# Waste to Energy: A Focus on the Impact of Substrate Type in Biogas Production

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*Abstract:*

> Anaerobic digestion is an efficient technology for a sustainable conversion of various organic wastes such as animal manure, municipal solid waste, agricultural residues and industrial waste into biogas. This technology offers a unique set of benefits, some of which include a good waste management technique, enhancement in the ecology of rural areas, improvement in health through a decrease of pathogens and optimization of the energy consumption of communities. The biogas produced through anaerobic digestion varies in composition, but it consists mainly of carbon dioxide methane together with a low quantity of trace gases. The variation in biogas composition are dependent on some factors namely the substrate type being digested, pH, operating temperature, organic loading rate, hydraulic retention time and digester design. However, the type of substrate used is of greater interest due to the direct dependency of microorganism activities on the nutritional composition of the substrate. Therefore, the aim of this review study is to provide a detailed analysis of the various types of organic wastes that have been used as a substrate for the sustainable production of biogas. Biogas formation from various substrates reported in the literature were investigated, an analysis and characterization of these substrates provided the pro and cons associated with each substrate. The findings obtained showed that the methane yield for all animal manure varied from 157 to 500 mL/gVS with goat and pig manure superseding the other animal manure whereas lignocellulose biomass varied from 160 to 212 mL/gVS. In addition, organic municipal solid waste and industrial waste showed methane yield in the ranges of 143?516 mL/gVS and 25?429 mL/gVS respectively. These variations in methane yield are primarily attributed to the nutritional composition of the various substrates.

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Review

# Waste to Energy: A Focus on the Impact of Substrate Type in Biogas Production

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**Abstract:** Anaerobic digestion is an efficient technology for a sustainable conversion of various organic wastes such as animal manure, municipal solid waste, agricultural residues and industrial waste into biogas. This technology offers a unique set of benefits, some of which include a good waste management technique, enhancement in the ecology of rural areas, improvement in health through a decrease of pathogens and optimization of the energy consumption of communities. The biogas produced through anaerobic digestion varies in composition, but it consists mainly of carbon dioxide methane together with a low quantity of trace gases. The variation in biogas composition are dependent on some factors namely the substrate type being digested, pH, operating temperature, organic loading rate, hydraulic retention time and digester design. However, the type of substrate used is of greater interest due to the direct dependency of microorganism activities on the nutritional composition of the substrate. Therefore, the aim of this review study is to provide a detailed analysis of the various types of organic wastes that have been used as a substrate for the sustainable production of biogas. Biogas formation from various substrates reported in the literature were investigated, an analysis and characterization of these substrates provided the pro and cons associated with each substrate. The findings obtained showed that the methane yield for all animal manure varied from 157 to 500 mL/gVS with goat and pig manure superseding the other animal manure whereas lignocellulose biomass varied from 160 to 212 mL/gVS. In addition, organic municipal solid waste and industrial waste showed methane yield in the ranges of 143–516 mL/gVS and 25–429 mL/gVS respectively. These variations in methane yield are primarily attributed to the nutritional composition of the various substrates.

**Keywords:** biogas; organic waste; methane yield; microorganism; anaerobic digestion

## 1. Introduction

Energy is of great importance in facilitating the socioeconomic development of a country. The increasing world population has consequently increased the demand for energy. However, the combustion of fossil fuel resources to meet these energy needs leaves a negative footprint. It contributes to global warming due to the emission of carbon dioxide ($CO_2$), methane ($CH_4$) and nitrous oxide ($N_2O$) all classified as greenhouse gases (GHGs). In addition, the depletion of fossil fuel resources due to its non-renewable nature and massive utilization has brought the need for an alternative energy resource that are renewable, abundant and cost effective [1,2].

Biogas production from locally available renewable organic resources can be a good alternative because it contributes to the reduction of GHG emissions. Biogas technology provides an attractive route for the utilization of different categories of biomass for meeting energy needs [3]. This technology

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offer a unique set of benefits, some of which include good waste management technique, enhancement in the ecology of rural areas, decrease in pathogenic diseases, optimization of the energy consumption of rural communities and promotion in agricultural structure [4].

Biogas is a mixture of gases comprising mostly of methane and carbon dioxide as well as a low quantity of other gases such as hydrogen sulphide ($H_2S$), ammonia ($NH_3$), oxygen ($O_2$), hydrogen ($H_2$), nitrogen ($N_2$) and carbon monoxide (CO) [5,6]. This mixture of gases results from a biochemical process known as anaerobic digestion (AD). Anaerobic digestion is a biochemical process that involves the degradation of organic resources to simple substances to produce biogas and digestate through the activities of a microorganism. Digestate is a biofertilizer, which when used in an agricultural integrated system aids in closing the nutrient demand gap [7]. AD technology is employed in the treatment of various organic wastes [1]. These organic wastes include animal manure, municipal solid wastes and agroindustrial wastes. They serve as a substrate for the anaerobic digestion process.

In biogas production, various factors are of great importance, however the type of organic substrate used has been found to play a significant role in the yield and composition of the biogas [3]. A number of biogas digesters operating worldwide utilize different types of substrates and this results in a unique microbial community and variation in methane composition in such digesters. Some studies have used a sequencing technology to analyze the structure of these microorganism communities involved in the AD process. These microorganisms consisting of bacteria, fungi and archaea are responsible for all the reactions occurring within the digester system [8,9].

The variation in biogas compositions are dependent on the substrate types used, which is traceable to the difference in their chemical composition as well as their biodegradability. However, there is a lack of comprehensive studies in the literature, which evaluates the contributions of various substrates used in biogas production and the limitations associated with each substrate. Therefore, the aim of this review study is to provide a comprehensive analysis on the different types of organic wastes that has been used as a substrate for the sustainable production of biogas via the anaerobic digestion process. Biogas formation from various substrates reported in the literature will be investigated and their pros and cons will be addressed to enable the synthesis of knowledge for proper means of maximizing biogas yield from organic matters.

## 2. Anaerobic Digestion Metabolic Pathways

The biological decomposition of organic substrates during anaerobic digestion is divided into four phases namely hydrolysis, acidogenesis, acetogenesis and methanogenesis. These biochemical phases are directly linked in such a manner that the byproduct of one phase is the substrate of the next phase. They occur simultaneously in an oxygen-free environment and results in the formation of biogas and digestate as a byproduct [10]. These biochemical decomposition phases are associated with a series of chemical reactions as shown in Equations (1)–(13) presented in Table 1.

Hydrolysis Reactions

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2 \tag{1}$$

Acidogenesis Reactions

$$C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2 \tag{2}$$

$$C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O \tag{3}$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \tag{4}$$

$$C_3H_7O_2N + 2H_2O \rightarrow C_2H_4O_2 + NH_3 + CO_2 + 2H_2 + ATP \tag{5}$$

$$C_4H_9O_3N + H_2O \rightarrow C_3H_6O_2 + NH_3 + CO_2 + H_2 + ATP \tag{6}$$

$$4CH_3COCOO^- + 4H_2O \rightarrow 5CH_3COO^- + 2HCO_3^- + 3H^+ \tag{7}$$

Acetogenesis Reactions

$$CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^- + HCO_3{}^- + 3H_2 \tag{8}$$

$$C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2 \tag{9}$$

$$CH_3CH_2OH + 2H_2O \leftrightarrow CH_3COO^- + 2H_2 + H^- \tag{10}$$

Methanogenesis Reactions

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{11}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{12}$$

$$2CH_3CH_2OH + CO_2 \rightarrow CH_4 + 2CH_3COOH \tag{13}$$

**Table 1.** Biochemical reactions associated with anaerobic digestion phases.

| AD Phase | Associated Chemical Reactions | Ref. |
|---|---|---|
| Hydrolysis | $C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2$ | [11] |
| Acidogenesis | $C_6H_{12}O_6 \leftrightarrow 2CH_3CH_2OH + 2CO_2$ | [12–16] |
| | $C_6H_{12}O_6 + 2H_2 \leftrightarrow 2CH_3CH_2COOH + 2H_2O$ | |
| | $C_6H_{12}O_6 \rightarrow 3CH_3COOH$<br>$C_3H_7O_2N + 2H_2O \rightarrow C_2H_4O_2 + NH_3 + CO_2 + 2H_2 + ATP$<br>$C_4H_9O_3N + H_2O \rightarrow C_3H_6O_2 + NH_3 + CO_2 + H_2 + ATP$<br>$4CH_3COCOO^- + 4H_2O \rightarrow 5CH_3COO^- + 2HCO_3{}^- + 3H^+$ | |
| Acetogenesis | $CH_3CH_2COO^- + 3H_2O \leftrightarrow CH_3COO^- + H^- + HCO_3{}^- + 3H_2$ | [17] |
| | $C_6H_{12}O_6 + 2H_2O \leftrightarrow 2CH_3COOH + 2CO_2 + 4H_2$ | |
| | $CH_3CH_2OH + 2H_2O \leftrightarrow CH_3COO^- + 2H_2 + H^-$ | |
| Methanogenesis | $CH_3COOH \rightarrow CH_4 + CO_2$ | [18] |
| | $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ | |
| | $2CH_3CH_2OH + CO_2 \rightarrow CH_4 + 2CH_3COOH$ | |

At the hydrolysis phase as shown in Table 1 complex biopolymer compounds such as carbohydrate, protein and lipids are degraded into water-soluble compounds. A typical example is shown in Equation (1) in which cellulose is hydrolyzed in water to produce glucose and hydrogen. This phase prepares the substrate for further degradation by making its products available for the fermentative microorganisms in the next phase [19]. In the next phase, known as the fermentation stage, the acidogenic bacteria converts glucose, amino acids and lipids into organic acids, volatile fatty acids (VFAs), carbon dioxide ($CO_2$) and hydrogen gas ($H_2$) as shown in Equations (2)–(7). The most significant organic acid produced at this phase is $CH_3COOH$, which serves as substrates for methanogenic microorganisms [20]. At the acetogenesis stage, the VFAs particularly acetic acid and butyric acid are converted to acetate, $H_2$ and $CO_2$ as shown in Equations (8)–(10). Equation (8) shows the conversion of the phase product to acetate ($CH_3COO^-$) and $H_2$, which are utilized in the next stage [17]. In the final phase, known as the methanogenesis stage, $CH_3COOH$ is converted to $CH_4$ and $CO_2$ as depicted by Equation (11). Furthermore, the produced $CO_2$ reacts with $H_2$ gas to produce more $CH_4$, while $CH_3CH_2OH$ undergoes decarboxylation to yield $CH_4$ as shown in Equations (12) and (13) respectively. Acetophilic methanogenic bacteria are responsible for the decarboxylation of acetate into $CH_4$ while the hydrogenophilic methanogenic bacteria group produces $CH_4$ through a $CO_2$ and $H_2$ reaction [21]. These products form the biogas that emerges as the final product of an anaerobic digestion process.

### *Microbial Groups Involved in Anaerobic Digestion*

The production of biogas from organic substrates (biomass material) is a complex microbiologically dependent process. The organisms that catalyze the conversion of organic substrates into biogas and other inorganic subunits operate under interdependent microbial activities, involving a consortium of different microbes namely bacteria, archaea and fungi. These complex microbial community that facilitate the conversion of organic polymers under anaerobic condition into biogas has until now been understudied as most of them could not be cultured in the laboratory. Recently, the advent of high throughput sequencing has revealed the different microbial groups involved in biogas production [6,22–25].

A recent study showed that fungi, though the group least present within the microbial community, is the most stable member of the community within the system. Bacteria and archaea are less stable and fluctuates as the system's chemical conditions changes during the biogas production processes. *Methanoculleus* belonging to the Methanomicrobiales order was found to be abundant at the completion phase of the methanogenesis compared to Methanosarcinales and Methanobacteriales. This shows that the hydrogenotrophic pathway is the main methanogenesis channel within the biogas digester system. These microbes account for 8–15 percent of the entire microbial community and perform the most important role that results in the production of biogas. Methylotrophic methanogenesis are carried out mostly by species of Methanosarcinales and *Methanosphaera* within the order Methanobacteriales. Acetate is used as a growth substrate for methanogens such as *Methanosarcina* and *Methanosaeta* spp. The former has been found to be a predominant group of methanogen in the digester due to its ability to adapt and tolerate stressful conditions such as heat, salt, ammonia and organic matter load of the digester better than the latter [26–28].

However, bacteria are equally an important agent in the production of biogas as their activities result in the production of substances (acetic acids), which serve as a substrate for methanogens. These bacteria can best be described as facultative anaerobes (*Clostridium, Paenibacillus, Ruminococcus, Streptococci* and *Thermoanaerobacteriaceae*) as well as acetogenic bacteria (*Acidaminococcus* and *Aminobacterium*) and sulphate reducing bacteria (*Desulfovibrio*). Other bacteria groups identified to participate in the process are *Proteobacteria, Chloroflexi, Verrucomicrobia, Actinobacteria, Acidobacteria, Spirochaetes, Plantomycetes, Fibrobacteres, Tenericutes* and *Cloacimonetes*. Some of these bacteria participate in the hydrolysis of organic molecules, while *Acidaminococcus*, and *Desulfovibrio* are responsible for the production of acetic acids from the substrates [29–32]. In addition, syntrophic acetogens, which are responsible for the breakdown and oxidation of alcohols and organic acids to acetate, hydrogen and carbon dioxide, are *Syntrophorhabdus, Syntrophus, Syntrophobacter* and *Pelobacter*. They are very abundant in the biogas digester. They are cellulolytic microbes capable of cellulose breakdown to simple sugars [33,34]. The type of substrate used and temperature of the biogas digester will determine which group of microbes will dominate in the system. At higher temperature, Thermotogae dominates. At the substrate level, municipal wastewater has more of *Chloroflexi* than animal waste or organic manure and *Firmicutes* are the most dominant bacteria in the digester containing animal waste and/or organic manure [25,35,36].

Although, bacteria and archaea are the predominant microbes in the digester, fungi are equally key players in the biogas formation process. They are facultative anaerobes and are capable of converting carbohydrate molecules via fermentation to acetate, carbon dioxide, formate, ethanol, hydrogen and lactate. They belong to the phyla Mucoromycotina, Pucciniomycotina, Agaricomycotina, Saccharomycotina, Pezizomycotina and Neocallimastigomycota. Studies have shown that fungi operate best in synergy with methanogens in the breakdown of cellulose [37–39]. Therefore, to achieve a maximum yield of biogas in the digester a symbiotic relationship between these microbes mentioned above should be maintained and efforts should be made to monitor the activities of detrimental organisms such as bacteriophages and protozoans that prey on the bacterial community, which could affect the performance of the system–biogas digester.

## 3. Substrates for Biogas Production

The suitability of a biomass as a substrate for the production of biogas is majorly dependent on its nutritional composition. These compositions influence the biogas yield, methane content, biodegradability and degradation kinetics of the biomass involved. The major nutritional composition of interest in substrates include carbohydrate, protein and fats [10]. Previous studies showed the theoretical estimation of the possible methane yield and biogas percentage realizable from these nutrients using the Buswell formula as shown in Table 2.

**Table 2.** Estimation of the maximum theoretical methane yield and biogas percentage composition.

| Nutrient | Methane Yield ($m^3$/kg VS) | $CH_4$ (%) | $CO_2$ (%) | Reference |
|---|---|---|---|---|
| Carbohydrate | 0.42 | 50 | 50 | [24] |
| Protein | 0.50 | 50 | 50 | [24] |
| Lipid | 1.01 | 70 | 30 | [40] |

As observed in Table 2, substrates rich in lipids such as fats hold a greater potential for methane yield. Nevertheless, its degradation releases long-chain fatty acids that could be toxic to the microbial community and causes a drop in pH. This could be minimized, by using a start-up strategy that enhances the development of a special group of microorganism that is resistant to toxicity [41–43]. Protein rich substrates also have a high potential for methane yield. Degradation of such substrates releases ammonium ($NH_4^+$) that could increase the alkalinity of the anaerobic digestion process. This will consequently enhance the digestate value as a fertilizer as well as inhibit the activities of the methanogens. This inhibition occurs because of a shift in equilibrium from ammonium to ammonia ($NH_3$) usually in a varying concentration ranging from 53 to 1450 mg/L [44]. Previous studies have indicated that microorganisms can acclimatize in an environment of high $NH_3$ concentration and still produce biogas efficiently [45].

Besides protein and lipid-rich substrates, some other biomass with a high degree of lignocellulose are used as a substrate for the production of biogas. Although this class of biomass is usually difficult to degrade because of their heterogeneous structure, recalcitrant nature and low accessibility by enzymes (carbohydrate polymers) [46–48]. Different pretreatment mechanisms are adopted in breaking down the heterogeneous matrix, increasing the surface area and porosity of the lignocellulose biomass for enhanced biogas production. For efficient production of biogas from any given substrate, it is paramount to supply sufficient nutrients in the right proportion to meet the microorganisms' nutritional requirements and sustain an optimal growth of these microbial communities. However, these requirements are usually difficult to meet with one type of substrate explaining the reason for exploration of various types of substrates in a monodigestion process as well as codigestion of two or more substrates. Substrates for the production of biogas can be broadly divided into three groups, namely agricultural waste, municipal organic waste and industrial waste.

### 3.1. Agricultural Waste

Agricultural waste emanates from different agricultural activities. They include animal waste, lignocellulosic biomass usually in the form of crop residue, forest residue and energy crop.

### 3.1.1. Animal Waste

Animal waste is a renewable and cost-effective substrate for the production of biogas through anaerobic digestion. This organic waste if not properly handled and disposed poses a threat to the environment because of its high concentration of nitrogen and phosphorus. In addition, the presence of pathogens, antibiotics, heavy metals and microorganisms in animal waste can contaminate water bodies, air and the soil [1]. However, the transformation of these animal wastes using anaerobic digestion technology could offer the dual benefits of producing sustainable biogas energy and good waste management technique. Animal wastes identified as a viable substrate for biogas production are manure derived from cattle, pig, sheep, goat and poultry. This is due to its high nutrient content, high organic matter concentration and high buffering capacity. Typically, the amount of animal waste that can be derived from a given farm varies based on type, size and age of the animal, feed and feeding mechanism and type of breeding [49].

Generally, manure from different animals show diverse characteristics, which can be a consequence of their management system, diet, digestive system and animal type. Apart from feces and urine that make up the major part of animal slurry, materials such as sand, straw from bedding material, water from cleaning and small branches are also found in it. All these constitute variation in the characteristics of animal waste. The volatile solid (VS), total solid (TS), pH and carbon to nitrogen ratio are important quantitative characteristic parameters for determining the methane production potential of animal waste. Table 3 presents the physiochemical characteristics of various animal manure and their corresponding methane yield.

**Table 3.** Physiochemical characteristics and methane yield of various animal manure.

| Animal Manure | pH | TS (%) | VS (%) | C/N Ratio | $CH_4$ Yield (mL/gVS) | Reference |
|---|---|---|---|---|---|---|
| Cattle Manure | 7.1–8.6 | 14.5–22.7 | 11.9–72.0 | 14.59–18.9 | 157.0–395.0 | [50–54] |
| Pig Manure | 6.4–7.5 | 8.2–36.7 | 6.2–82.8 | 5.7–13.5 | 204–438.4 | [53,55–60] |
| Chicken Manure | 6.9–7.4 | 20.0–92.6 | 18.3–84.1 | 7.5–9.75 | 160.0–396.0 | [53,61–65] |
| Sheep Manure | 7.16–8.1 | 22.3–40.0 | 18.7–72.7 | 11.3–14.7 | 207.0–357.0 | [50,66,67] |
| Goat Manure | 7.9 | 33.7–55.5 | 27.7–89.4 | 18.0 | 402–500 | [66–68] |
| Donkey Manure | 6.8 | 19.8 | 14.4 | - | 380 | [69] |

It was observed from the literature that the methane yield of various animal manure varies significantly worldwide as evident in Table 3. This can be attributed to a range of factors such as a difference in the origin of the animal manure, animal diet, variation in animal digestion, management system, manure storage mechanism prior to the anaerobic digestion process and intestinal microorganism [70]. The methane yield from pig manure (204.0–438.4 mL/gVS) and goat manure (402–500 mL/gVS) were found to supersede that of other manure. The high methane yield in pig manure can be related to its high buffering capacity that protects the digestion process against problems such as acidification associated with high TS. The accumulation of volatile fatty acids usually causes instability and AD system failure particularly at a high organic loading rate [57]. However, with good buffering capacity of the substrate an adequate environment is provided for optimum functioning of microorganisms. The TS and VS concentration of the animal manure has its contribution towards the methane yield. As observed from Table 3, chicken manure gave the highest TS content of 92.6% obtained in Bojti et al.'s [62] study. This resulted in a lower methane yield of approximately 160 mL/gVS, which is comparable to the lowest methane yield of cattle manure. With a higher percentage of TS in a substrate, the amount of water decreases and this reduces the activities of the microorganism. This is because of the main contribution of water in the growth of microorganisms that facilitates the dissolution and transport of nutrients [71]. Cattle manure with the reported TS content that ranged from 14.5 to 22.7% and VS content that ranged from 11.9 to 72.0% gave the lowest methane yield. This could be traceable to a higher lignin content in cattle manure originating from their feed that contains a structural carbohydrate (cell wall components) as compared to other farm animal manure [72]. In a recent review study, it was shown that the highest lignin content was recorded in cattle manure (11.5%) as compared to pig manure (8.5%) and poultry manure (4.2%). This lignin content inhibited methane production in cow manure as evident in the average methane yield of 168.0 mL/gVS reported compared to 215.0 mL/gVS and 255.0 mL/gVS reported for pig and poultry manure respectively [73]. Li et al.'s [2020] study further showed a higher lignin content (14.0%) in cattle manure as compared to sheep manure (8.6%), which resulted in a theoretical methane yield (357 mL/gVS) of cattle being lower than that of sheep (395.0 mL/gVS). The pH for all the animal manure as gathered from the literature presented in Table 3 ranged from 6.4 to 8.6, where cattle manure and sheep manure gave the highest pH value of 8.6 and 8.1 as recorded in a recent study [50]. The reported pH range efficiently supports the methanogenesis process and enhances the activities of hydrolytic enzymes [74].

### 3.1.2. Lignocellulosic Biomass

The abundant production of lignocellulosic biomass, which approximates to 200 billon tons per year, made it a viable resource for sustainable energy production. Anaerobic digestion identified as a less energy intensive process is a sustainable route for the conversion of a variety of lignocellulosic biomass into biogas [75]. Lignocellulosic biomass is comprised of three major components namely cellulose, hemicellulose and lignin that primarily influences its biodegradation. Cellulose, being the most abundant and main component of all plant cell walls, usually constitutes about 35–50% of the entire composition. It is a linear polymer formed by D-glucose subunits linked through β-(1-4) covalent bonds [76]. The β configuration gives cellulose a structure, which could be in the crystalline or amorphous form. Its biodegradation particularly crystalline cellulose involves a number of enzymes namely endo-cellulases, exo-cellulases and β-glucosidases. These enzymes are responsible for splitting of β-1, 4 glucosidic bonds, degradation of polymers and cellobiose to glucose. In addition, an extracellular multi-enzyme called cellulosome performs the complete degradation by binding to the substrate [77].

Hemicellulose, the second most dominant fraction of the lignocellulosic biomass, accounts for about 20–35% of the total composition. It consists of a variety of polysaccharides including xylan, glucomannan, glucuronoxylan, xyloglucan and arabinoxylan depending on the plant tissue and species [78]. Hemicellulose degradation are majorly attributed to a key enzyme called xylanases that breaks β-1,4 backbone of the xylan polymers. This key enzyme exists in a variety of forms depending on substrate specificities, action mechanisms and hydrolytic activity. The third component known as lignin, encapsulates hemicellulose and cellulose to produce a hydrophobic 3-dimensional structure called "Lignin-Carbohydrate Complexes" (LCC). Lignin recalcitrant nature limits its degradation in an anaerobic environment [75]. However, various pretreatment mechanisms are usually adopted to break the lignin and polysaccharides linkage, thus, making the hemicellulose and cellulose more accessible to microorganisms and hydrolytic enzymes. Some lignocellulosic biomass with their respective hemicellulose, cellulose and lignin composition are shown in Table 4.

**Table 4.** Composition of some lignocellulosic biomass for anaerobic digestion.

| **Biomass Type** | **% of Dry Weight** | | | **Reference** |
|---|---|---|---|---|
| | **Cellulose** | **Hemicellulose** | **Lignin** | |
| Eucalyptus | 38.0–45.0 | 12.0–13.0 | 25.0–37.0 | [79] |
| Switch grass | 43.1 | 31.7 | 11.3 | [80] |
| Nut shell | 25.0–30.0 | 25.0–30.0 | 30.0–40.0 | [81] |
| Grasses | 25.0–40.0 | 35.0–50.0 | 10.0–30.0 | [81] |
| Corn Stover | 33.7 | 19.1 | 15.2 | [82] |
| Bagasse | 38.2 | 27.1 | 20.2 | [79] |
| Rice straw | 37.8 | 29.6 | 14.8 | [54] |
| Cotton stalk | 50.4 | 15.6 | 16.3 | [83] |
| Wheat straw | 48.6 | 29.4 | 7.3 | [84] |
| Corn cob | 45.0 | 35.0 | 1.05 | [81] |
| Rice Husk | 41.4 | 18.0 | 20.4 | [80] |
| Pineapple leaves | 30.0 | 37.0 | 22.0 | [85] |
| Pineapple stem | 37.0 | 34.0 | 20.0 | [85] |
| Pineapple root | 42.0 | 32.0 | 19.0 | [85] |

From Table 4, it can be observed that cellulose dominated in the composition for all lignocellulosic biomass particularly in the cotton stalk, wheat straw and corncob, with lignin accounting for the lowest composition with an exception of *Eucalyptus* and nutshell. The high lignin content in *Eucalyptus* is attributed to it been a woody biomass that derives its high thermal stability from high lignin content. It is evident from Table 4 that the total composition of cellulose, hemicellulose and lignin in all biomass did not amount to 100%. The remaining percentage is a summation of organic, and inorganic compounds such as lipids, protein and other extractives.

Extractives are classified as plant cell wall chemicals constituting of fatty alcohols, fatty acids, phenols, resin acid, terpenes, rosin, steroids and waxes. These extractives increases the biodegradability of lignocellulose and are responsible for its durability, color as well as smell [85,86]. It is important to highlight that cellulose, hemicellulose and lignin composition does not only vary with biomass species as observed in Table 4, but also varies based on biomass maturity and growth conditions. These variations in composition influence the biogas production potentials of lignocellulosic biomass. A recent study focused on AD performance of cellulose, hemicellulose, lignin and their mixtures to understand their individual contribution towards biomethane production. Table 5 presents the AD performance of these components as reported.

**Table 5.** Anaerobic digestion performance of lignocellulose compositions. Adapted from [75].

| Substrates | TMMY (mL/gVS) | EMY (mL/gVS) | BD (%) |
|---|---|---|---|
| MC | 407.8 | 211.8 | 51.9 |
| XY | 382.5 | 133.9 | 35.0 |
| MC + XY | 394.6 | 185.1 | 46.9 |
| MC + XY + AL | 414.8 | 178.1 | 42.9 |
| MC + XY + SL | 450.2 | 160.1 | 35.6 |

MC: microcrystalline cellulose, XY: xylan (hemicellulose), AL: alkali lignin and SL: sodium lignosulfonate.

In Table 5, the theoretical maximum methane yield (TMMY), experimental methane yield (EMY) and biodegradability (BD) of cellulose, hemicellulose, lignin and their combination are presented. TMMY and BD were determined using Equations (14)–(16) along with the elemental compositions of cellulose, hemicellulose and lignin.

$$C_aH_bO_cN_d + \left(a - \tfrac{b}{4} - \tfrac{c}{2} + \tfrac{3d}{4}\right)H_2O \rightarrow \left(\tfrac{a}{2} + \tfrac{b}{8} - \tfrac{c}{4} - \tfrac{3d}{8}\right)CH_4 + \left(\tfrac{a}{2} - \tfrac{b}{8} + \tfrac{c}{4} + \tfrac{3d}{8}\right)CO_2 + dNH_3 \tag{14}$$

$$\text{TMMY} = \frac{22.4 \times 1000 \times (a/2 + b/8 - c/4 - 3d/8)}{12a + b + 16c + 14d} \tag{15}$$

$$\text{BD} = \left(\frac{\text{EMY}}{\text{TMMY}}\right) \times 100 \tag{16}$$

where $C_aH_bO_cN_d$ is the chemical formula for the substrate derived experimentally. As observed from Table 5, hemicellulose gave the lowest experimental methane yield when fermented separately. This can be attributed to acidification of hemicellulose that inhibits the activities of methanogens responsible for methane production. As hemicellulose was codigested with microcrystalline cellulose, its biodegradability was enhanced from 35.0 to 46.9%. This is because of an increase in the nutritional balance brought about by the addition of cellulose. Contrarily, the addition of alkali lignin (AL) and sodium lignosulfonate (SL) to the fermentation system of hemicellulose and cellulose caused a decrease in EMY. This in turn resulted in a decrease in biodegradability from 46.9 to 42.9% and 35.6% for AL and SL respectively. This decrease is traceable to the inhibition effect of lignin and the presence of sulphur. Similarly, in another study, lignin showed the lowest biodegradability of 0.1% as compared to cellulose (57.8 and 59.9%) and hemicellulose (43.6–55.3%). The methane production characteristics of these lignocellulosic components were equally investigated in the study. Lignin gave the least EMY of 0.7 mL/gVS followed by hemicellulose with EMY of 178.6–223.5 mL/gVS and cellulose giving the highest EMY of 241.7 mL/gVS and 251.4 mL/gVS [61]. Comparably, Xu et al.'s [87] study evaluated the methane potential of different parts of corn stover namely stem bark, stem pith and leaves with varying compositions of cellulose, hemicellulose and lignin. The cumulative methane yields obtained for corn stover stem bark, stem pith and leaves were 0.194 L/gVS, 0.210L/gVS and 0.198 L/gVS respectively. The lower methane yield of stem bark is attributed to its lignin content (17.61%), which is higher compared to the lignin content of 7.16% and 5.16% for stem pith and leaves respectively. The higher lignin content of stem bark created a stronger binding for its cellulose and hemicellulose content thus resulting in a lower degradation rate for both compositions. As observed from the literature, lignin is confirmed to contribute the most in limiting the biodegradability of lignocellulosic biomass. Previous studies showed that an increase in lignin content by 1% would cause a reduction of 7.49 L $CH_4$/kg total solid on average [88,89]. In addition, a lignin content of any lignocellulose biomass in excess of >100 g/kg VS will result in a significantly lower yield of methane [90]. Li et al.'s [91] study further indicated that lignin content of 15% could be a critical point in AD of lignocellulosic biomass.

Comparing only the cellulose and hemicellulose degradation rate, Zhao et al.'s [92] study showed a significant difference in the degradation of the hemicellulose and cellulose composition of oat straw when digested as a monosubstrate. Hemicellulose degradation (68.85–81.44%) was observed to be greater than cellulose degradation (28.06–33.61%) as the total solid of the oat straw varied from 2 to 10% in steps of two. Additionally, in Song and Zhang's [84] study, hemicellulose was reported to have decomposed more compared to cellulose and lignin. According to the study, their decomposition rates were recorded to be 12.5–45.2% for hemicellulose, 9.3–30.2% for cellulose and 5.4–21.9% for lignin. Recalling that hemicellulose hydrolyzes more easily compared to cellulose and has a lower degree of polymerization than cellulose; hemicellulose can be expected to degrade faster. Although, some studies are of the view that cellulose has a higher biodegradability and yields more methane than hemicellulose, some other studies have a different view where the reverse is the case. Both cellulose and hemicellulose contain D-glucose molecules but hemicellulose is easily hydrolyzable than cellulose, which forms an association with other plant substances that limit its biodegradability. In addition, the ease of hemicellulose biodegradability could be attributed to its composition of short side chains consisting of a variety of sugars and its inability to form an aggregate when crystallized with cellulose. However, due to cellulose, dominating in the percentage composition (35–50%) compared to hemicellulose (20–35%), [93,94] cellulose methane yield per unit biomass under complete degradation will be higher compared to hemicellulose. This conclusion might not entirely hold for all biomass as the high rate of biodegradation of hemicellulose could result in higher yield of methane than cellulose. Hence, further studies are required to ascertain between cellulose and hemicellulose the one that yields more methane.

### 3.2. Codigestion of Lignocellulose and Animal Manure Studies

Anaerobic microorganisms differ in their requirements of organic and micronutrients needed for their growth and degradation of substrates for biogas production. To satisfy these nutritional requirements of microorganisms, a combination of substrates are codigested to improve their characteristics. For instance, the low and imbalanced carbon to nitrogen ratio in animal manure can be compensated through codigestion with carbon-rich substrates. As it has been noted that the protein, fats and carbohydrate content of a given substrate influence the percentage of methane in biogas. Substrates that are rich in these compositions can be combined with other substrates to achieve process stability and subsequently improve biogas production. This section presents an overview on anaerobic codigestion of a variety of substrates particularly lignocellulose and animal manure. Table 6 presents a summarized overview of some studies on codigestion of lignocellulosic biomass and animal manure.

**Table 6.** A summary on some studies of codigestion of lignocellulose and animal manure.

| Substrate Type | Mixing Ratio | pH | Pretreatment | $CH_4$ Yield (mL/gVS) | Ref. |
|---|---|---|---|---|---|
| Wheat Straw + Cattle manure | 40:60 | 6.5–7.0 | 3% *w/w* $H_2O_2$ | 320.8 | [84] |
| Wheat Straw + Cattle manure | 30:70 | 6.8–7.1 | None | 254.6 | [84] |
| ASW + Cow dung | 60:40 | 8.1 | None | 297.7 | [95] |
| ASW + Cow dung | 60:40 | 8.1 | 1 g $NaHCO_3$/g of VS | 386.3 | [95] |
| Corn stover + Chicken manure | 3:1 | 6.9–8.2 | Wet-AD | 218.8 | [91] |
| Corn stover + Chicken manure | 3:1 | 7.4–8.3 | HSS-AD | 208.2 | [91] |
| Corn stover + Chicken manure | 1:1 | 8.0–9.3 | SS-AD | 147.8 | [91] |
| Goat manure + Wheat straw | 30:70 | 6.5–7.5 | None | 12.8 | [67] |
| Goat manure + Corn Stalk | 70:30 | 6.5–7.5 | None | 16.0 | [67] |
| Goat manure + Rice Straw | 50:50 | 6.5–6.8 | None | 15.7 | [67] |
| Sugarcane Bagasse + Cow dung | 1:2 | 6.8 | 2% *w/w* NaOH | 386 | [96] |
| Sugarcane Bagasse + Cow dung | 1:2 | 6.8 | 2% *w/w* $Ca(OH)_2$ | 334 | [96] |
| Sugarcane Bagasse + Cow dung | 1:2 | 6.8 | None | 322 | [96] |
| Animal manure+ Grape by-products | 1:2 | 4.3–8.8 | None | 348 | [97] |
| Animal manure+ Tomato pulp | 1:2 | 3.6–8.8 | None | 404 | [97] |
| Animal manure + Olive by-product | 1:2 | 4.6–8.8 | None | 398 | [97] |

A summary of the discussed studies on codigestion of lignocellulosic biomass and animal manure presented below are provided in Table 6. All studies presented in Table 6 were conducted under the mesophilic temperature (35–38 °C) condition but at varying retention times.

Wheat straw, a typical example of an agricultural waste presented in Table 6, is a suitable substrate for the production of biogas, although its lignocellulose content slows down the degradation process. Song and Zhang's [84] study presented in Table 6 explored the monodigestion and codigestion of pretreated wheat straw with cattle manure. In the study, wheat straw was pretreated with four concentrations of $H_2O_2$ (1%, 2%, 3% and 4%) prior to its digestion as a monosubstrate and cosubstrate in varying ratios of dairy cattle manure. The methane yield for monodigestion of $H_2O_2$-treated wheat straw were 94.8, 108.5, 128.4 and 118.7 mL/gVS for the 1%, 2%, 3% and 4% pretreatment and 84.3 mL/gVS for untreated wheat straw. A significant improvement in the methane yield was observed as $H_2O_2$-treated wheat straw and cattle manure were codigested. The mixing ratio of 40:60 for $H_2O_2$-treated wheat straw and cattle manure gave the highest methane yield of 320.8 mL/gVS while codigestion of untreated wheat straw/cattle manure gave an optimum methane yield of 257.6 mL/gVS at a 30:70 mixing ratio. Additionally, with codigestion the methanogenic community moved from acetoclastic methanogens to hydrogenotrophic methanogens.

Almomani and Bhosale's [95] study proposed a means of optimizing the biogas yield of some agricultural solid wastes (clover, grass and wheat straw) by addition of cow dung. A maximum cumulative methane production (CMP) of 297.99 NL/kgVS was recorded at a mixing ratio of 60:40 for the agricultural solid wastes and cow dung as shown in Table 6. The CMP of the codigested substrates were further enhanced through chemical pretreatment by addition of different doses (D1 = 0.25, D2 = 0.5, D3 = 0.75, D4 = 1.0, D5 = 1.25 and D6 = 1.5 g) of $NaHCO_3$. A maximum CMP of 386.3 NL/kgVS was obtained with 1.0 g of $NaHCO_3$/gVS (D4) at a mixing ratio of 60:40. Another study investigated the contribution of the organic loading rate in codigestion of rice straw and cow manure using a continuous feeding mechanism. An optimal mixing ratio of 1:1 for the volatile solids was obtained through a batch test analysis prior to the continuous experiment. An organic loading rate of 6 g/Ld resulted in an efficient and stable codigestion with an average biogas production and daily volumetric biogas production rate of 383.5 L/kgVS and 2.3 $m^3$/day respectively. A further increase in organic loading led to accumulation of VFA, which in turn caused a severe inhibition to the codigestion process [32].

Corn stover is a potential substrate for biogas production that usually results as a leftover from maize harvest. In Li et al.'s [91] study shown in Table 6, corn stover was codigested with chicken manure under three conditions namely: the hemi-solid state (HSS-AD), wet (W-AD) and solid-state (SS-AD) anaerobic digestion. The study was focused on determining the best mixing ratio for the optimum methane yield and achieving process stability under the three anaerobic digestion conditions. An optimum methane yield of 218.8 mL/gVS and 208.2 mL/gVS occurred at a substrate-mixing ratio of 3:1 for corn stover and chicken manure under wet and hemi-solid state anaerobic digestion conditions respectively. In addition, a mixing ratio of 1:1 gave the maximum volumetric methane productivity of 14.2 $L_{methane}/L_{reactor\ volume}$. Moreover, a synergistic effect was observed when the substrates were mixed in the ratio of 3:1 and 1:1 under the solid-state condition. Zhang et al. [67] investigated the codigestion of goat manure with three crop residues namely corn stalk, rice straw and wheat straw under mesophilic conditions and at varying mixing ratios for efficient biogas production. An optimum biogas yield presented in Table 6 were obtained at mixing ratios of 30:70, 70:30 and 50:50 for goat manure/wheat straw, goat manure/corn stalk and goat manure/rice stalk respectively. The total biogas yield of 12.8 L/kgVS from the codigestion of goat manure and wheat straw at a mixing ratio of 30:70 were 62.1% and 23.0% higher, compared to their monodigestion. On the other hand, at a mixing ratio of 50:50, the codigestion of goat manure/rice straw gave a total biogas yield of 15.7 L/kgVS that is 111.28% and 51.31% higher than digesting rice straw and goat manure separately. Whereas, the total biogas yield of 16.0 L/kgVS for goat manure/corn stalk when codigested is 83.02% and 54.44% higher than that of corn stalk and goat manure alone. A significant improvement in biogas production was achieved through codigestion by overcoming the carbon to nitrogen imbalance associated with single substrates.

Sugarcane bagasse is another agricultural waste that can serve as a substrate for codigestion purposes due to its energy potential. It is a byproduct of the sugar milling industry that results from milling of the sugarcane crop. A recent study investigated the anaerobic codigestion of pretreated sugarcane bagasse with cow dung. The bagasse was pretreated with a solution of NaOH and $Ca(OH)_2$ for one day before mixing it with cow dung in the ratio of 1:2. As presented in Table 6, NaOH treated bagasse gave a maximum biogas yield of 386 mL/gVS, $Ca(OH)_2$ treated bagasse gave about 334 mL/gVS and pure bagasse (untreated) yielded about 322 mL/gVS of biogas at 35 °C. With the addition of cow dung to the pure bagasse and an increase in temperature from 35 to 55 °C, an increase in biogas yield of 27 mL/gVS was observed. This could be attributed to the shift in the carbon/nitrogen ratio (130:1) of pure sugarcane bagasse to 29:1 when cow dung was added [96]. The higher biogas yield in the codigestion of pretreated sugarcane bagasse with cow dung as compared to pure sugarcane bagasse is due to increase in the internal surface area and decrease in the degree of polymerization of the lignocellulose material. This in turn breaks the linkage between carbohydrate and lignin due to applied alkaline pretreatment.

A study developed an assay for codigestion of animal manure (a mixture of 45% VS of calf manure, 41% VS of lamb manure and 2% VS of pig manure) with agro-food byproduct silages (grape byproduct, tomato pulp and olive agro-food byproduct). The study showed that a more synergetic effect existed in the codigestion of animal manure and tomato pulp due to a higher methane yield of 404 mL/gVS attained, compared to the grape byproduct and olive agro-food byproduct shown in Table 6. The highest methane yield was recorded when the animal manure was higher in proportion compared to the agro-food byproduct. This could be attributed to an elevation in the chemical oxygen demand of the assay. Additionally, a correlation was observed with alkaline parameters and ammonia nitrogen at a higher ratio of animal waste [97]. Mukumba et al.'s [98] study mathematically modeled the performance potential of a biogas digester fed with selected types of a substrate. An optimal methane percentage composition of 75% was reported with an equal mixture of cow dung, goat dung, donkey dung and horse dung. It has been shown from the reviewed studies that codigestion of animal manure with agricultural residues leads to the optimization of biogas production and stabilization of the anaerobic digestion process. This is attributed to more balanced nutrients achieved through codigestion particularly between carbon and nitrogen.

### 3.3. Municipal Solid Waste

Municipal solid waste (MSW) consists of solid wastes generated within a municipality by households, industries and a commercial setting. Its composition and amount are variable with organic matter constituting about 25–75% of the total MSW. The MSW production rate typically varies between 1.1 and 2.2 kg/person/day based on a country's income [10]. On a global scale, approximately 1.3 tonnes of MSW are generated annually. These MSW compositions consist of 46% of organic waste, 17% paper waste, 10% plastic waste, 5% glass waste, 4% metal waste, 3% textile waste, 13% inert and 2% miscellaneous waste [99]. The organic waste accounts for the highest composition among other waste types. Their percentage composition also varies from continent to continent with Africa having the highest composition of 66% and Australia having the least of about 25% as present in Table 7.

**Table 7.** Organic matter composition of municipal solid waste (MSW) by continent. Adapted from [100].

| Continent | Organic Percentage Composition of MSW (%) |
|---|---|
| Africa | 66 |
| Asia | 47 |
| Europe | 54 |
| North America | 26 |
| South America | 53 |
| Australia | 25 |

For low-income countries, the organic portion of the waste ranges from 50 to 70% while that of high-income countries ranges from 20 to 40%. The high rate of the organic fraction of MSW generated in Africa is traceable to urbanization due to rural–urban migration, rapid population growth and industrialization [101]. Effective conversion of this waste through innovative ways can be a sustainable waste management technique to adopt. Two major conversion pathways exist for MSW and they are the biochemical conversion process (anaerobic digestion) and thermochemical conversion (incineration). The thermochemical conversion mechanism is rarely used because of the low calorific value and high moisture content of MSW. Anaerobic digestion of MSW has attracted more attention because of the possibility of separating the organic biodegradable fraction from the total MSW [102]. Additionally, the generation of renewable energy, reduction of landfilling and mitigation of pollution are some other factors that steer the public interest in AD of MSW. Food waste makes up a greater proportion of the organic waste stream and has the highest biogas potential compared to other biodegradable stream. This is because of the high concentration of carbohydrates, proteins, fats and the absence of heavy metals. Table 8 presents the characteristics of different organic fractions of MSW as reported in the literature.

**Table 8.** Physicochemical characteristics of organic municipal solid waste.

| Substrate | TS (%) | VS (%) | C/N Ratio | pH | Reference |
|---|---|---|---|---|---|
| Food waste | 10.8 | 10.2 | 15.2 | 4.2 | [103] |
| Kitchen waste | 19.1 | 17.8 | 14.4 | 4.5 | [104] |
| OFMSW | 14.1 | 10.33 | 32.5 | - | [105] |
| Fruit and Veg waste | 13.8 | 12.88 | - | 4.5 | [106] |
| Catering food waste | 23.0 | 18.5 | 20 | 4.9 | [107] |
| SOW | 12.8 | 11.3 | 13.6 | 4.3 | [108] |
| Brown grease | 43.8 | 37.2 | - | 6.1 | [109] |

OFMSW—organic fraction of municipal solid waste and SOW—synthetic organic waste.

The synthetic organic waste (SOW) reported in Table 8 represents a typical composition of organic waste disposed in a landfill. It is comprised of leftover food such as meat, rice and beans accounting for about 79%, fruit and vegetable waste such as orange, banana and apple accounting for about 20% and 1% cardboard. As shown in Table 8 the TS and VS content of the organic MSW are in the ranges of 10.8–23.0 and 10.2–18.5 respectively, indicating that water accounts for about 80% of the total composition. This is acceptable, as moisture content is recommended in the literature to be as high as 90% to support a high methanogenesis rate [110]. The pH of the substrates as seen are low, thus a proper control is needed during AD of these substrates for optimal performance. The carbon to nitrogen ratio of organic municipal waste as observed ranged from 13.6 to 32.5, of which some wastes are within the optimum recommended ratio of 20–30:1 [111]. However, for substrates with a low C/N ratio, codigestion is suggested as a good approach to attain the optimal ratio. Generally, the microorganisms responsible for the AD process utilize carbon more compared to nitrogen. Hence, nitrogen concentration should not exceed the quantity needed by the microbial community to avoid ammonia inhibition [112]. Table 9 presents the methane potentials of the organic fraction of MSW reported in the literature.

**Table 9.** Organic municipal solid waste and their methane yield.

| Substrate Type | Methane Yield (mL/gVS) | Reference |
|---|---|---|
| Food Waste | 460.0 | [103] |
| OFMSW | 220.5 | [105] |
| Fruit and vegetable waste | 516.0 | [106] |
| Kitchen Waste | 501.0 | [113] |
| Vegetable food waste | 425.0 | [114] |
| Catering food waste | 287.0 | [107] |
| Cucumber waste | 143.0 | [115] |
| Onion skin | 400.0 | [116] |
| Potato skin | 267.0 | [116] |
| Banana skin | 277.0 | [116] |
| Carrot petioles | 309.0 | [116] |
| Orange peel | 230–332 | [117] |
| Strawberry Extrudate | 285–339 | [118] |
| Fluted pumpkin peel | 161–164 | [119] |
| Brown Grease | 400–490 | [109] |

The methane yield of all organic wastes presented in Table 9 fall in the range of 143–516 mL/gVS. Food waste, kitchen waste, fruit and vegetable waste showed the highest methane yield. This could be because of high lipid content of food waste and kitchen waste, which could be directly linked to the presence of animal fat and oil in the waste stream. Studies have shown the lipid content of food waste and the kitchen to be about 33.22% and 21.6% respectively [120,121]. As noted previously, substrates rich in lipids have a greater potential for higher methane yield compared to protein and carbohydrates. Although, high lipid content usually results in the formation of long-chain fatty acids that could cause system failure [111]. Additionally, the high moisture content in fruit and vegetables may have contributed to higher degradability of these substrates that led to high methane yield. Cucumber waste showed the lowest methane yield, which could be attributed to its lignin content as phytonutrients. Besides the nutritional composition of the substrates, other factors such as temperature, pH, C/N ratio, organic loading rate and hydraulic retention time influence their methane yield. However, temperature, organic loading rate and hydraulic retention time were not considered in the present review. In summary the organic fraction of MSW substrates shows some variation in characteristics as well as methane yield. Geographical change, seasonal variations as well as the type of collection determine the final characteristics of the waste stream.

### 3.4. Industrial Waste

Industrial wastes are byproducts, residues and wastes that result from various industrial activities. They include waste from the pulp and paper industry, food industry, petrochemical refinery waste, textile industry and liquid biofuel production waste. Besides waste from the food industry, other industrial wastes have not been widely used as a substrate in anaerobic digestion due to their recalcitrant chemical properties and low biodegradability of about 30–50% [122]. In the pulp and paper industry, a large quantity of wastewater with a high organic load is produced during the paper manufacturing process. These wastewaters typically have high chemical oxygen demand (COD) in the range of 800–4400 m/g, high biological oxygen demand (BOD) of about 300–2800 m/g and high dye content in the range of 1200–6500 color units [109]. Anaerobic treatment of this wastewater has an added benefit of lower treatment cost because of the possibility of utilizing the biogas produced for energy generation. Due to low solid content (TS < 1%) of this wastewater, they are codigested with other substrates or pretreated to improve their biodegradability. The textile industry is another industry that generates a significant quantity of wastewater through the production process of washing, dyeing and finishing. Some studies have reported on the anaerobic treatment of textile wastewater for the production of biogas. Table 10 presents the methane yield of different industrial wastes.

**Table 10.** Methane potential of industrial waste.

| Industrial Waste | Methane Yield (mL/gVS) | Reference |
|---|---|---|
| Textile wastewater | 200–400 | [123] |
| Paper mill effluent | 220–340 | [109] |
| Cheese whey and diary | 280–350 | [124] |
| Cane Molasses stillage | 168 | [124] |
| Barley waste | 25 | [125] |
| Biodiesel wastewater | 161 | [126] |
| Sunflower oil cake | 195 | [127] |
| Rapeseed oilcake | 310 | [128] |
| Pulp and paper mill sludge | 429 | [129] |
| Jatropha curcas oil cake | 250 | [130] |
| Sugarcane vinasse | 350 | [131] |

As observed from Table 10, the methane yield of all wastewater streams gave a significant methane yield that ranged from 25 to 429 mL/gVS. The paper mill effluent with an average methane yield of 280 mL/gVS resulted from a COD removal efficiency of 50–65%. The reported paper mill effluent is a mixture of four wastewater streams namely foul condensate milling from the chemical pulping process, liquid waste from the bleaching process, screw press liquor and alkaline extraction operating liquid [109]. Barley waste that results from the production of an instant coffee substitute gave the lowest methane yield of 25 mL/gVS with a TS and VS reduction of 31% and 40%. This low yield is due to the existence of complex heterocyclic compounds that emanates from the hydrolysis phase of the anaerobic digestion process. Moreover, knowing that the chemical structure of compounds has been found to have a direct influence on the methanogenic degradation mechanism, the alkaline hydrolysis pretreatment was applied, which resulted in an increase in methane yield (222 mL/gVS) [125]. Sugarcane vinasse is a recalcitrant wastewater that emerges from ethanoic distillation of sugarcane. The high methane yield (350 mL/gVS) of sugarcane vinasse could be traced to the organic matter and solid minerals content. Some of these organic compounds include alcohols, esters, aldehydes, acids, ketones and sugars. While the solid minerals are majorly potassium, calcium, sulphate ion, magnesium as well as phosphorus [131]. As noted in the literature calcium and magnesium are essential macronutrients that enhance the anaerobic digestion process.

## 4. Conclusions

Anaerobic digestion is a suitable technology for the efficient management of organic waste that contributes to the uncontrolled emission of methane and carbon dioxide when dumped in landfill sites. Biogas produced through AD has a wide range of applications; it can serve as a cooking fuel as well as being a good substitute for other cooking fuels such as coal gas, kerosene, charcoal, cow dung and firewood. In addition, biogas could be used in a direct combustion system for power generation, space heating, drying, water heating and fuel for vehicles. This review study has highlighted the various substrates used in biogas production and their limitations such as longer retention time for industrial wastes, slow hydrolysis for lignocellulosic materials and high nitrogen concentration of animal manure, which affect the overall yield of biogas. However, codigestion of these substrates is a good approach for the simultaneous treatment of solid and liquid organic waste. This will aid in solving the nutrient imbalance problem associated with the anaerobic treatment of single substrates and the effects of toxic compound build-up during the digestion process. Consequently, biogas production will be greatly enhanced by codigestion as compared to monodigestion.

## 5. Recommendation

The type of substrate digested, operating pH, temperature, organic loading rate, hydraulic retention time and digester design controls the efficient production of biogas through AD. For maximum growth and activities of microorganisms that enhances efficient biogas production, essential organic and mineral nutrients are needed in the substrate. The concentration and availability of these macro substances, microelements and vitamins in substrates vary. Lipid-rich and protein-rich substrates result in a higher yield of methane compared to carbohydrate-rich substrates. However, high lipid content in substrates results in the formation of long-chain fatty acids that causes anaerobic digestive system failure. Additionally, carbohydrate rich substrates can affect the C/N ratio, which results in nutrient restriction and quick acidification. Hence, a mixture of substrates is recommended to achieve nutrient balance, process stability and enhanced biogas yield. The study recommends that the choice of substrates for anaerobic digestion should be guided by their nutrient composition, availability, cost and pretreatment availability. Finally, future researchers should consider supplementing the organic wastes with a little quantity of inorganic fertilizer that is small enough to enhance microbial growth and activities as well as not cause salinization effects. This could enhance the yield of biogas per given digested organic waste substances.

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