in changing the microorganism's environment and metabolic activity within the digester.

Since biogas/biomethane production is a microbial process, the maintenance of suitable growth conditions for biogas/biomethane-producing bacteria is essential. It is only if these conditions are fulfilled that maximum bacteria activity and adequate gas production are assured [164]. Therefore, these conditions or variables require proper monitoring and control so as to obtain optimum or maximum biogas/biomethane yield [17]. The effect or influence of all these variables on the various aspects of AD is widely elucidated in the following subsections.

## 5.1. Feedstock Particle Size

Feedstock particle size is directly correlated with the substrate or feedstock contact surface [165]. The larger the particle size, the smaller the available contact surface. That is, as the particle size increases, the contact surface reduces or decreases, and thus the space available for enzyme contact is minimized [26]. In the AD process, very good contact between the feedstock or substrate and the microbial community (or inoculum) is essential as enzymatic processes are extracellular and are adsorbed onto a particulate surface [26,166]. A feedstock with smaller particle sizes possesses a higher or larger surface area and will thus, during the AD process, display higher reaction efficiency, which will, in turn, result in increased biogas and/or biomethane yield [163].

## 5.2. Total Solid Content

The total solid content (TSC) of solid waste influences the performance and stability of AD [120,167]. Generally, TSC represents or indicates the amount or concentration, or percentage of the solids (materials) present in the solid wastes (feedstock) [168]. That is, TSC describes the dry matter of a substrate, and it is expressed as the percentage of the total weight in g/kg [169,170]. To obtain the TSC of the solid waste feedstock, the amount of feedstock is weighed and then dried at 105 °C until its water or moisture content is zero; thereafter, the dried weight is divided by the original feedstock weight [170]. TSC affects the solid sedimentation, fluid dynamics, clogging, and digester contents' rheology and viscosity, which can directly impact the overall rates of mass transfer within the digester [121]. The bacterial activity could be hampered depending on the TSC level if it is too high or too low [169]. The adjustment of TSC is commonly done by the addition of water [169]. The optimum TSC is different for each kind of biogas feedstock [169]. For example, the optimum TSC for the AD of cattle manure, agricultural wastes, and municipal solid waste was found to be 7.4–9.2% [73], 9% [171], and 10% [172], respectively. The ideal solid concentration in sewage sludge for AD ranges from 8 to 10% [32]. There are several studies that concern the effect of the TSC on the AD process performance [10,169,173]. From these several studies, it can be deduced that biogas/biomethane yield often increases with increasing the low-percentage TSC range of 1 to 10% [169,174,175], while in most cases it decreases with increasing the high-percentage TSC that is greater than the range of 10-20% [10,173,176].

## 5.3. Carbon/Nitrogen (C/N) Ratio

The ratio of the amount of carbon (C) and nitrogen (N) present in the feedstock is denoted as the carbon: nitrogen ratio or C/N ratio. The C/N ratio is an essential parameter for the AD process. A high C/N ratio indicates the presence of a low amount of nitrogen, and so there will be rapid nitrogen consumption by methanogens which consequently leads to lower biogas and biomethane production. On the other hand, a low C/N ratio depicts the presence of a high amount of nitrogen which results in ammonia accumulation and high pH values that are toxic and inhibitory to methanogens [125]. Therefore, there

must be an optimal balance between the carbon and nitrogen (i.e., C/N ratio), as well as other factors being at the optimum value to achieve process stability [177] and higher biogas/biomethane production. The suitable or optimal C/N ratio required for the effective microbial metabolic processes, maintenance of process stability, microbial growth, and better AD performance lies within the value range of 20 to 30 [121,178]. In some cases, there is a rapid occurrence of the AD process when the C/N ratio falls between 25 and 35.1 [179]. Karthikeyan and Visvanathan [121] achieved a maximum biomethane potential at a C/N ratio of 27, while Zhang et al. [56] obtained it at a C/N ratio of 15.8 when they co-digested FW with cattle manure. However, the optimal C/N ratio gossess the poor buffering capacity and produce excess amounts of volatile fatty acids during AD fermentation, while substrates that are characterized by lower C/N ratios possess a high buffering capacity and generate high amounts of ammonia during the AD fermentation process, which eventually leads to the inhibition of microbial growth [125].

#### 5.4. Nutrients and Metals (Light and Heavy)

Light metals, such as sodium, potassium, and calcium, as well as heavy metals, such as chromium, selenium, cobalt, zinc, nickel, manganese, iron, molybdenum, and copper, together with nutrients (carbon, hydrogen, oxygen, and nitrogen), are essentially required by anaerobic microbial species for the optimal growth, development of enzyme synthesis, and the maintenance of microbial activity [125,180]. The addition of these metals into the anaerobic bioreactors or biodigesters, not in excess, can improve the AD process system performance [125,181]. Nevertheless, an excess of metal level or concentration can result in the inhibition of the AD process due to the enzyme function and microorganism structure disruption [182].

#### 5.5. Presence of Inhibitory Compounds

Inhibition is a common problem for AD process systems, with dry AD process systems being more prone to the accumulation of inhibitory compounds (volatile fatty acids and ammonia). The occurrence of this inhibition in the AD system can be due to the imbalance between the rates at which hydrolysis and methanogenesis take place. A rapid or fast methanogenesis step over the hydrolysis step is required to prevent the accumulation of volatile fatty acids from lowering the pH to the point that it can inhibit methanogenesis [125]. The inhibitory compound's accumulation, associated with dry AD processes, is due to the high OLR and TSC, as well as low or no stirring/mixing, which did not allow for proper homogenization [29,127], and thus facilitated the inhibitor's accumulation [29,183]. Nevertheless, dry AD processes have a higher inhibitor tolerance [29,184] and can function at higher volatile fatty acid or ammonia concentrations, as these inhibitory compounds are localized as a result of the poor diffusion that occurs in the ADs. This does not frequently affect the entire bioreactor or biodigester volume [29].

#### 5.5.1. Volatile Fatty Acids

Volatile fatty acids are one of the paramount parameters that affect AD process technologies [185]. Volatile fatty acids are short-chain fatty acids, which are intermediate compounds produced during the acidogenesis step, where more hydrolyzed substrates are broken down. The major volatile fatty acids present during the AD process are acetic acid, propionic acid, and butyric acid [186], as well as valeric acid, caproic acid, and enanthic acid [27,187], which are commonly accumulated at the start-up period in the ADs. At a pH of 8.0, most of the volatile fatty acids (approximately 99.9%) exist in the dissolved form, while at a pH of 6.0, approximately 90% of the volatile fatty acids occur in the dissolved form [31]. Accumulated volatile fatty acids, depending on the types and concentrations or levels, can be toxic and inhibitory to the AD process [27]. The AD process inhibition takes place when the volatile fatty acids are produced in the hydrolysis/acidogenesis steps at a faster rate than they are taken up by the acetogenesis and methanogenesis steps which results in the drop of pH and, in turn, the inhibition of the methanogenic bacterial groups [188]. Several approaches have been proposed that can result in the reduction of volatile fatty acid accumulation. Among these approaches, the utilization of appropriate OLR, pH, reactor type, chemical additives, temperature, and hydrogen partial pressure have been widely considered to be important, all of which have been comprehensively reviewed by Sarker et al. [27]. The operational strategies applied to reduce the volatile fatty acids accumulation in both batch and continuous AD process systems are different. For the batch AD process system, the most common strategies are: (i) to increase the inoculum/substrate ratio and (ii) to recirculate the percolate, while for the continuous AD process system, the most common strategy used is OLR reduction [29].

## 5.5.2. Ammonia

Ammonia is produced from a nitrogen-containing substance such as protein and urea that could be present in the feedstock. It can be present in the aqueous phase as ammonium ions or ionic ammonia ( $NH_4^{+}$ ) and un-ionized ammonia ( $NH_3$ ) or free ammonia (FA), where the sum or totality of both is called the total ammonia nitrogen (TAN) [125,189]. Most of the ammonia generated during the AD process is usually produced during the stage of hydrolysis [190]. The type of ammonia produced is often influenced by variables such as a change in pH, microbial community or inoculum, and temperature [27]. Free ammonia or un-ionized ammonia is membrane permeable, and when it diffuses through the cell wall of the organisms, it causes an intracellular pH variation or proton imbalance leading to enzymatic reactions inhibition [27]. Therefore, it is a strong candidate for the inhibition of methanogens. Generally, a free ammonia concentration that ranges from 1.7 to 14 gN/L is inhibitory to methanogenic organisms, especially to the acetoclastic species, which results in a 50% or more decrease in the yield of biomethane [27]. Free ammonia values that range from 300 to 800 mg/L have been reported to be inhibitory, while the higher range values of 1500 to 3000 mg/L for ammonium are tolerated [125]. The degree to which ammonia concentration or level affects methanogenic organisms varies depending on environmental conditions and bacteria type. Thus, to achieve an optimum AD process, there should be a careful and right choice of process variables, essentially feedstock type, operating pH, type of inoculum, and temperature so that the level of free ammonia can be kept below 0.2 g/L, as recommended in the literature [182]. Different methods have been employed to overcome the accumulation of ammonia, including (i) OLR reduction, (ii) the use of co-digestion with other carbon-rich wastes or the adjustment of the C/N ratio [191], and (iii) bioaugmentation [192] and substrate dilution [182].

## 5.6. pH

The pH is a measure of the acidity or alkalinity of an aqueous fluid. It has a vital role to play in the biological activities of bacteria. Therefore, the maintenance of the appropriate pH is essential in the production of biogas/biomethane. Before the feedstock is to be fed into the digester, it is important to ascertain the pH condition. Where the feedstock pH is very low or high, it is pertinent to artificially neutralize the feedstock by adding a base or acid to the reactor (digester) [31,193]. Low or high pH decreases can inhibit the performance of methane-producing bacteria, which in turn adversely affects the yield of biogas. For example, a pH equal to or greater than 9.0 results in a significant rise in ammonia which has a strong inhibitory effect. While a pH  $\leq$  6 leads to a significant increase in volatile fatty acids, which is indicative of inhibition [30]. In general, a pH range of extremely acidic ( $\leq$ 3) or extremely alkaline ( $\geq$ 12) can be inhibitory to acidogenesis [194] and limit the rate of hydrolysis.

The pH requirement of the AD process is a compromise, as the optimal pH for methanogenic micro-organisms is reported to be most effective at pH 6.5–8.2 with the optimal pH of 7.0 [195], while for hydrolytic and acidogenic microorganisms, it is between 5.5–6.5 and 6.5–8.5, respectively [29,153]. Hence, the optimal pH for the AD process is often near neutral at a range of 6.8–7.4 [111,196]. The generation of certain chemical species

(e.g.,  $CO_3^{2-}$ ,  $NH_3$ , and  $CH_3COO^-$ ) and basic cations (e.g.,  $K^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ ) as well as multivalent anions (such as  $SO_4^{-2}$  and Fe(OH)<sub>3</sub>) reductions that occur during biochemical interaction in the course of AD processing can cause a considerable pH variation or rise in the digestate [27]. Fluctuation in pH is dangerous since it can inhibit the process of biomethanation. It is highly necessary that the pH must be properly controlled so that the normal activity of the bacteria will not be disrupted [197]. Improper control of pH will result in a large accumulation of volatile acids and, consequently, lead to a lower pH in the digester which could inhibit the biomethanation process [198]. Thus, the pH of the AD process is controlled by the bicarbonate acid–base system [199]. In a modern biogas plant, an automatic pH controller is often installed to be able to operate the AD process at the desired pH range and to control pH fluctuation.

## 5.7. Temperature

Temperature is considered to be one of the most significant operation parameters for the stability of the AD process [26]. This is because it influences enzyme and coenzyme activities of the anaerobic bacteria responsible for biogas generation [26], as they can only survive in certain ranges of temperature. That is, temperature affects the rate of reaction of AD or the biomethanation process [164,200]. Therefore, constant control of the AD temperature is pertinent to maintaining stable AD digester operation, and in order to make the AD bacteria work at their maximum efficiency, a suitable temperature is required. The temperature at which the maximum activity of bacteria occurs varies, and as a result, bacteria are classified into three categories according to the range of temperature where their maximum growth is attained. These are the psychrophilic bacteria (below 25  $^{\circ}$ C), the mesophilic bacteria (between 25 °C and 40 °C) and the thermophilic (between 40 °C and 60 °C) or extremophilic bacteria (>65 °C) [27]. The AD duration is temperature dependent, and methanogenic bacteria are very sensitive to sudden thermal changes. Thus, any drastic temperature change should be avoided [200]. This is because for a given process temperature, a few degrees of temperature fluctuation and permanent changes can have a severe effect by inhibiting the bacteria's metabolic activity and decreasing population and, thus, reducing or stopping the stoppage of biogas/biomethane production [117]. Anaerobic bacteria are most active in the mesophilic and thermophilic ranges of temperature [200]. The amount of biomethane produced in AD subjected to thermophilic temperature is almost identical to that subjected to mesophilic AD, though a higher temperature improves the rate of production [27] as well as reduces the high HRT operational requirement and hence reduces the reactor volume or size [27,201]. On the other hand, Li et al. [202] reported that the mesophilic AD system generates less biomethane than the thermophilic AD system. As a general rule, the bacteria metabolic rate, growth rate, and biogas production rate, as well as the performance of AD, increase with temperature [27]. Despite its advantages, thermophilic AD systems can be challenging to operate, unstable, energy-intensive, and sensitive to inhibition [27,203]. Consequently, mesophilic AD processes are currently the most preferred technology implemented on an industrial scale [27,204].

#### 5.8. Regular Agitation/Stirring

It is essential to stir the reactor at short intervals in order to prevent the thickening and caking of the scum, which prevents the gas from escaping into the gas holder [164]. According to Nandi et al. [205], crust formation hampers effective reactor operation and biogas formation. Mixing can be an engineering approach to solve this problem. Agitation or mixing, or stirring to a large extent, can influence the performance and cost of the ADprocessing system. Agitation promotes intimate contact between the bacteria, substrates, and nutrients to encourage more active metabolism and provides a uniform temperature or heat distribution (i.e., avoidance of pronounced temperature gradients) and uniform bacterial population density within the digester [17,27]. Adequate agitation or stirring can also set free gases that may be trapped in the substrates or remove gas bubbles produced by methanogens, reduce or prevent sedimentation and scum/foam formation, and prevent dead spaces formation that would reduce the effective digester volume [17,206,207]. The main factors that influence agitation, stirring, and mixing are the strategy of agitation, intensity, and duration of agitation, as well as the agitator/stirrer location [207].

Agitation or stirring, or mixing can be achieved by means of mechanical agitators or mixers, pneumatic agitators/mixers, hydraulic agitators, and the recirculation of the digester's contents or the recirculation of produced biogas using recirculation pumps at various frequencies and intensities (minimal (gentle), intermittent, and continuous rotation speeds) as well at different duration (several hours or several times in an hour during a day) [27,205,208]. An increase in stirring rate enhances mass transfer from the substrate in the bulk phase to the granulated biomass, thus providing nutrients to the micro-organisms [209]. Also, this increases the amount of water within the porous area of the waste, so sufficient hydrogen is made available in the water-filled pores. This hydrogen is used by methane-forming species to generate methane with carbon dioxide [210]. Reactors or digesters equipped with agitation/stirring tend to produce more biogas/biomethane [211–214] than those without agitation. However, some researchers have reported contrasting or negative results [207,215]. The use of intermittent agitation or stirring leads to the great enhancement of mass transfer from the liquid phase to the gas phase, resulting in an increased release of biogas by as much as 70% higher than is the case without mixing [216]. High intense agitation/stirring during startup can generate negative effects due to high shear forces that break microbial flocs and syntrophic relationships that exist between methanogens and bacteria, thus resulting in the acidification of the system due to the accumulation of volatile fatty acids [214,217]. In addition, among the various agitation intensities, gentle or minimal agitation leads to aggregate formation and prevents biogas/biomethane-producing organisms from being washed out and, hence, proves to be more effective [211]. For instance, Aworanti et al. [17] reported higher biogas/biomethane yield at an agitation speed of 30 rpm than at an agitation speed of 70 rpm. Thus, according to Sulaiman et al. [218], Rojas et al. [219], and Jaman et al. [214], low, gentle, or minimal-intensity agitation is preferable as it allows for proximity between microorganisms and, thus, maintains the juxtaposition of the microbes. Despite the merits of increased biogas/biomethane generation, agitation does require energy input and possesses an extra cost [27]. To this end, continuous agitation or stirring can demand as much as approximately 50% of the total biogas plant energy, with 2.5% additional energy being consumed by the agitator motor during startup [27,220]. Therefore, agitation/stirring should be carefully chosen or compromised, given the type of AD technology and the type of feedstock.

## 5.9. Hydraulic Retention Time

Retention time is a crucial parameter used for the design and optimization of AD. It encompasses both solid retention time (SRT) and hydraulic retention time (HRT). SRT refers to the retention of the microbial culture in the bioreactor [27] or the time required for feedstock degradation and microbial growth [221], while HRT, measured in days, refers to the retention time of the liquid phase [27], the time needed for complete feedstock (raw material) degradation [9] or the average amount of time that the feedstock spends in the bioreactor before being removed [222,223]. In an AD bioreactor system where the microbial mixed cultures and feedstock are present at the same phase, the SRT equals HRT. SRT and HRT can be represented using Equations (15) and (16) [27]:

$$SRT = \frac{V \times X}{Q_X \times X_X} \tag{15}$$

$$HRT = \frac{V}{Q} \tag{16}$$

where V = biodigester volume (m<sup>3</sup>); Q = influent flow rate [m<sup>3</sup>/d]; X = mixed liquidsuspended solids in the biodigester (mg/L);  $Q_x$  = removal rate of excess biosolids (m<sup>3</sup>/d);  $X_x$ : mixed liquid suspended solids in excess of biosolids flow (mg/L). HRT has an influence on biogas production, biomass or microbial concentration, kinetic model parameters, and AD system operation stability [149]. In general, HRT depends on the feedstock composition, temperature, organic loading rate (OLR), and biodigester or bioreactor volume, and is associated with the growth rate of bacteria [27,113]. To achieve constant and maximum biogas/biomethane yields, a longer or higher HRT and a lower OLR are the best options required [9]. Meanwhile, there could be significant high-molecular-weight volatile fatty acids (VFA) accumulation and bacterial washout (mobilization) at a shorter or lower HRT and a higher OLR, resulting in AD failure [27,111]. A high biodigester or bioreactor temperature increases the rate of feedstock degradation or decomposition rate and reduces the HRT. This is the reason for most thermophilic bioreactors generally being operated at a shorter or lower HRT than mesophilic bioreactors [27]. Conversely, the use of a longer or higher HRT leads to an increase in the biodigester size [27,201]. It has been reported that a minimum of 10 days of HRT is required to prevent bacteria from being washed out [32]. Therefore, the optimum operational HRT is neither very long nor very short and, in most cases, ranges from 10 to 25 days. Nevertheless, a very long HRT in the magnitude of 50–100 or more days could be required for biodigesters or bioreactors operated in colder climates [27]. Bouallagui et al. [224], Kim et al. [225], and Shi et al. [226] have, respectively, reported that there is a stable AD performance as well as increased biogas/biomethane yield as HRT increases.

## 5.10. Organic Loading Rate

The organic loading rate (OLR) is defined as the amount of feedstock or volatile solids (VS) added to an AD biodigester per unit volume per day [27,166]. This is expressed in Equation (17):

$$OLR = \frac{C}{HRT}$$
(17)

where C is the feedstock or raw-material concentration in g.VS/L and HRT are the hydraulic retention time.

Typically, biogas and biomethane yields, to some degree, increase with increasing OLR [32]. An OLR that is very low may adversely affect AD [227], while an OLR that is very or too high may result in the generation of insufficient products that promote microbial growth, as well as contribute to the accumulation of volatile fatty acids in the biodigester or bioreactor which prevents microbial growth [228]. In general, OLR is affected or influenced by factors such as TSC, HRT, microbial concentration (i.e., number of microbes) in the biodigester, and temperature within the digester [229]. For a typical AD biodigester utilization, a high-operating OLR is often preferred. This is because it allows for reduced bioreactor sizes, reduced investment cost, enriched bacterial species, and has a lower heat requirement [230]. Lowered HRT may result in high operational OLR which in turn may lead to microbial washout and overloading and, due to overloading, could result in volatile fatty acid accumulation and the eventual failure of the biodigester [27,231]. That is, there will be a decrease or reduction in biogas/biomethane production if the OLR (feeding rate) in the biodigester or bioreactor is above the optimal level, and then, eventual collapse or failure of the system due to overloading [9,124]. Several approaches to OLR optimization that lead to enhanced biogas/biomethane production are continually being researched. Some of these approaches include keeping OLR constant and simultaneously reducing the HRT [148], utilization of additives [24], and microbial management [232].

## 5.11. Pressure

Extensive studies on the effect of pressure on AD have not been conducted. Typically, AD occurs at atmospheric pressure. However, lower pressure or high pressure can be developed on the liquid surface due to different gas accumulations and exchange into the reactor headspace [27]. Petersson and Wellinger [233] reported that, as biomethane gas solubility increases with pressure, there is a lower pressure on the liquid surfaces

that results in higher yields of biogas. Singh et al. [234] have reported that a reduction in the height of a high digester (over 10 m) to a lower height (i.e., depth of about 4–5 m, horizontally oriented) resulted in a lowering of the hydrostatic pressure, thereby improving methanogenesis activities. That is, the level of hydrostatic pressure within the digester can also affect the production of methane. High pressure leads to an increase in the solubility of carbon dioxide, and thus, as the biogas has been produced, there is a partial carbon dioxide stripping, which in turn gives rise to a net increase in biomethane concentration [27]. According to Lindeboom et al. [235], the use of high pressure in the biodigester results in a methane level that is above 95%. However, it has been reported that, in some cases, high pressures in the AD bioreactor did not result in satisfactory improvement in the production of biogas [27]. Anaerobic bioreactors that make use of high pressures (i.e., pressurized bioreactors) have been developed. However, high investment costs, pH reduction, and the technical challenges associated with leakages in the bioreactor systems are recognized as a few of the drawbacks of the pressurized bioreactor [27].

## 6. Kinetics Modelling of AD

The mathematical kinetic modeling for the AD of complex organic biomass is often challenging as a result of its complicated nature and that of the substrate [25]. Nevertheless, the kinetic data of AD can be utilized to create correlations between the efficiency of the process and kinetic characteristics, as well as to reveal the mechanisms of kinetics that can cause the instability of the process [217,236]. The mathematical kinetic model used for the AD process can represent the major aspects of the biological system and predict, simulate, and quantify the system's empirical behavior under different conditions [33], as well as predict the process variable that is most influential in the system [237] and identify parameters that can be optimized [34]. It plays a vital role in monitoring the performance of the process under various conditions [25]. It is a useful predicting tool for large-scale anaerobic digester or reactor design since it helps in comprehending the design, operation, and maximization of biogas and biomethane output [217]. According to Donoso-Bravo et al. [33], the several mathematical kinetic models that have been proposed for the AD of organic waste can be divided into three generations.

The models that were modeled based on either methanogenesis or hydrolysis as the limiting step are referred to as first-generation models. The models modeled, based on the intermediate products (volatile fatty acids), redox potential (NADH/NAD<sup>+</sup> ratio), and their effects on the AD process, were designated as second-generation models, while models that considered the different substrates used in the AD and incorporated additional species and processes, as well as detailed inhibitory kinetics, were referred to as third-generation models. There have been several reviews of kinetic models, from the simplest to the more complex models for the AD process, that have been published in the literature in recent times [25,37]. Nevertheless, most of the models that deal with the production of biogas and biomethane are based on mechanistic and empirical models (data based or experimental) [34,36,238]. The mechanistic models are models formed based on the chemical, physical, or biological laws that govern the behavior of the process in relation to biogas production, while the empirical models are black-box models formed using mathematical equations to stochastically relate different factors or variables based on observation and measure extensive-process data [36]. Some examples of empirical models include response surface methodology (RSM), neuro-fuzzy models, fuzzy-logic models, partial least-square (PLS) models, and artificial neural networks (ANN), which are particularly used for nonlinear systems [34]. PLS models are used for linear systems. These models have been used to describe and predict the performances of anaerobic reactors that have been used to treat different organic wastes for biogas generation [239-241]. The mechanistic model can further be subdivided into dynamic models and steady-state (or static) models [36].

Steady-state models are those mathematical models that use input parameters that are constant to predict the constant values of the product, while dynamic models are the models that describe the temporal variability of a process system and its physical behavior. The models consist of ordinary differential equations (ODE) that are based on mass balances [34]. These models predict the biodigester's transient behavior based on the different substrates and bacterial cultures' mass balances represented by a set of differential equations [36]. Time is one of the factors or variables that is considered in dynamic models [117]. An example of the dynamic model is the anaerobic digestion model number one (ADM1) proposed by Bastone et al. [242], which involves the four stages of the AD process. ADM1 focuses on kinetics and the optimum reaction conditions but neglects the microbial degradation of different substrates [36]. Amongst the mechanistic models, ADM1 is the most widely used model in the AD process for biomethane production from wastewater [36,243]. Furthermore, reaction kinetic models and stoichiometric models are other forms of models that can be applied in modeling AD process systems.

Stoichiometry models are nondynamic white-box models which are time-independent and are based on stoichiometry, as well as rely on the organic substrates' basic elements/components data [244]. They are only applied for biogas and biomethane production calculation. That is, they are helpful for CH<sub>4</sub> and CO<sub>2</sub> theoretical values estimation. Reaction kinetic models are based on microbial growth, substrate conversion or degradation, and byproduct formation [245] and thus can be categorized into growth-kinetic models, substrate-degradation models, and product-formation models [244]. These different kinds of reaction-kinetic models have been utilized to model the influences of physical and chemical conditions (such as temperature, total solid content, pH, inhibitors, etc.) on the AD of a feedstock [35,246]. Kythreotou et al. [35] reported that the kinetic model of biogas production (i.e., product-formation model) was the most important among the reaction-kinetic models. Therefore, understanding the kinetics of biogas and biomethane production from substrates is very significant for designing and evaluating AD digesters or reactors. Among the numerous reaction-kinetic models utilized in evaluating and describing AD processes, the most common reaction-kinetic model expressions that have been employed in recent times, as presented in Table 4, include (i) the first-order kinetic model [202,247–249] or exponential rise to maximum [144,250], (ii) the Gompertz kinetic model [251], (iii) the modified Gompertz kinetic model [202,248,252], (iv) the logistic model [251-253], (v) the Chen-Hashimoto model [247,254], (vi) the anaerobic-digestion model one (ADM1) [255,256], (vii) the Richards model [251,253], (viii) the modified Richards model [251,252], (viii) the cone model [251,257,258], and (ix) the Monod model [257,259].

Model	Equation	Ref.
First-order kinetic model	$C(t) = C_0 \times \left(1 - e^{(-kt)}\right)$	[20]
Gompertz model	$C(t) = a \exp[-\exp(-kt)]$	[21]
Modified Gompertz model	$C(t) = A \exp\left\{-exp\left[\frac{\mu_{max}e}{A}(\lambda - t) + 1\right]\right\}$	[22]
Logistic model	$C(t) = rac{a}{1+b\exp(-kt)}$	[23]
Modified logistic model	$C(t)=rac{A}{\left[1+ ext{exp}\left(rac{4\mu_{max}}{A}(\lambda+t)+2 ight) ight]}$	[24]
Chen-Hashimoto model	$C(t) = C_0 \left( 1 - \frac{K_{CH}}{HRT \times \mu_{max} \times K_{CH} - 1} \right)$	[25]
Richards model	$C(t) = a\{1 + v \exp[k(\tau - x)]\}^{(-\frac{1}{v})}$	[26]
Modified Richards model	$C(t) = A \left\{ 1 + v  \exp(1 + v) \times exp\left[\frac{\mu_{max}}{A}(1 + v)\left(1 + \frac{1}{v}\right) \times (\lambda - t)\right] \right\}^{\left(-\frac{1}{v}\right)}$	[27]
Cone model	$C(t) = \frac{C_0}{1 + (kt)^{-n}}$	[28]
Monod model	$C(t) = C_0 \left(rac{kt}{1+kt} ight)$	[29]

Table 4. Most common kinetic models used for AD process reaction kinetics.

Where, C(t) is the cumulative-specific biogas or biomethane yield (production) at the hydraulic retention time or digestion time t (dm<sup>3</sup>/g or mL/g VS); *A* is the maximum-specific biogas or biomethane production potential (dm<sup>3</sup>/g or mL/g VS),  $\mu_{max}$  is the maximum-specific biogas or biomethane production rate (dm<sup>3</sup>/g /day),  $\lambda$  is the lag-phase period or the minimum time required to produce biogas or biomethane (day); e is a constant that is equal to 2.7183; HRT is the hydraulic retention time (days); K<sub>CH</sub> is the Chen and Hashimoto kinetic constant (dimension less); n is the shape factor; C<sub>o</sub> is the biogas or biomethane production-rate constant (day<sup>-1</sup>); t is the hydraulic retention time (days); a, b are the logistic constants; and v is the shape coefficient.

The above models are basically used to model the cumulative biogas and biomethane production with time and thus comprehensively represent the basic framework for the simulation of the biogas and biomethane production process. Several researchers have reported on the application of these models to determine the kinetic parameters of AD processing of different organic feedstocks and to simulate the biogas and biomethane yielding rates and the cumulative biogas and biomethane production [9,176,214,260–262]. Most of these researchers reported that the modified Gompertz model fitted best to most of the AD kinetic data [9,176,251,262].

#### 7. Knowledge Gap and Future Research

Based on this review, herein are presented prospects for potential research areas that could be investigated in future work.

(i) The feedstock composition itself is of great importance concerning the quality of the biogas and biomethane, being the main product of AD process technology. Components that are not desirable will affect its potential utilization as fuel. That is, the relative amounts of these undesirable components in the starting feedstock need to be carefully put into consideration, along with their fate, during the AD process to ensure that relatively clean biogas can be obtained. Hence, one of the main challenges, which should be addressed, is to carry out more systematic research studies with a wide biomass waste or feedstock diversity so as to establish a comprehensive relationship between the feedstock composition and the AD performance under different operating conditions and how the AD performance is affected by these conditions;

(ii) MS-AD (three-stage and above) is more complex in operation, more expensive, and requires more maintenance and operation energy when compared to TS-AD process technology. However, its performance has not been adequately improved compared to the TS-AD process technology. Thus, its application on a large scale is currently not advisable, and so it is suggested or proposed that there should be further research studies on its operation with the aim of reducing the cost involved;

(iii) There is also the need for AD economic cooperation in order to improve and establish a circular economy. Thus, there should be further research development where the AD process technology can be merged or integrated with biorefineries such that the intermediates products (volatile fatty acids) of AD can be utilized for the production of high-value products. It can as well be integrated with thermochemical processes (e.g., hydrothermal liquefaction (HTL) or hydrothermal carbonization (HTC)) such that the digestate as a byproduct from AD process technology can be passed into the thermochemical process unit and be used for further production of biogas and value-added products such as hydrochar. Thus, performing the AD-HTL in a continuous mode needs to be investigated, and this also requires research on the design of novel thermochemical (e.g., HTL) reactors;

(iv) The process or liquid water from the HTL or HTC section contains nutrients (nitrogen and phosphorus) that can be recovered and utilized as fertilizer. The methods that have been used in full scale for nutrient recovery are ammonia stripping and struvite formation (chemical precipitation) [263–265]. Other methods that have been utilized are ion exchange and adsorption [263–265]. These methods have their drawbacks, and therefore further research should be carried out on nutrient recovery using other methods, such as pressurized and nonpressurized membrane technologies. Techniques for the disposal of solid volatiles and liquid residuals after nutrient recovery should also receive research attention.

#### 8. Conclusions

Anaerobic digestion process technology suggests being a very reliable and feasible technology for recycling and recovering organic biomass waste. In terms of socioeconomic and environmental considerations, AD process technology appears to be the best option or alternative for waste management due to its potential to extract renewable green energy with low emissions from waste. That is, the AD process technology provides an effective technology to treat organic biomass waste in order to reduce waste, improve air pollution, and improve energy security through meeting local energy (biogas, heat energy, and electricity) demand. Biogas/biomethane is a renewable green energy that can be utilized as an alternative to fossil fuels for heat and power generation. However, the currently perceived complexity of the AD process operation tends to limit its full implementation. Understanding the operational factors or variable impact on AD performance and how a stable operation without inhibition can be sustained is thus very critical. Therefore, a more thorough and adequate knowledge of the process is required for the proper development and stability of the AD process technology. This paper, therefore, reviewed the AD process technologies for the treatment or processing of organic biomass waste with regard to its classification, the mechanisms involved in the process, process variables that affect the performance, and the kinetic models utilized for describing the process reaction kinetics. Gazing into the future, research studies on reduced MS-AD operational cost, integrated or hybrid AD-biorefinery technology, integrated or hybrid AD-thermochemical process, novel thermochemical reactor development, nutrient recovery from integrated AD-thermochemical process, and solid and liquid residual disposal techniques are more likely to receive increased attention for AD process technology of biomass wastes. It can be concluded from this review that the AD process technologies are of different classifications based on the feedstock properties, mode of operations, growth temperature of microorganisms involved in the process, and type of digester or reactor configuration. Each of these technologies has its merits and demerits.

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