REVIEW



Effects of co-substrate on biogas production from cattle manure: a review

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Abstract This literature review surveys the previous and current researches on the co-digestion of anaerobic processes and examines the synergies effect of co-digestion with cattle manure. Furthermore, this review also pays attention to different operational conditions like operating temperature, organic loading rate (OLR), hydraulic retention time (HRT), chemical oxygen demand (COD) and volatile solid (VS) removal efficiency and biogas or methane production. This review shows that anaerobic mono-digestion of cattle manure usually causing poor performance and stability. Anaerobic studies were generally performed under mesophilic conditions maintained between 35 and 37 °C. Organic waste loading rate generally ranges from 1 to 6 g VS-COD L^{-1} day⁻¹ stable condition in anaerobic digester. Generally, studies show that HRT for co-digestion of fruit-vegetables waste and industrial organic waste appears to exceed 20 days. However, the anaerobic co-digestion process is generally operated at HRT of between 10 and 20 days. VS and COD removal efficiency usually reaches up to 90 % due to codigestion with different type organic waste. Methane-biogas production is generally obtained between 0.1 and 0.65 L CH₄-biogas g^{-1} VS.

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Introduction

Anaerobic co-digestion technology allows concurrent digestion of different solid and liquid wastes (Dias et al. 2014). Anaerobic treatment has been considered as the waste-to-energy technology and has been largely used in the digestion of different organic wastes, like animal manure, food waste, organic fraction of municipal solid waste and sewage sludge (Li et al. 2009; Kavitha et al. 2015a).

The production of animal manure in large-scale farms has substantially expanded in the world (Gungor-Demirci and Demirer 2004). Livestock manure causes most environmental problems such as greenhouse gas, odor problems, airborne ammonia, high counts of fecal coliform bacteria and pathogens, rodents, insect, flies and other pests, release of animal pathogens, surface- and groundwater contamination, deterioration of biological structure of the earth and catastrophic spills (Nelson and Lamb 2002; Sakar et al. 2009; Sung and Santha 2003; Packyam et al. 2015).

Most livestock manure is generally produced by cattle in the world. Cattle manure is a complex type of substrate composed of carbohydrates, proteins and fats (McInerney 1998). During anaerobic digestion (AD) process, complex organic matter is hydrolyzed and fermented to short-chain fatty acids (such as acetic, propionic, butyric and smaller amounts of isobutyric, valeric, isovaleric acids), alcohols, H₂ and CO₂ (Ahring et al. 2001; Ozturk 2007; Sawyer et al. 2003). Acetic acid, H₂ and CO₂ are directly utilized by methanogenic phase. Other hydrolysis and acidogenesis



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products are transformed by acetogenic bacteria into H₂, CO_2 and acetic acid (Ozturk 2007).

Ruminants manure, especially cattle, is very helpful for beginning the fermentation phase, because it already has the necessary methanogenic bacteria. However, the fermentation of manure alone results in lower methane generation due to moderate anaerobic biodegradability of about 45-50 % (Rico et al. 2007). Moreover, the biogas production from cattle manure is lower than that obtained from other farm animals, since cattle manure contains leftover lignin complexes from fodder that are very resistant to AD (Monteiro et al. 2011). However, the high water content (70-90 %) and buffer capacity of manure have a positive effect on AD stability. Consequently, most of the farm-type anaerobic digesters are operated manure together with organic wastes (called co-digestion) (Rico et al. 2014).

The substrate-to-inoculum ratios between 2 and 6 (as VS) are typically used at the laboratory scale, and it is suggested that substrate-to-inoculum ratio really applied in industry can be optimized. By considering only the first days of operation, some studies showed an inefficiency of anaerobic digestion for substrate-to-inoculum ratio higher than 4 (Motte et al. 2013). At the same time, anaerobic digestion of microalgae has highest productivities at substrate-to-inoculum ratios of 1/2 (Alzate et al. 2012).

Mixing substrates for co-digestion have many advantages including environmental, technology and economic benefits when contrasted with a single substrate processing (Brown and Li 2013). Over the last years, several authors investigated the effect on the performance of the AD process by simultaneously treating cattle manure as well as wastes containing high levels of organic matter or energy crops (Alvarez and Liden 2008; Comino et al. 2009; Lehtomaki et al. 2007; Nasir et al. 2012; Yangin-Gomec and Ozturk 2013). This co-digestion method, if co-substrate is used at the appropriate rate, can give interesting results because the synergistic impact indicated by different organic substrates when processed simultaneously (Angelidaki and Ellegaard 2003; Chen et al. 2010; Dias et al. 2014; El-Mashad et al. 2004; Hills and Roberts 1981; Lehtomaki et al. 2007; Li et al. 2009, 2011; Macias-Corral et al. 2008; Mata-Alvarez et al. 2000; Rao and Baral 2011; Umetsu et al. 2006). For optimal carbon-to-nitrogen ratio and pH diverse substrates are mixed for best biogas production (Khan and Martin 2016). One of the techniques for the economic sustainable of biogas systems is to improve their biogas production about 50 % by co-digesting the Fig. 1 Parametres of operating or performance compared to biogasmethane production; a temperature (T °C), b OLR (g VS-COD L⁻ d^{-1}), c HRT (day), d VS-COD removal (%)

animal manure with more degradable wastes containing high levels of organic matter as long as such organic wastes are reachable in the digester region (Xie et al. 2011; Khan and Martin 2015).

The benefits of co-digestion are evidently and clearly inexpensive, and to a simple technology and to remember ecological advantages, such as reduction in concentration toxic compounds, arranged demand of nutrients, synergistic effects of anaerobic bacteria, improved biodegradable substrate loading, increased in biogas production, hygienic stabilization and enhanced rate of digestion (Sosnowski et al. 2003), adjustment percent of moisture and pH, supply of buffer capacity. All these benefits are very important for stability and performance of the anaerobic process (Esposito et al. 2012).

Organic-rich wastes and residues include a considerable amount of biodegradable organic carbon. The range of biogas generation from several biodegradable waste is stated as 0.20–1.11 m³ kg⁻¹ of dry matters (CH₄ content of 57-69 %); e.g., biogas yield per unit weight of dry matters is stated as 0.31 m³ kg⁻¹ for the cattle manure (Yangin-Gomec and Ozturk 2013).

The anaerobic biomethanization studies from digestion of cattle manure alone and co-digestion of fruit and vegetable wastes, organic household wastes, industrial organic wastes and sewage sludge wastes are reported in Fig. 1. The aim of this study is not only to review the previous and current researches on the co-digestion of anaerobic processes by various wastes containing high levels of organic matter, but also to indicate the synergies effect of co-digestion with cattle manure. Furthermore, this review also pays attention to different operational conditions like operating temperature, organic loading rate, hydraulic retention time, COD and volatile solid removal efficiency and biogas or methane production.

Feedstocks for anaerobic digestion

The most important premise of producing high-quality digestate is the utilization of high-quality feedstock for the digestion process. Some feedstocks are difficult or unsuitable for mono-digestion because of their unfavorable C/N







ratios or high lipid content. Under these circumstances, codigestion is the best approach to resolve any imbalance and improve volumetric methane productivity (Wellinger et al. 2013). In general, cattle manure biodegrades more slowly than other organic waste because of hay materials. The addition of co-digestion feedstocks can improve the biodegradability and the VS in the anaerobic reactor by including the co-digestion of cattle waste and the addition of food waste, fruit or vegetable waste, industrial organic waste or sewage sludge (Callaghan et al. 1998; Naik et al. 2010; Rao and Baral 2011; Zhang et al. 2013). The physical and chemical characteristics of the feedstocks have significant effect on the overall anaerobic phase for designing and operating anaerobic reactors because they affect biogas generation and digestion stability during anaerobic process. The production of biogas from any feedstocks is highly dependent on the C/N ratio of the substrate, concentration, pH and temperature (Dioha et al. 2013). Nitrogen provides an essential element for synthesis of amino acids and is converted to ammonia which neutralizes the volatile acids produced by fermentative bacteria, thus providing suitable pH conditions for digestion. Also, the small amount of nitrogen causes nutrient limitation and ammonia toxicity occurs when nitrogen has too much levels in the substrate. The proper C/N ratio for anaerobic digestion (AD) is between 20 and 35 (Abbasi et al. 2011; Ghasimi et al. 2009; Zhang and Zhang 1999). Cattle manure has low C/N ratio of 11-14 the nutrients requirement for anaerobic bacteria (Hashimoto 1983; Hills and Roberts 1981). C/N ratios of cattle manure are observed between 5 and 26.5 (Bah et al. 2014; Chen et al. 2010; Corro et al. 2013; Dias et al. 2014; García and Pérez 2013; Lehtomaki et al. 2007; Li et al. 2009; Risberg et al. 2013; Solli et al. 2014).

The nutrients content of organic substrates determines the biogas quality and quantity. Maximum methane yield requires adequate and efficient nutrient supply for microorganisms in the digester (Amon et al. 2007). Macronutrients elements (C, H, N, O and S) must be present in the substrate for microbial growth to occur. More balanced macronutrients in anaerobic co-digestion process increased buffering capacity are sufficient to maintain a stable digestion situation (Chen et al. 2010). Significant parts of the C, H and O are converted to CH₄ and CO₂, whereas any N and S that are not join into new biomass are rapidly reduced to ammonia and sulfides in either soluble or gaseous form. Both ammonia and sulfides are toxic to methanogens in a critical concentration (Wellinger et al. 2013). Ammonia toxicity occurs at concentration above

2500 mg L^{-1} (Boria et al. 1996; Chen et al. 2008; Hashimoto 1986). If the concentration of soluble sulfides exceeds 50 mg L^{-1} , the inhibition starts in anaerobic process (Imai et al. 1998; Koster et al. 1986; Lawrence and McCarty 1969; Speece 1983). The micronutrients (trace elements) such as Ni, Co, Mo, Fe, Se, Wo, Zn, Cu and Mn are required for AD (Wellinger et al. 2013). The lack of the micronutrient requirement of methanogens failed many anaerobic digester (Khanal 2011). Manures provide a wide range of nutrients, while the addition of other organic wastes increases the methane yield of the process (Seppälä et al. 2013). Compared with cattle manure, the concentration of micronutrients was obviously fewer in food waste (Zhang et al. 2013; 2015), in plant-based material and waste (Demirel and Scherer 2011; Schattauer et al. 2011; Seppälä et al. 2013), higher in fresh leachate (Zhang et al. 2015), in sewage sludge (Ishaq et al. 2005).

Important parameters for operating and performance

The biogas generation highly depends on the temperature (Appels et al. 2011; Sanchez et al. 2001; Rani et al. 2012), but the HRT, OLR and substrate content in the feeding are also other significant operation parameters (Alvarez et al. 2006; Ashekuzzaman and Poulsen 2011; Khalid et al. 2011; Sakar et al. 2009; Kavitha et al. 2015b). The appropriate operation parameters of an anaerobic digestion related to the suitable factors are temperature, pH, volatile fatty acids, alkalinity, NH₃-N, supplement of nutrients, trace elements, sulfides and heavy metals (Borja et al. 2006; Sakar et al. 2009; Yadanaparthi et al. 2014, Kavitha et al. 2015c). Hence, the stability parameters for a highly biogasification especially depend on temperature, HRT, OLR and substrate content in the feeding. For that reason, many authors have investigated about these parameters (Garcia-Pena et al. 2011; Wu et al. 2010). Furthermore, the most functional parameters for evaluating the efficiency of biogas production are the reduction in VS or COD (Debik and Coskun 2009; Demir et al. 2011; Demirer and Chen 2005; Razaviarani et al. 2013; Yangin-Gomec and Ozturk 2013; Ye et al. 2013). Figure 1 shows important parameters of operating or performance compared to biogas-methane production from different substrates.

Generally, most of the studies on AD of organic substrate have been experimented with one-stage mesophilic CSTR or semi-CSTR; informed sustainable and economic ways to enhance CH₄-biogas production or to success



higher VS-COD reduction are based on operation parameters.

During the period of time examined, some studies focused on comparing mesophilic and thermophilic conditions. The CH₄-biogas production at thermophilic digestion was slightly higher than at mesophilic digestion. Thermophilic digestion is the most commonly used in particular cattle manure alone treatment. However, thermophilic digestion could not increase the biogas production and waste removal at a desired level. Also, the heating costs of thermophilic digestion are far higher. When we examine different temperature combinations of co-digestion in Fig. 1a, it is observed that more use of mesophilic conditions. The literature review shows that co-digestion of physical, chemical or biological pretreatments waste seems to be most suitable together with cattle manure in respect of their biogas production compared to raw waste. Pretreatments could result in reduced HRT, increased biogas yield, but most of the fruit-vegetables co-digestion study is generally operated higher than 20 days HRT. In order to provide essential nutrient balance in the waste mixture, codigesting macro- and micronutrients biodegradable rich substrate is beneficial for co-digestion. Organic loading rates were reported between 0.67 and 15.06 g VS-COD L^{-1} day⁻¹ and are shown in Fig. 1b. The higher biogas production of 0.7 L g⁻¹ VS removed is achieved by codigesting organic kitchen waste (OKW) and cattle manure (OKW:CM mixing ratio 75:25) (Aragaw et al. 2013), but also cattle manure, food waste with glycerin (87:10:3) (Castrillon et al. 2013) and cattle manure, food waste, sewage sludge (70:20:10 TS concentration around %4) (Marañón et al. 2012) give very high methane generation of 0.64, 0.61 L g $^{-1}$ VS with 93 % COD, 53 % VS removal, respectively. In a field study, biogas yield of 0.41 and 0.47 $L g^{-1} VS$ loaded is conducted by co-digesting CM, chicken manure without or with maize silage around 50 % VS reduction in mesophilic condition (Yangin-Gomec and Ozturk 2013). The higher than 60 % VS-COD reduction is often reported by co-digestion organic household waste and industrial organic waste (Bah et al. 2014; Bertin et al. 2013; Comino et al. 2012; Comino et al. 2009; Corro et al. 2013; Solli et al. 2014).

The performance data reveal that mesophilic condition of anaerobic process is more widely used compared to thermophilic condition because of higher system stability and low-cost operation managements. Nevertheless, thermophilic condition is used a lot of investigation in cattle manure alone study because of its more efficient to produce biogas at cattle manure digestion (Abubakar and Ismail 2012; Ahring et al. 2001; Boe and Angelidaki 2009; El-Mashad et al. 2004; Mohaibes and Heinonen-Tanski 2012; Omar et al. 2008; Sung and Santha 2003). In cattle manure alone digestion studies, HRTs were conducted between 10 and 20 days, while biogas production usually ranged from 0.15 to 0.30 L CH₄ g^{-1} VS day⁻¹ with COD-VS removal ranged from about 30–55 % (Abbasi et al. 2011; Ahring et al. 2001; Demirer and Chen 2005; El-Mashad et al. 2004; Ghaly 1989; Gungor-Demirci and Demirer 2004; Omar et al. 2008; Rico et al. 2011; Sung and Santha 2003).

Anaerobic mono-digestion of cattle manure often caused poor performance and stability (Arici and Koçar 2015). The insufficiency of essential trace elements of organic waste is regarded as an important factor limiting anaerobic digestion. Anaerobic co-digestion of different kind of organic waste, especially cattle manure, allows for resolving any imbalance (pH, alkalinity, macro- and micronutrients elements) and improving the biogas production with an effective bioreactor performance (Amon et al. 2007; Chen et al. 2010; Seppälä et al. 2013). Anaerobic co-digestion of cattle manure exhibits the synergies effect such as buffering capacities on inhibition of pH and ammonia, supplying trace elements and supporting necessary methanogenic bacteria (Hashimoto 1986; Macias-Corral et al. 2008; Rao and Baral 2011; Rico et al. 2007; Yangin-Gomec and Ozturk 2013).

According to the data shown in Fig. 1a, most of the anaerobic digestion was operated mesophilic condition with a temperature range from 35 to 37 °C. According to the data presented in Fig. 1b, organic waste VS-COD loading rate generally ranges from 1 to 6 g VS-COD per liter of active reactor volume per day (g VS-COD L^{-1} day^{-1}) stable condition in anaerobic digester. However, suitable organic loading rate changes according to HRT and type-mixing ratio of waste. The study shows that HRT for co-digestion of fruit-vegetables waste and industrial organic waste appears to exceed 20 days in Fig. 1c. However, the anaerobic co-digestion process is generally operated at HRT of between 10 and 20 days. This review study shows that the anaerobic co-digestion could be operated at lower HRT and higher OLR together with higher biogas yield and better waste treatment (Fig. 1b, c) when organic waste such as cattle manure, household waste, industrial waste and sewage sludge, which are exposed to physical, biological and chemical pretreatment, are used for co-digestion. Chemicals addition for co-digestion is not needed, or very little addition is needed.



The previous studies exhibited that up to 90 % VS–COD removal was observed co-digestion of household and industrial organic wastes (Fig. 1d). Methane–biogas production was obtained between 0.1 and 0.65 L CH₄–biogas g^{-1} VS added. Furthermore, there seems to be a remarkable success of approximately 0.4 L CH₄–biogas g^{-1} VS production in anaerobic co-digestion. Figure 1d shows that where VS–COD reduction and CH₄–biogas production from fruit–vegetables waste digestion are less when compared with household waste, industrial waste and sludge waste anaerobic digestion. Improving the operating parameters seems apparent in co-digestion process (Fig. 1a–d).

Conclusion

Anaerobic digestion of organic waste has been widely implemented in the waste stabilization process because of the need to be treated before being disposed in nature. Accordingly, several treatment processes have been developed. Due to the high organic matter content, anaerobic treatment technologies have been receiving significant attention for this type of waste. However, anaerobic digester which fed with monotype of substrates would not achieve waste reduction efficiency and production of biogas potential. Therefore, anaerobic co-digestion process has synergistic effects to increase biogas yield from the substrate and to decrease the volume of effluent waste because of suitable anaerobic process parameters with mixing waste. For this reason, many kinds of organic waste have been treated anaerobically in an appropriate way, such as fruit and vegetable waste, household organic waste, industrial organic waste, sewage sludge and livestock manure.

Most livestock manure was generally produced by cattle. Cattle manure is a complex type of substrate. Anaerobic mono-digestion of organic waste generally caused poor performance and stability. However, anaerobic co-digestion of different kind of organic waste, especially cattle manure, allows for resolving any imbalance and improving the biogas production with an effective bioreactor performance and anaerobic co-digestion of cattle manure exhibited the synergies effect. Treatment of waste in the anaerobic biodegradation depends on several conditions. The main conditions are related to reactor operating parameters such as temperature, OLR, HRT and feeding characteristics. Suitable intervals of parameters and their effects are very important on the anaerobic digestion and biogas production performance. However, unstable intervals of parameters can inhibit biodegradation process. Therefore, appropriate mixing strategies can help to solve these biodegradation process problems and to increase biogas production with treatment of waste.

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