

# A review of hydrogen production from anaerobic digestion

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#### Abstract

Recent advances in the utilization of hydrogen as an alternative fuel source to conventional fossil fuels have led to a search for a renewable process of producing hydrogen. Most hydrogen today is produced from hydrocarbons in a process that also releases high levels of carbon dioxide and carbon monoxide, two established greenhouse gasses; because of this harmful means of production, research has been directed toward using anaerobic digestion to produce useful levels of hydrogen gas. Anaerobic systems have been shown to produce a biogas that is easily used in producing energy, but certain processes can be performed to further enhance the concentrations of hydrogen. These processes include the inhibition of microorganisms that lower hydrogen concentrations have shown this process to be environmentally viable with limited, but promising, economic potential. With a constant increase for the need of hydrogen gas, the sustainable production of hydrogen is becoming more important. This review explores some of the recent research on this topic and explores the processes behind using anaerobic digestion for hydrogen production.

Keywords Hydrogen production · Anaerobic digestion · Renewable fuels · Sustainability

# Introduction

With the increasing need for alternative fuel sources, hydrogen production is a topic of growing interest. Hydrogen is a unique fuel source in that one of the only product released from its use is water vapor, in addition to small amounts of nitrogen oxides and other air combustion products (Hashem Nehrir and Wang 2015). It also has an energy storage capacity per weight three times greater than the average liquid hydrocarbon (Mcwhorter et al. 2011). Analysis on the economic capabilities of hydrogen fuel cells also shows the promising results for large-scale use in certain parts of the country and perhaps anywhere with the right incentives (Emerson 2008). Hydrogen as a fuel source has a large potential in the transportation industry where it can

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<sup>2</sup> Department of Chemical Engineering, University of Louisiana Lafayette, Madison Hall, Room 217, 131 Rex St., Lafayette, LA 70503, USA serve as renewable source of energy. Many countries have encouraged the use of hydrogen for vehicles, passing legislation to make its use more viable; these countries have seen an obvious spike in the use of hydrogen as a result (Markets&Markets 2020). Most hydrogen-fueled vehicles use pressurized tanks of hydrogen to provide a source of providing electricity in addition to an onboard battery (DOE 2020a). Another major use of hydrogen is within the chemical production industry. In fact, the largest use of hydrogen globally is for the production of ammonia, requiring twothirds of global production (Jolly 2020). Furthermore, it also has shown potential for use in rocket fuels for its high energy density and low weight (Jolly 2020). Hydrogen is also used in processes of hydrogenation, a common chemical synthesis process (Patterson 2011). Hydrogen production normally involves the use of fossil-based fuels as a feedstock in a process called catalytic steam-hydrocarbon process (Alvarez-Murillo et al. 2015). This process accounts for nearly three-fourths of the entire global hydrogen production and involves the release of carbon monoxide and carbon dioxide, two established greenhouse gases (Markets&Markets 2020). Ever since the energy crisis of the 1970s, hydrogen has become a focus of great potential for future energy needs (Volkov 2012). Currently, the global hydrogen market was



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valued at USD 117.49 billion in 2019 with a great potential to grow as the incentives for its use become more widespread (GrandviewResearch 2020). Hydrogen is also expected to increase in value as its demand increases in the near future; from 2010 to 2018, the demand for pure hydrogen increased by around 12 Mt and will continue to increase as more technology is developed (GrandviewResearch 2020).

Though the process of producing hydrogen is important, the process of separation also controls the overall efficiency and sustainability of a hydrogen sourcing system. Traditionally, a large portion of hydrogen separation methods were dominated by pressure swing adsorption and cryogenic distillation (Volkov 2012). However, these processes, though effective, are very costly and energy demanding, impacting both the overall costs and environmental impacts. This shows the need for more research in alternative processes. One process of particular focus in recent years is using selective hydrogen membranes; these allow for the selective permeability of specific membranes to separate hydrogen from a gas stream (Shirasaki and Yasuda 2013). These can also be added to reactors to further enhance the efficiency of this process (Lu et al. 2007). These membranes can serve a special role in reactors to lower the concentration of a desired gas to direct the reaction toward the products (Yin and Yip 2017). In the case of anaerobic digestors, it has been shown that high levels of hydrogen can affect the microbes responsible for hydrogen production, leading to lower yields; the use of these types of membranes in conjunction with anaerobic digestors can lead to an increase in hydrogen production. However, care must be taken to ensure the proper membrane is chosen for use within a biomass system. One particular type of membrane with potential in this application is polymeric membranes. These membranes show poor separation potential (selectivities of around 39, 24, and 23 for hydrogen/nitrogen, hydrogen/methane, and hydrogen/carbon monoxide, respectively), but they show great resistance to chemicals found in biogases (Henis and Tripodi 1977). Another type of membrane under consideration for this type of use is dense metal membranes which use metals like palladium to achieve a chemical potential to transfer hydrogen selectively. This type is much more efficient as it can produce a pure hydrogen stream with a greater than 99.99 mol percent composition (Yin and Yip 2017). However, this type is much more susceptible to damage from biogas components, and it has a much higher cost as it requires the use of noble metals (gold, palladium, etc.).

This growing need for hydrogen has led to a search for a more renewable hydrogen source as a large majority of today's hydrogen production comes from a process that releases carbon monoxide and carbon dioxide into the atmosphere; this process is also not sustainable for the future as it relies on hydrocarbons (GrandviewResearch 2020; Markets&Markets 2020; Jolly 2020; Arreola-Vargas

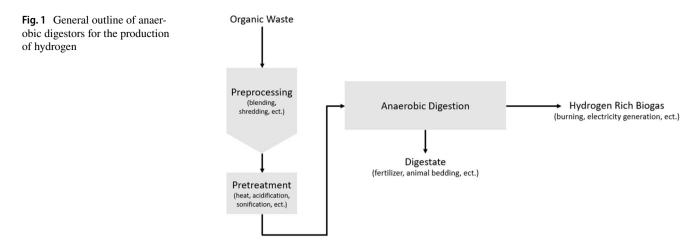


et al. 2016). Continued use of this process as the need for additional hydrogen sources increase will lead to dangerous levels of greenhouse gases being released for the production of hydrogen. This ongoing search for a renewable source of hydrogen has promoted research into anaerobic digestors as a possible source. Conventional anaerobic digestion systems produce a biogas that is rich in methane and contains nominal levels of hydrogen (Gujer and Zehnder 1983; Opus 2017). Recent findings have suggested that it is possible to maximize hydrogen production and limit methane through various processes of influent pretreatment and control of operating conditions, making anaerobic digestion a possible source for hydrogen (Emerson 2008; Peña Muñoz and Steinmetz 2012; Muthudineshkumar and Anand 2019). Not only would this use of anaerobic digestion produce viable sources of hydrogen, it would also increase the use of anaerobic digestion, a process that could treat organic wastes and minimize the spread of pathogens. The combination of treating organic wastes while producing viable amounts of hydrogen and a usable organic liquid/solid mixture called digestate suggests that this process is sustainable and environmentally friendly (Fu et al. 2017; Muthudineshkumar and Anand 2019; Biomass 2005; University of Michigan 2019). There are many design considerations that must be controlled and maximized in order to make this process both efficient and sustainable to the greatest degree possible for each particular set of conditions. Figure 1 shows a basic schematic of the process of anaerobic digestion with some processes that help maximize the production of a hydrogen-rich biogas.

#### **Anaerobic digestion**

Anaerobic digestion is the process in which microorganisms break down organic materials in an oxygen-deprived environment (EPA 2020a). Conventionally, this process results in the production of biogas, biosolids, and an organic liquor (Uçkun Kiran et al. 2016). The biogas contains high levels of methane and carbon dioxide with trace amount of oxygen, nitrogen, hydrogen sulfide, and ammonia, and it is often used as a fuel source to replace common fossil fuels (Parvathy Eswari et al. 2020). The biosolid and organic liquor contain nitrogen, phosphorus, and other nutrients making them good potential sources for fertilizers and other industrial products (Xu et al. 2018). Anaerobic digestion is used to treat organic materials which include industrial organics; fats, oils, and greases; food scraps; sewage sludge; and animal manures (EPA 2020a). This process is often used to minimize the amount of harmful gasses released and contain them for future use (Jarvie 2018).

Anaerobic digestion was first used by humans over two hundred years ago, but one of the first times it was industrially utilized was 1911 when activated digest sludge was treated in an anaerobic lagoon. In the 1940s, it was used for



methane production in Germany and France during the fuel crisis of World War II. After a decline in interest due to fuel costs and digester malfunctions, anaerobic digestion became a focus of research for treating organic matter and producing environmentally friendly energy in the 1990s, and this interest continued through today (Humenik et al. 2011). With an increasing need to focus on the environmental effects of conventional fueling systems, anaerobic digestion offers an alternative source that can both mitigate the release of greenhouse gasses and treat organic matter safely (Jarvie 2018). Anaerobic digestion systems allow the capture of energy-containing gasses for use later on thus lowering the net amount of methane and carbon dioxide released into the atmosphere (EPA 2020b).

#### Uses of anaerobic digestion

Anaerobic digestion systems are used in markets where organic matter is created and often disposed of; these include farm-based, food-based, and municipal waste systems (Environmental Protection Agency 2020). The use of digestors is increasing, especially as the efficiency of these systems are improved (Zhang et al. 2012). Europe was the first continent to heavily invest in these systems, but as North American countries began to push legislation to encourage their use, more began to appear in the USA (Environmental Protection Agency 2020). In 2015, Europe supported more than 244 large-scale anaerobic digestion plants treating almost 8 MMT of organic waste per year; the USA had around 175–240 large-scale anaerobic digestion plants (Linville et al. 2015). It is predicted that by 2030, with the continued increase of government incentives and developing technologies, 11,000 additional biogas systems could be added in the USA (Linville et al. 2015).

One particular use of anaerobic digestors is in the agricultural industry to treat farm-based wastes. It is most commonly found in large-scale farms that can afford to support this type of system in an economically viable manner (Anderson et al. 2013). The benefits of such a system are that they control odor and allow for a cheap source of energy (USDA 2008). There are currently 288 documented digesters, of all sizes, being used or built within the USA for farm-based purposes; these digesters mainly process animal manure but sometimes co-digest other organic wastes (agricultural residues, dairy processing wastes, and food processing wastes) (Environmental Protection Agency 2020). Anaerobic digestion can be used in a large array of farm types including dairy, swine, beef, and poultry farms. Recent studies into economic requirements show that at the current state of energy prices and the extensive capital costs, it is usually not reasonable to construct a digester system. However, if fossil fuel prices increase and research into these digesters lead to better development, there is a chance that they become more common in the agricultural industry (USDA 2008).

The most common use of industrial-scale anaerobic digesters is with water resources recovery facilities (WRRFs). There are currently around 1250 municipal WRRFs in the USA that use anaerobic digesters (Environmental Protection Agency 2020). Anaerobic processes are preferred to aerobic digestors in these situations as they can have five to ten times higher treatment rates on a volume basis as well as minimizing land area required for treatment; they also tend to produce less excess sludge (Wilkie 2005). These systems also use the biogas to minimize the energy costs (Linville et al. 2015). For a better understanding of the scope of these large-scale processes, the EPA reports some statistics of three major anaerobic digestion facilities from across the USA. These values are summarized in Table 1.

These facilities use the resultant biogas (methane and carbon dioxide) for power, but an alternative process of hydrogen use will be explored later in this paper for the potential to enhance power production.

Another use of anaerobic digestion that has been gaining increased attention is the process of co-digestion within municipal solid waste landfills (Cazier et al. 2015a, b).



	City of Fresno reclamation facility	Los Angeles county sanitation district	Des Moines Metro WRF
Feedstock processed	Wastewater, FOG, and HSW	Sludge and food waste	Sludge, FOG, and HSW
Capacity	13 Digestors (various capacities)	24 Digesters (3.7 MG each)	6 Digestors (2.7 MG each)
Throughput	0.9 MG sludge/day and 7.7 MG HSW/day	4.4 MG sludge/day and 0.02 MG food waste/ day	0.4 MG sludge/day, 0.03 MG FOG/day, and 0.11 MG HSW/day
Biogas generation	1.4 million ft <sup>3</sup> /day	7.2 million ft <sup>3</sup> /day	1.5 million ft <sup>3</sup> /day
Biogas use	Co-generation and boiler heat	Total energy facility and boilers	Combined heat and power
Generation	3.3 MW	20 MW	1.60 MW

Table 1 Comparison of three major anaerobic digestor facilities for wastewater treatment (EPA 2016)

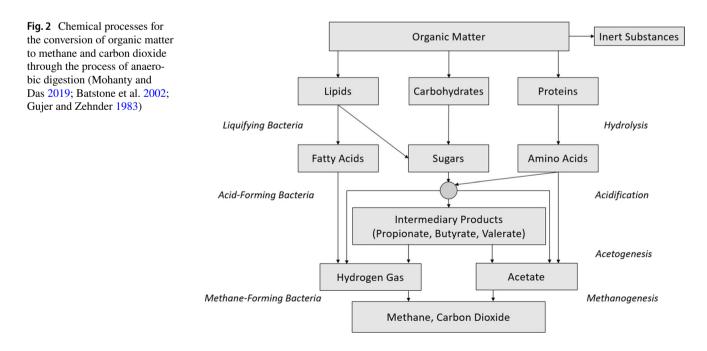
HSW, high strength wastes; FOG, fats, oils, and greases

Though the bulk of the biogas from landfills come from landfill gas systems, about ten landfills in the USA support separate anaerobic digestion systems on their sites (Environmental Protection Agency 2020).

#### Anaerobic digestion mechanisms

The process of anaerobic digestion begins with organic matter (usually waste) and produces a methane/carbon dioxide gas mixture (Mohanty and Das 2019). It is important to note that due to the ubiquitous nature of the microorganism consortium, there is no need for sterilization steps or for separation as the biogas will naturally separate from the liquid phase in which the reactions occur (Wilkie 2005). The time it takes for this process to occur depends on a series of factors including the feedstock, the bacteria consortium used, the temperature, the pH, mixing procedures, and more; some processes take a few hours to

complete while others can take up to a few days or weeks (Humenik et al. 2011; Parvathy Eswari et al. 2020; EPA 2016, 2020b). Original research into this process listed two main steps: acidification and methanogenesis; though these steps are important, recent studies have shown that much more must be included when analyzing such a system and that it is much too broad for proper understanding (Gujer and Zehnder 1983). This chart (Fig. 2) and flow process will include an in-depth analysis of multiple steps expanded from the original view and expanded from multiple research papers and reviews. It is also important to understand that these steps occur simultaneously in solution and are being continually performed during the process (Wilkie 2005; Linville et al. 2015; Mohanty and Das 2019). That being said, the process for each molecule occurs in four main steps with certain bacteria from the consortium performing specific roles; this process is outlined in Fig. 2 with an explanation for each step beneath it.



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Organic matter consists of three major groups of macromolecules: lipids, carbohydrates, and proteins (Siyavula 2011). The first major step of anaerobic digestion is the breaking down of those macromolecules into more usable forms of monomers through a chemical process called hydrolysis (Wilkie 2005). The following processes occur for each type of macromolecule: Lipids are converted into long chain fatty acids (87%) and sugars (13%); carbohydrates are converted to sugars; and proteins are converted to amino acids (Gujer and Zehnder 1983). This

(Wilkie 2005). The second major step is acidogenesis; this is where the microorganisms break down molecules of sugar and amino acids and convert them into intermediate volatile acids (Gujer and Zehnder 1983; Opus 2017; Rivière et al. 2009). This process is caused by the fermentation of amino acids and sugars by acid-forming bacteria (Opus 2017; Jarvie 2018; Wilkie 2005). This process affects amino acids and sugars almost exclusively while nearly none of the fatty acids undergo this process (these fatty acids are converted directly to hydrogen through obligate syntrophic bacteria) (Gujer and Zehnder 1983; Wilkie 2005). The intermediate acid concentration is usually made up of propionate, butyrate, and valerate (Wilkie 2005; Opus 2017). This conversion is only an intermediate for further conversion into hydrogen and acetic acid, as displayed in the next step.

process is initiated by a group of liquifying bacteria found

in the large and ubiquitous consortium of microorganisms

The next step is acetogenesis. As implied by its name, it involves the conversion of fatty acids and the intermediate acid solution into acetic acid, but it also results in carbon dioxide and hydrogen (Wilkie 2005; Batstone et al. 2002; Gujer and Zehnder 1983). This process involves anaerobic oxidation, thus requiring a system that is completely devoid of oxygen (Jarvie 2018; Opus 2017; Batstone et al. 2002). This step has been of major focus of recent research to maximize the rate and efficiency in which it occurs (Gujer and Zehnder 1983). This focus is a result of the feedstock for acetogenesis: acids. If the pH reaches acidic levels, the microorganisms needed for the following steps may be killed; that is why current research is working to maximize the rate of this process to better control ideal conditions (Wilkie 2005; Atasoy et al. 2018).

The final step in most anaerobic digestion systems is the conversion to methane and carbon dioxide; this process is called methanogenesis (Jarvie 2018; Batstone et al. 2002). This process is performed by methanogens, microorganisms that produce methane; the predominant methanogens that can exist in an aceticlastic environment are those of the genera *Methanosarcina* and *Methanosaeta* (Wilkie 2005; Jarvie 2018). After this step, the products of the total process are the resulting biogas and influent constituents (Wilkie 2005; Batstone et al. 2002).

The process product of greatest value is the biogas which is used as a substitute for natural gas or for further processing for renewable natural gas (RNG) (Han et al. 2011). RNG is a special type of renewable fuel in that it can be used in conventional natural gas systems with no change in their design making their widespread application more reasonable (Church 2015). RNG is produced from a purifying process that involves the removal of water, carbon dioxide, hydrogen sulfide, and other trace elements (DOE 2017). The use of anaerobic digestion in the production of renewable natural gas offers a promising source of easy-to-use renewable fuel (Han et al. 2011). That being said, currently, biogas is most used directly for fueling and heating (Mohanty and Das 2019). This leads to the overall anaerobic digestion to become even more economically feasible for a number of reasons. One way is using the biogas as a fuel source to produce electricity and interconnecting it to the electricity grid (Han et al. 2011). Another way is through using the biogas for direct combustion for heat; when the biogas is burned, mainly for electricity, the heat released can be used in the place of conventional heating systems that require energy (Han et al. 2011). Given that its composition is 50-75%methane with carbon dioxide, hydrogen sulfide, water vapor, and trace amounts of other gases, the biogas is very combustible (500-650 Btu per cubic foot) making it a great alternative fuel source for a variety of uses (Environmental Protection Agency 2020; EPA 2020b).

The other major product of this process is the digestate which includes the residual material left over after the digestion process; it normally contains undigested inert material and water (Environmental Protection Agency 2020). The undigested matter could be a result of several factors including temperature, mixing, or simply just being nonbiodegradable material (Environmental Protection Agency 2020). The digestate contains two main parts for later use: a liquid phase and a solid phase. Both phases can be used to maximize efficiency and generate revenue; these uses include fertilizer, animal bedding, bioplastics, compost, or a combination of these (Environmental Protection Agency 2020; Wilkie 2005; EPA 2020b). The selling of digestate would help minimize costs, especially in conjunction with the use of the biogas, making this process even more economically favorable.

#### Hydrogen

The hydrogen market is one that offers a unique potential to reduce the current means of energy use and carrying, greatly shifting the conventional means of the power industry (IEA 2020). Hydrogen is an energy carrier that has the chemical energy per mass capacity of more than three times the average of liquid hydrocarbons, but it is much lower on a volume basis (Mcwhorter et al. 2011). It is an environmentally safe



energy source that usually only produces water vapor when used as a fuel source, though it can also produce some levels nitrogen oxides and other combustion products (Hashem et al. 2015). The more conventional processes for the production of hydrogen can be somewhat harmful as it is often done through the burning of coal and other fossil fuels; however, recent research into alternative methods (as the one analyzed in this paper) shows that more environmentally, and perhaps economically, beneficial methods exist (Arreola-Vargas et al. 2016; De Beni and Marchetti 1970; Mcwhorter et al. 2011). These alternatives could offer the opportunity for hydrogen to replace conventional energy feedstocks (Mcwhorter et al. 2011).

The global hydrogen generation market was valued at USD 117.49 billion in 2019 and is expected to grow (GrandviewResearch 2020). The use of hydrogen has been encouraged by many countries, including the USA, so incentives and pro-hydrogen legislation further promote the hydrogen market to expand over time (DOE 2020b). The demand for hydrogen has been increased by three times since 1975 with a large spike in growth expected soon from emerging technologies (GrandviewResearch 2020). From 2010 to 2018, the global demand for pure hydrogen has been increased by almost 12 Mt (GrandviewResearch 2020). Though the uses for hydrogen are broad and mostly expanding, the transportation segment is expected to grow by the most over the few years with the increase in fuel cell vehicle sales, especially as countries (Japan, China, and South Korea) are proposing strong fuel cell-based vehicle implementation to lower their overall use of imported gasoline fuels (Markets&Markets 2020). These implementations have led the Asia Pacific region to be the area with the largest market growth, but most global regions are expecting to grow as well (Markets&Markets 2020). Hydrogen's growth can be credited mainly to the energy market, but a few others must be recognized as well for a complete analysis of its prevalence. Three examples of these markets are the semiconductor, fertilizer, and pharmaceuticals, in which hydrogen plays an important role in their production (IndustryARC 2020).

Pure hydrogen is used in many applications and can be found in the production of many common industries. The largest use of hydrogen is in the production of ammonia; this process consumes almost two-thirds of the world's hydrogen production (Jolly 2020). Often used for a source of hydrogen storage and fertilizer, ammonia requires the presence of hydrogen and nitrogen for its creation and makes up a major part of the global chemical market for its presence in many products (Jolly 2020; Lamb et al. 2019). This process is performed at very high temperatures and reacts one molecule of gaseous nitrogen with three molecules of gaseous hydrogen (Hignett 1985). Another common use of hydrogen is in the catalytic hydrogenation of organic compounds for the conversion of animal fats and oils to margarine and vegetable



shortening; it serves as the reducing agent for aldehydes, fatty acids, and esters (Lamb et al. 2019). This use is just one example of how hydrogen is used in the process of hydrogenation (adding hydrogen to a molecule) (Patterson 2011). Another interesting use of hydrogen is in rocket fuel. This is because hydrogen serves as one of the lightest forms of an energy carrier making it ideal for space exploration where weight is one of the most important considerations (Jolly 2020). Hydrogen is also used in hydrogen fuel cells where they produce energy for vehicles (cars, forklifts, etc.) and other systems (Markets&Markets 2020; Houf et al. 2013). Hydrogen fuel cells are a developing industry due to the incapability to successfully minimize size in relation to energy potential when using hydrogen; though its energyto-mass ratio is extremely high, its energy-to-volume ratio is extremely low (Manoharan et al. 2019). It does, however, hold great potential for its ability to use hydrogen in the large vehicle industry which would greatly lower carbon emissions (Manoharan et al. 2019; Mcwhorter et al. 2011). These are just a few of the many uses of hydrogen in modern production; full inclusion of all of its potential uses is not possible as it such a versatile and common chemical in many products and industries.

#### Mechanisms of hydrogen production

Conventionally, hydrogen production is dependent on natural gas and other fossil-based fuels as a feedstock (Álvarez-Murillo et al. 2015; IndustryARC 2020). These practices usually lead to the release of harmful gases including carbon dioxide, carbon monoxide, and sometimes dangerous levels of gaseous oxygen, a potential risk for industrial applications (Alvarez-Murillo et al. 2015; Jolly 2020). Though fossil fuels are the overwhelming main sources of hydrogen, water and biomass both contain the potential for more renewable and environmentally friendly sources; though widespread prevalence of these technologies are still far away, they could offer the opportunity to make hydrogen production a more sustainable practice for the future (Markets&Markets 2020; DOE 2020b ). Listed below are the current trends for hydrogen production with an explanation of their chemical processes as well as an analysis of their history and current prevalence in the hydrogen market as a whole.

*Catalytic steam-hydrocarbon process* The most common industrial method for producing hydrogen has been a process called catalytic steam-hydrocarbon process; this involves treating hydrocarbons, mostly methane, with steam and a catalyst at high temperatures to produce hydrogen gas (Álvarez-Murillo et al. 2015; Jolly 2020). This process is currently the cheapest and most widespread technique used to produce hydrogen, and it accounts for nearly three-fourths of the entire global hydrogen production of around 70 million tons and accounts for around six percent of the total natural gas used internationally (GrandviewResearch 2020; Markets&Markets 2020). The chemical reactions for this process are listed below (Jolly 2020):

$$\begin{split} \mathbf{C}_{n}\mathbf{H}_{2n+2} + n\mathbf{H}_{2}\mathbf{O} &\rightarrow n\mathbf{CO} + (2n+1)\mathbf{H}_{2} \\ \mathbf{C}_{n}\mathbf{H}_{2n+2} + 2n\mathbf{H}_{2}\mathbf{O} &\rightarrow n\mathbf{CO}_{2} + (3n+1)\mathbf{H}_{2} \end{split}$$

This means of production is efficient, but it also releases two common greenhouse gases, (carbon dioxide and carbon monoxide) that must be controlled and monitored (Markets&Markets 2020). This technique also relies on access to fossil fuels making long-term dependence on this method less likely; the United States Energy Information Administration expects natural gas reforming to be a nearterm solution as it lacks the sustainable practices to make long-term use feasible (Pinto 1978). That being said, there are ways to increase its sustainability such as collecting the natural gas from landfills or biogases (Pinto 1978).

Electrolysis The process of electrolysis is very rarely used on an industrial scale but offers some potential of a more renewable source of hydrogen, if performed in conjunction with a renewable source of energy (Santos et al. 2013). The process involves running an electric current through water in order to cause it to decompose into gaseous oxygen and hydrogen (Shiva Kumar and Himabindu 2019). It is normally seen as a more environmentally favorable process than catalytic steam-hydrocarbon processes, but potential issues arise from the source of the electrical power (Santos et al. 2013; Shiva Kumar and Himabindu 2019; DOE 2020c). If the energy came from a renewable source (hydroelectric, solar, wind power, etc.), then the process would be more environmentally favorable, but when finding its sustainability factor, it is important to consider the fossil fuels required to generate conventional power (DOE 2020c; Shiva Kumar and Himabindu 2019; Santos et al. 2013). Most estimates conclude that electrolysis only accounts for about four percent of the total hydrogen produced globally (Santos et al. 2013). The following reaction demonstrates the overall reaction that occurs in this process (Santos et al. 2013):

 $H_2O \rightarrow H_2 + 1/2O_2$ 

This reaction shows the overall reaction of electrolysis on water, but there are two reactions that occur on the cathode and anode, respectively (Santos et al. 2013; DOE 2020c; Shiva Kumar and Himabindu 2019):

 $2\mathrm{H}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2}$  $\mathrm{H}_{2}\mathrm{O} \rightarrow 1/2\mathrm{O}_{2} + 2\mathrm{H}^{+} + 2\mathrm{e}^{-}$ 

*Hydrogen from coal or coke* This method is somewhat outdated, but it is worth mentioning as it is still used in some situations even today. Before 1940, hydrogen was almost exclusively collected from coal or coke from combustion or

gasification (Jolly 2020). This process had extremely low yields relative to today's more prevalent techniques and also released harmful amounts of carbon monoxide making it unfavorable in most situations; though after 1970 very little hydrogen was produced using this system for the stated shortcomings, in order to demonstrate the simplicity of the reaction, the reaction for this process is demonstrated below (Jolly 2020):

$$H_2O + C \rightarrow H_2 + CO$$

Selective membrane technology This method is a developing technology to more easily and effectively separate hydrogen from a gas (usually biogas). This allows for more efficient separations and further adds to the production of hydrogen (DOE 2020a). This can also allow for hydrogen to be produced by steam reforming at lower temperatures, adding to the efficiency of this process (Kikuchi 2000). One membrane developed by Kikuchi (2000) shows a great example of the effectiveness of this technique. They developed a palladium-covered composite membrane that achieved nearly complete selectivity of hydrogen.

These are only four of many techniques that are employed, but it is important to remember that all of these techniques still lack a completely sustainable solution that is feasible for large-scale industrial applications. Therefore, a more environmentally favorable and scalable solution must be offered to best meet these needs and the future global demand.

# Anaerobic digestion for hydrogen

One promising alternative for hydrogen production is offered from the use of an anaerobic digestor that is modified to maximize hydrogen production while minimizing the release of carbon dioxide and methane (DigitalCommons et al. 2008). There are many techniques to achieve this and many conditions to modify in order to enhance the process (pH, temperature, rate of stirring, time, feedstock, etc.) (Lim 2019; Anantharaj et al. 2020). The basic technique involves inhibiting the microorganisms that convert hydrogen into methane; in reference to Fig. 2 this means preventing the process of methanogenesis from occurring which ensures that only the desired products are produced in larger volumes (Uçkun Kiran et al. 2016; DigitalCommons et al. 2008; Lim 2019). It is important to inhibit methanogens from consuming hydrogen (DigitalCommons et al. 2008). Most processes to inhibit methanogens require the use of pretreatment technologies to create conditions unsuitable for methanogenic bacteria while still allowing liquifying and acid-forming bacteria to flourish during digestion (Kim et al. 2013). This process is also sustainable as it treats wastes while producing hydrogen as a fuel source without having to also release



harmful greenhouse gases. Large-scale implementation of this technique would (1) find a cheap solution to disposing of organic wastes, (2) require little energy in its execution, (3) produce hydrogen for future energy needs, (4) produce digestate for a variety of uses, (5) produce acids that are highly valued in many markets (thus lowering costs and increasing sustainability), and (6) can also produce small amounts of methane which can be used in the production of other chemicals (DigitalCommons et al. 2008; Lim 2019; Kim et al. 2013; Anantharaj et al. 2020; Anantharaj and Arutchelvan 2019; EIA 2020; Zhang et al. 2012; Anderson et al. 2013; USDA 2008; Uçkun Kiran et al. 2016). These benefits are explored in more detail in the following paragraphs:

Organic wastes are abundant in modern society with agriculture, food waste, and municipal liquid wastes playing major parts (Barik 2018). Organic wastes from agricultural are produced in very high quantities (about 998 million tons a year), encompassing animal manure, animal waste, cultivation activities, aquaculture, and many more (Obi et al. 2016). Food wastes are also an enormous portion with 133 billion pounds of food waste reported by the USDA in the USA (USDA 2020). The treatment of wastewater is also very common with over 14,500 publicly owned treatment works in the USA generating over 8 million dry tons of sludge annually (University of Michigan 2019). All of these sources require the use of treatment processes to minimize pathogens, reduce the volume of dispersed sludge, and mitigate the possibility of contamination. Anaerobic digestion would successfully accomplish this goal (Obi et al. 2016; USDA 2020; Lim 2019). The resulting biogas and digestate safely lower the spread of pathogens, killing off any dangerous diseases allowing for the effluent to have more uses. Thermophilic digesters (those operating at high temperatures) have been shown to kill more than 99.99% of all pathogens (Biomass 2005). Though we are currently far from a dependence on anaerobic digestion for this processing, it does offer great potential for the future of treating organic waste on a large-scale basis while also generating hydrogen.

It is important to note that most anaerobic digestors produce large amounts of methane relative to hydrogen, and when targeting the production of hydrogen, the specific gas can be targeted before or during treatment (as outlined before and for most of these analyses) or after the process of anaerobic digestion is allowed to completion (allowing the steps of methanogenesis) (DeBruyn and Hilborn 2015; Cazier et al. 2015a, b; Baldi et al. 2019). Separation of hydrogen from methane in the biogas stream can be accomplished through a large variety of methods; one such method is using a single proton exchange membrane (PEM) to isolate hydrogen from methane (Ibeh et al. 2007). This process uses very little energy to achieve near-complete separation (Ibeh et al. 2007). For further conversion to a high hydrogen



output, this technique can be accompanied with a process to harvest the hydrogen from the separated methane stream. Methane has the potential to follow a steam-catalytic process to produce hydrogen gas; the high levels of methane in the biogas can be separated and used with steam for a hydrogen source (though some carbon monoxide and carbon dioxide will be produced as well) (Saur and Milbrandt 2014; Linville et al. 2015; Jolly 2020; Rostrup-Nielsen 1984). This process would also work well in addition to two-stage digestors where the second bioreactor produces copious amounts of methane. Though most current anaerobic digestors conventionally produce methane-rich streams, the bulk of this paper focuses on the developing techniques to produce hydrogenrich streams.

Anaerobic digestion for hydrogen is also relatively cheap in terms of construction and energy costs. In terms of purely energy, anaerobic digestors offer a net positive energy potential as the gas released (in this case hydrogen) can be immediately used for fuel, and in many digestors, the energy can be sold resulting in a profit (E3A 2012; Moser et al. 1998). The electrical costs for running such a system are very small and are easily cancelled by the energy profit of the system (Moriarty 2013). However, the main costs for these digestors, as with most industrial systems, are from construction. Estimates from the EPA show that the costs for an on-farm conventional anaerobic digestor range anywhere from \$400,000 to \$5,000,000 with the average being around \$1.2 million (Moriarty 2013; Moser et al. 1998; E3A 2012; Biomass 2005). This, however, does not account for the modifications required for a hydrogen-focused design (acids extraction and pretreatment systems), but due to little research available in this area and a current lack of realworld examples, exact pricing is difficult to estimate. However, these costs may be overcome by the benefits, especially as hydrogen prices increase; the benefits of energy production, odor reduction, generation of chemical feedstocks, and safety of effluent could help save money in terms of selling costs and liability prevention (Moriarty 2013; E3A 2012). Many countries also offer grants for the construction of these systems and for hydrogen usage as a fuel source further supporting this process (USDA 2008; Moriarty 2013; E3A 2012).

Perhaps the biggest draw for using this type of system is the hydrogen that is produced (DigitalCommons et al. 2008; Kim et al. 2013). As discussed earlier, hydrogen is a much more environmentally favorable energy carrier as opposed to conventional fossil fuel system or even standard biogas, and when hydrogen is used, the only chemical produced is water (IEA 2020; Jolly 2020; Kim et al. 2013). As extensively detailed above, hydrogen is an expanding market with great potential in the future. The biggest issue has mainly been production, which is almost exclusively dependent on fossil fuels, but by using an anaerobic digestor, hydrogen almost becomes a completely renewable process (Anantharaj and Arutchelvan 2019; E3A 2012; Moriarty 2013).

Another beneficial product of this system is the digestate, a mixture of usually around 30% biosolids and 70% liquids (Moriarty 2013). This product can often be used directly on farmlands as a source of fertilizer which can be done without treatment in the case of the liquid digestate, making this system ideal for onsite farm-based treatment, but it is important to note that hydrogen-focused anaerobic digestors tend to produce high levels of acids as well that need to be monitored before use (Moriarty 2013). The solids can be further treated for use as a fertilizer or treated as a source for animal bedding (Rigby and Smith 2011; Moriarty 2013; Moser et al. 1998). Processes for acid extraction include gas stripping, adsorption, electrodialysis, and membrane contractors (Atasoy et al. 2018). These acids could be sold as chemical feedstocks. Table 2, as presented by Moriarty in an analysis of local anaerobic digestion systems, shows the chemical makeup of food waste digestate.

Though these data were analyzed for food waste digestate, it is important to note that the composition may vary dependent on the influent used in the digestor. Though there is little research into the selling of the digestate available, it may be possible to lower costs and maximize profits by selling and multipurposing the digestate between industries, but it requires their markets to be further developed (Rigby and Smith 2011; E3A 2012; Moser et al. 1998).

In digestors that are suited for hydrogen production, the process of methanogenesis is often avoided; this leads to an increase in the amount of volatile acids present in the digestor (Rigby and Smith 2011; E3A 2012). Studies have shown that an increase in hydrogen partial pressure results in a higher concentration of volatile fatty acids in the effluent (Sbarciog et al. 2018). These acids may also have the opportunity for use, as they are relatively prevalent in the effluent of some of the anaerobic digestion techniques that are configured for hydrogen production, further adding to the list of useful products of this set of reactions (Biomass 2005; Rigby and Smith 2011; Moser et al. 1998). The

 
 Table 2
 Chemical composition of food waste digestate (Rigby and Smith 2011; Moriarty 2013)

Digestate composition	Percentage
Total solids	6
Volatile solids	69
Nitrogen	15
Potassium	4.7
Phosphorus	0.7
Calcium	0.34
Sulfur	0.3
Magnesium	0.19

most important concern for this source is determining the proper method to separate the volatile fatty acids from the digestate. A number of possible techniques can be used, determined by the construction constraints and the acids desired for extraction; these include gas stripping, adsorption, electrodialysis, solvent extraction, and membrane contactors (Atasoy et al. 2018). One particular method of promise is the use of vapor permeation membrane contactors to separate mixed volatile fatty acids from anaerobically digested wastes. This was demonstrated in a study by Aydin et al. where over 95% of volatile fatty acids were recovered (Aydin et al. 2018; Atasoy et al. 2018). This study also concluded that the process is both economically and environmentally friendly.

Also, in the bioproduction of hydrogen, methane is often produced as well, as is the case in most two-stage reactors; for this reason, the methane could also be used as a fuel source or sold for other uses as well (Uçkun Kiran et al. 2016; Jarvie 2018; Environmental Protection Agency 2020). Though the point of hydrogen production from anaerobic digestion is to avoid the production of methane, benefits for its use are available and should be considered when constructing an anaerobic digestor, even for hydrogen production (UCAR 2012; Moser et al. 1998).

Despite these benefits, there are still some major issues with the industrial-scaling of anaerobic digestion for the purpose of hydrogen production. Mainly, there is great difficulty in creating a large-scale system that can pretreat the microorganism consortium and maintaining adequate flow through the system (DigitalCommons et al. 2008; Anantharaj et al. 2020). There also needs for more research and designs on how to implement a system that can sufficiently pretreat, separate, and store all influents and effluents efficiently and effectively. That being said anaerobic digestion is not a new technology; the only newer aspect to this process is the use of it for hydrogen production. Another issue is the overwhelming prevalence of fossil fuels over hydrogen; currently, fossil fuels are relatively easy to obtain making other techniques dependent on fossil fuels economically viable as compared to the newer and less tested technique of using anaerobic digestion (DigitalCommons et al. 2008). More research and large-scale applications of these systems are required before a thorough and accurate statement can be made on their economic feasibility. One study, performed by Emerson, showed that in most parts of the USA, a hydrogen-focused anaerobic digestor is not feasible due to a lack of incentives, but this could easily be corrected in the future (Emerson 2008). Though these issues are of concern, the benefits of such a process offer great hope for a sustainable source of hydrogen and efficient means of disposing of wastes.



# Microorganisms in anaerobic digestors producing and/or consuming hydrogen

The number of microorganisms used in the consortium for anaerobic digestion is large and is often unknown in terms of the exact composition of the consortium members (EPA 2020b; Environmental Protection Agency 2020). Though it is difficult to identify and quantify the types of microorganisms, much research has sought to identify the microorganisms responsible for each step (Anukam et al. 2019; Hassan and Nelson 2012; Cazier et al. 2015a, b). In the production of hydrogen, it is important to promote acetogenesis, which produces hydrogen (Anukam et al. 2019). Maximum hydrogen production can be achieved through an understanding of the physiology of microorganisms in the anaerobic digestor.

The most important biological component in hydrogen production from anaerobic digestion is the group of bacteria and archaea responsible for actually producing the hydrogen; these are groups of acetogenic bacteria that convert small organic material into acetate and hydrogen gas (Anukam et al. 2019). However, the hydrogen produced by these bacteria is toxic to them, leading to an overall increase in hydrogen causing a decrease in hydrogen production; for that reason, it is important to limit the partial pressure of hydrogen through collection during the process (Krzysztof Ziemiński 2012; Kim et al. 2013). In conventional anaerobic digestion systems, where methane is produced as the main product, a symbiosis is formed between the acetogenic bacteria with methanogenic bacteria where the hydrogen levels are controlled (Ziemiński 2012). There are two main types of microorganisms involved in acetogenesis: syntrophic acetogens and non-synthrophic homoacetogens (Cazier et al. 2015a, b). Syntrophic acetogens convert fatty acids, alcohols, and volatile fatty acids into hydrogen, carbon dioxide, and acetate and are especially prone to inhibition from high levels of hydrogen, and the most common species of these contain Syntrophobacter wolinii and Syntrophomonas wolfei (Cazier et al. 2015a, b). Non synthrophic homoacetogens produce acetate from hydrogen and carbon dioxide, often lowering hydrogen levels; common species include *Clostridium aceticum.* Other species of acetogenic bacteria include Methanobacterium suboxydans and Methanobacterium propionicum (Anukam et al. 2019).

Another important form of bacteria in the digestor consortium are those that produce methane. They are of particular concern when aiming for hydrogen production as they most often use hydrogen gas as the hydrogen source, targeting the desired product (Anukam et al. 2019). They are used in most digestors to limit the partial pressure of



hydrogen gas, but in the case of producing hydrogen, this is counter-productive. These are also divided into two main types depending on their energy sources: acetotrophic and hydrogenotrophic methanogens; the acetotrophic methanotrophs (such as *Methanosaeta concilii* or *Methanosarcina acetivorans*) use acetate as substrate while hydrogenotrophic methanogens (such as *Methanobacterium bryantii* or *Methanobrevibacter arboriphilus*) use carbon dioxide and hydrogen gas as substrates (Cazier et al. 2015a, b). Common species of methanotrophs include *Methanobrevibacter ruminantium*, *M. Bryantic*, *Methanogenium cariaci*, and *M. marinsnigri* (Anukam et al. 2019).

# Hydrogen biogas co-production

When trying to produce a specific gas from the process of anaerobic digestion, two main setups are used: single-stage reactors and two-stage reactors (DigitalCommons et al. 2008). Both of these techniques successfully treat the wastewater, but the difference is mainly found in the composition of the effluent (predominately the gas phase composition) (Nasr et al. 2012). Each type allows for different control systems and have different construction and maintenance costs (DigitalCommons et al. 2008). Their benefits in relation to hydrogen production are explored below which includes their construction, product composition, and how to control the process for hydrogen production.

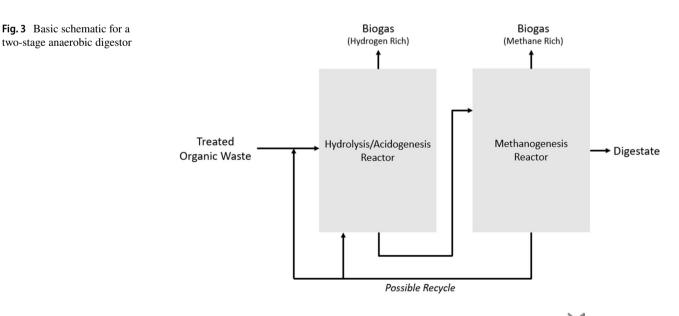
Single-stage anaerobic digestors are seemingly simpler but require much greater control of the bioreactor conditions (pH, temperature, etc.) in order to sustain all of the microorganisms in the consortium, because, unlike twostage designs, single-stage systems have all of the required microorganisms performing their tasks simultaneously (Van et al. 2019). Though this is a hindrance in the conventional production of methane as the most sensitive bacteria are the methanogens, for hydrogen production, the sensitivity of the methanogenic bacteria is advantageous, as creating unstable conditions for methanotrophs eliminates the conversion of hydrogen to methane (Van et al. 2020; DigitalCommons et al. 2008). Generally, methanogens cannot convert hydrogen into methane at pH values less than 6.2 and begin to die off around 6.0 (Van et al. 2019). In a study performed by Eniyon et al., they determined that the ideal pH for singlestage anaerobic digestors for the purpose of hydrogen production is around 5.9 (Anantharaj and Arutchelvan 2019). Steps can also be taken to ensure that methanogens are killed off or inhibited before treatment; these sometimes involve ultrasonication, alkalization, acidification, heating, or a combination of multiple methods (Van et al. 2019). Though an exact amount cannot be given as so many characteristics are given on a case-by-case basis, an example of hydrogen production from anaerobic digestion has shown hydrogen to

be produced at a concentration between 28 and 40% of the biogas (DigitalCommons et al. 2008; Kyazze et al. 2007; Nasr et al. 2012; Van et al. 2020). This process is easier to construct and maintain as opposed to large-scale two-stage digestors which require much more labor and material costs; however, for better production, two-stage digestors have been shown to be more successful, especially when in conjunction with methane production (Van et al. 2019, 2020; Kyazze et al. 2007; Nasr et al. 2012).

As opposed to deactivating the methanogenic bacteria, two-phase systems separate the processes of acidogenesis and methanogenesis into two separate reactors, allowing hydrogen to be extracted from one and methane from the other (Pham Van et al. 2019; Zhang et al. 2012; Environmental Protection Agency 2020). This process prioritizes acid-forming bacteria in the first bioreactor which produce hydrogen gas, acetate, propionate, butyrate, valerate, and other acidic compounds; extraction processes could extract hydrogen before moving to the second bioreactor (Uckun Kiran et al. 2016; Kim et al. 2013; Van et al. 2020). The second bioreactor has a higher concentration and better conditions for methanogenic bacteria in the consortium leading to an increase in the amount of methane produced (Sbarciog et al. 2018; Van et al. 2019; Nasr et al. 2012). This process has much higher yields than a single-reactor system. An example of such a setup was performed by Zhu et al. in which the first reactor was held at a pH of 5.5 (to prevent methanogenesis) and the second at 7 (to encourage it) (Zhu et al. 2008). In a study by Baldi et al., they compared the biogas production of two-stage systems as opposed to single stage; they concluded that the two-stage technology increased the total biogas production by 35% (Digital-Commons et al. 2008). However, little research has been performed on two-stage anaerobic digestion for the main purpose of hydrogen production, but some studies show that it does allow for an overall biogas production that has more hydrogen than conventional systems (Nasr et al. 2012; Biomass 2005; E3A 2012; Rigby and Smith 2011; Baldi et al. 2019; Kim et al. 2013) (Fig. 3).

Other than overall design, one of the most important factors in controlling the biogas produced is the feedstock fed into the digestor (Fu et al. 2017; Environmental Protection Agency 2020). Feedstocks include, but are certainly not limited to, food and drink waste, including restaurant waste, cafeteria waste, and organic landfill recoveries; processing byproducts and residues, such as vinasse, fats from food production, and dairy residues; agricultural residues, mainly manure and crops; and sewage sludge (Muthudineshkumar and Anand 2019; OIPAD 2020; Zhu et al. 2008; Fu et al. 2017; Pham Van et al. 2019). It has been shown that the greatest yielding feedstocks, for biogas, are crude glycerin, fats, and rape meal (OIPAD 2020). For hydrogen production, Thompson performed a study to find which feedstock produced the most hydrogen; he concluded that municipal wastewater, though possible, was not the ideal feedstock for hydrogen production (DigitalCommons et al. 2008). Rather, food wastes, in this case cheese whey, offered a better feedstock for hydrogen; however, the best feedstock in this study was a combination of both cheese whey and wastewater, a process referred to as co-digestion (the treatment of two feedstocks combined in the same solution) (DigitalCommons et al. 2008). In another study, it was determined that the optimal combination of food waste-to-sewage sludge was 2:1 which increased hydrogen production to 5 mL/g VSS, and it also increased the amount of acids produced to a concentration of around 41,000 mg/L (Kim et al. 2013).

In the production of hydrogen, pretreatment of the feedstock and microbial seed has been shown to isolate hydrogen and prevent its conversion to methane. The basis of this technique is that it prevents methanogenic bacteria from



converting hydrogen to methane, thus increasing the partial pressure of hydrogen and the concentration of volatile fatty acids (Kim et al. 2013; Lim 2019; Kyazze et al. 2007). Various pretreatment techniques can be utilized on the microorganism consortium prior to digestor reactions; these include alkalization, acidification, heat treatment, microwave treatment, and chemical additions to inhibit methanogens (Peña Muñoz and Steinmetz 2012; Sbarciog et al. 2018). Munoz and Steinmetz performed an analysis to determine the most effective method for pretreating anaerobic digestor feedstock and seed for the goal of producing bio-hydrogen while factoring in environmental and economic considerations (Peña Muñoz and Steinmetz 2012). They used 21 different conditions of pretreatments to determine which produced the most hydrogen in a two-stage digestor. Their results concluded that the most effective method was chemical acidification (using HCl) in combination with heat shock. They also recommend analysis on a case-by-case basis for the efficacy of heat treatment on a large-scale system as it could become expensive; they also recommend an environmental impact analysis on the use of HCl (Peña Muñoz and Steinmetz 2012).

# Hydrogen production through anaerobic digestion

Hydrogen production using anaerobic digestion is a developing point of research with each potential method having advantages, along with its challenges. In order to better outline the benefits of each method, the following table outlining these methods is included below (some of these can be integrated into a single process):

This table outlines some key factors in designing and implementing hydrogen production techniques from anaerobic digestion, and it is encouraged to use some of these factors in conjunction with each other. For example, for maximum hydrogen production, one design may use a two-stage reactor with food waste feed using both continuous hydrogen extraction and pretreatment techniques; however, this does not account for costs and the multiple concerns considered for design (for example, usually feed is the initial consideration and is less controllable) (Table 3).

The following paragraphs outlines some key studies in the development of anaerobic digestion as a source of hydrogen. They summarize reviews/assessments, experimental designs, and examples of large-scale applications. They were collected from a variety of sources, mainly database searches but also articles and government records regarding proprietary information.

In a study performed by Kim et al., the maximization of biological hydrogen was sought by modifying the composition of a food waste and sewage sludge feedstock as well as finding the most efficient pretreatment technique (Kim et al. 2013). The experiments were performed in a batchtype reactor with multiple sampling ports in a pH-controlled environment while being stirred at a rate of 150 rpm. The hydrogen gas was measured immediately after generation to prevent a partial pressure that could inhibit more hydrogen production. The sewage sludge was collected from a local wastewater plant while the food waste was collected from a local restaurant. They tested multiple pretreatment techniques including ultrasonication, alkalization, acidification, and heat shock; they also measured the effectiveness of different ratios of food waste-to-sewage sludge. They made several key conclusions: The process of alkalization with ultrasonication is the preferred method for pretreating sewage sludge as it most effectively destroys cell walls and aids in microbial digestion; the optimal pH levels were found to be around 5-5.5 for maximum hydrogen production; the best

 Table 3
 Summary of the current status of hydrogen production from anaerobic digestion

Method	Advantages	Challenges
Single stage	Relatively cheap costs of construction No other targeted biogas is produced	Difficult to maintain optimal conditions (pH of around 5.9) Production of hydrogen is relatively low
Two-stage	Conditions are easy to maintain Option to co-produce other biogases Relatively high yields	High costs of construction Larger size considerations
Sewage sludge fed	Ubiquitous Relatively easy adaptation of treatment facilities	Not optimum levels of hydrogen produced
Food waste fed	Produces optimum levels of hydrogen Ubiquitous (especially in developing countries)	Difficult construction requirements Difficult to collect food waste exclusively
Continuous hydro- gen extraction	Higher yield of hydrogen Maintains good growth conditions for bacteria in the digestor	More costly (construction and energy) Difficult to maintain
Pretreatment	Higher yield of hydrogen Many options: Alkalization, acidification, heat treatment, microwave treat- ment, chemical additions, etc.	Difficult to determine best pretreatment options Extra costs



ratio of food waste-to-pretreated sewage sludge is 2:1; and the maximum rate of hydrogen production they achieved was around 13.8 mL  $H_2$  per gram volatile suspended solids consumed (Kim et al. 2013).

Another study performed by Thompson further emphasized the importance of pretreatment when targeting the production of hydrogen, but in this case, they focused on wastes from agricultural systems: cheese whey and dairy manure (DigitalCommons et al. 2008). The microbial seeds were pretreated prior to experimentation by exposure to an environment of pH 3, at 37 degrees Celsius for 48 h; this ensures that the methanogenic bacteria are killed off prior to reaction. Dairy manure was collected from a local dairy, and the whey was collected from two cheese production plants. The digestion took place in three batch reactors (2 L, 2.5 L, and 2.5 L) equipped with temperature control and agitation control. The trials were maintained at a pH between 5 and 6 to ensure a high partial pressure of hydrogen. Different concentrations of whey and manure mixtures were analyzed. The results showed that manure alone produced little to no hydrogen, and it was discovered that a mixture was required for adequate production. The cheese whey trials showed very promising results as 45% cheese whey produced 83.03 mmols of hydrogen per liter of substrate; the biogas contained between 27.9 and 39.02% hydrogen. The mixture of cheese whey and manure produced around 63.16 mmols of hydrogen per liter of substrate (slightly lower than just whey). This study showed that hydrogen can effectively be produced in an agricultural setting, but proper pretreatment techniques and feedstocks must be utilized.

One interesting example of a large-scale anaerobic digestor for hydrogen was constructed by S. Venkata Mohan and his team where they designed an anaerobic digestor to be fed from food waste from his institute's cafeteria (Lim 2019). The food waste was ground up, filtered, and drained of oils and was added to the microorganism blend in the bioreactor. This tower was able to produce 5 kg of hydrogen a day. This success led Mohan to suggest that digestors ten times larger could be constructed to treat local municipal waste.

Some attention has been paid to more innovative uses for anaerobic digestion. One such example is reviewed in a paper by I. Khan (Khan 2020). He explores the possibility of using wastes in developing countries as a means to produce hydrogen as well as provide safe waste treatment facilities. Using Bangladesh as a case example, he found that organic food wastes made up around 50–87% of the overall waste produced in these areas. He found that an anaerobic system would provide a more sustainable source of hydrogen while simultaneously help solving a sanitary problem in developing countries, creating a more sustainable future.

Emerson evaluated the economic viability of using anaerobic digester gas to generate electricity using stand-alone hydrogen fuel cells at wastewater treatment plants (Emerson 2008). He concluded that from a strictly quantitative approach such a system would not be viable in most parts of the country due to the cost of energy in those places; however, he does suggest that the Northeast and some states in the Western, and Pacific Noncontiguous states represent possible markets for this type of system. He did mention that incentives could definitely make it possible for development in other parts of the country as well. He suggests also exploring the viability of similar systems at landfills and farms.

### Conclusion

Using anaerobic digestors to produce hydrogen offers an opportunity to (1) treat dangerous organic waste, preventing the spread of dangerous pathogens; (2) decrease dependence on fossil fuels, a limited resource, as a hydrogen source; (3) create more access to a fuel carrier that does not harm the environment; (4) integrate multiple systems to be more economically and environmentally viable; and (5) produce other products that can be used in multiple markets further enhancing the sustainability factor of this process. Though more research needs to be done to ensure full integration into society in a successful manner, current trends show that this technology may help to greatly support the need for hydrogen and the need to lower the amount of greenhouse gases into the atmosphere. By using pretreatment methods and a close control of conditions to favor hydrogen-producing microbes, hydrogen production from anaerobic digestion can be further maximized. Ultimately, this technology may serve a large role in making an energy sustainable future.

# **Future research needs**

Though more attention is being paid for this process to be used for hydrogen production more research needs to be done before large-scale applications can be completely integrated into society. Studies need to be performed to study other possible areas for using anaerobic digestion with a focus on those that produce high levels of organic wastes. Moreover, multiple analyses need to be done to further understand the economic status required to support these systems and where they may be most effective. In addition, more development of using hydrogen as an energy source needs to be performed, especially for integration into modern applications (vehicles, power plants, wastewater treatment facilities, etc.). A better understanding of the preferred microbes and optimal conditions is also needed. The overall goal of future research in this area needs to be on how to implement these kind of systems in an environmentally and economically favorable manner.



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#### **Compliance with ethical standards**

Conflict of interest The authors declare no conflict of interest.

# References

- Álvarez-Murillo A, Ledesma B, Román S, Sabio E, Gañán J (2015) Biomass pyrolysis toward hydrocarbonization. Influence on subsequent steam gasification processes. J Anal Appl Pyrol 113(May):380–389. https://doi.org/10.1016/j.jaap.2015.02.030
- Anantharaj C, Arutchelvan V (2019) International journal of scientific research and reviews biological hydrogen production from distillery spent wash using mixed anaerobic micro flora sludge eniyon, UK. https://www.researchgate.net/publication/335755994\_Inter national\_Journal\_of\_Scientific\_Research\_and\_Reviews\_Biolo gical\_Hydrogen\_production\_from\_Distillery\_Spent\_Wash\_using \_mixed\_anaerobic\_micro\_flora\_sludge\_Eniyon\_UK
- Anantharaj C, Veeraraghavan A, Ashok Kumar N (2020) Effects of PH and temperature on biological hydrogen production using mixed wastewater by dark fermentation in a continuous stirred tank reactor | request PDF. https://www.researchgate.net/publication/34041 6931\_Effects\_of\_pH\_and\_Temperature\_on\_Biological\_Hydro gen\_Production\_using\_Mixed\_Wastewater\_by\_Dark\_Fermentati on\_in\_a\_continuous\_stirred\_Tank\_Reactor
- Anderson RC, Hilborn D, Weersink A (2013) An economic and functional tool for assessing the financial feasibility of farm-based anaerobic digesters. Renew Energy 51(March):85–92. https://doi. org/10.1016/j.renene.2012.08.081
- Anukam A, Mohammadi A, Naqvi M, Granström K (2019) A review of the chemistry of anaerobic digestion: methods of accelerating and optimizing process efficiency. Processes 7(8):504. https://doi. org/10.3390/pr7080504
- Arreola-Vargas J, González-Álvarez V, Corona Gonzalez RI, Méndez-Acosta HO (2016) Mexican center for innovation in bioenergy view project succinic acid production by Actinobacillus succinogenes view project. https://doi.org/10.1016/j.ijhydene.2015.11.016
- Atasoy M, Owusu-Agyeman I, Plaza E, Cetecioglu Z (2018) Bio-based volatile fatty acid production and recovery from waste streams: current status and future challenges. Bioresour Technol. https:// doi.org/10.1016/j.biortech.2018.07.042
- Aydin S, Yesil H, Evren Tugtas A (2018) Recovery of mixed volatile fatty acids from anaerobically fermented organic wastes by vapor permeation membrane contactors. Bioresour Technol 250(February):548–555. https://doi.org/10.1016/j.biortech.2017.11.061
- Baldi F, Pecorini I, Iannelli R (2019) Comparison of single-stage and two-stage anaerobic co-digestion of food waste and activated sludge for hydrogen and methane production. Renew Energy

143(December):1755–1765. https://doi.org/10.1016/j.renen e.2019.05.122

- Barik D (2018) Comprehensive remark on waste to energy and waste disposal problems. In: Barik D (ed) Energy from Toxic Organic Waste for Heat and Power Generation. Elsevier, Amsterdam, pp 205–209. https://doi.org/10.1016/B978-0-08-102528-4.00013-4
- Batstone DJ, Keller J, Angelidaki I, Kalyuzhnyi SV, Pavlostathis SG, Rozzi A, Sanders WTM, Siegrist H, Vavilin VA (2002) The IWA anaerobic digestion model no. 1 (ADM1). https://iwapo nline.com/wst/article-pdf/45/10/65/425002/65.pdf
- Biomass, Michigan (2005) Anaerobic digester FAQs. https://www. focusonenergy.com/data/common/dmsFiles/W\_RB\_MKFS\_ Farmenergy%20from%20manure.pdf
- Cazier EA, Trably E, Steyer JP, Escudie R (2015a) Biomass hydrolysis inhibition at high hydrogen partial pressure in solid-state anaerobic digestion. Bioresour Technol. https://doi. org/10.1016/j.biortech.2015.04.055
- Cazier E, Trably E, Steyer J-P, Escudié R (2015b) Biomass hydrolysis inhibition at high hydrogen partial pressure in solid-state anaerobic digestion. Bioresour Technol 90:106–113. https://doi. org/10.1016/j.biortech.2015.04.055ï
- Church K (2015) Energy sources for district heating and cooling. In: Wiltshire R (ed) Advanced District Heating and Cooling (DHC) Systems. Elsevier, Amsterdam, pp 121–143. https://doi. org/10.1016/B978-1-78242-374-4.00006-9
- De Beni G, Marchetti C (1970) Hydrogen, key to the energy market. www.fastio.com
- DeBruyn J, Hilborn D (2015) Anaerobic Digestion Basics. Ministry of Agriculture & Food, Ontario
- DigitalCommons, Usu, Usu All Graduate Theses, Thompson RS (2008) Hydrogen production by anaerobic fermentation using hydrogen production by anaerobic fermentation using agricultural and food processing wastes utilizing a two-stage agricultural and food processing wastes utilizing a two-stage digestion system digestion systemhydrogen production by anaerobic fermentation using agricultural and food processing wastes utilizing a two-stage digestion system. https://digitalcommons.usu. edu/etd/208
- DOE (2017) Alternative fuels data center: renewable natural gas production. https://afdc.energy.gov/fuels/natural\_gas\_renew able.html
- DOE (2020a) Alternative fuels data center: hydrogen basics. https:// afdc.energy.gov/fuels/hydrogen\_basics.html
- DOE (2020b) Financial incentives for hydrogen and fuel cell projects | Department of Energy. https://www.energy.gov/eere/fuelcells/ financial-incentives-hydrogen-and-fuel-cell-projects
- DOE (2020c) Hydrogen production: electrolysis | Department of Energy. https://www.energy.gov/eere/fuelcells/hydrogen-produ ction-electrolysis
- E3A (2012) Anaerobic digesters: economics—E3A4U—exploring energy efficiency and alternatives. https://www.e3a4u.info/energ y-technologies/anaerobic-digesters/economics/
- EIA (2020) Production of hydrogen—U.S. Energy information administration (EIA). https://www.eia.gov/energyexplained/hydrogen/ production-of-hydrogen.php
- Emerson CW (2008) Hydrogen energy: a study of the use of anaerobic digester gas to generate electricity utilizing stand-alone hydrogen fuel cells at wastewater treatment plants. https://scholarworks.rit.edu/theses
- Environmental Protection Agency, US (2020) Project development handbook a handbook for developing anaerobic digestion/biogas systems on farms in the united states 3rd edition AgSTAR project development handbook I
- EPA (2016) Digester projects at water resource recovery facilities (WRRFs). https://www.epa.gov/anaerobic-digestion/digesterprojects-water-resource-recovery-facilities-wrrfs



- EPA (2020a) Basic information about anaerobic digestion (AD) | anaerobic digestion (AD) | US EPA. https://www.epa.gov/anaer obic-digestion/basic-information-about-anaerobic-digestion-ad
- EPA, US (2020b) Frequent questions about anaerobic digestion, Accessed June 21, 2020. https://www.epa.gov/anaerobic-diges tion/frequent-questions-about-anaerobic-digestion
- Eswari AP, Meena RA, Kannah RY, Sakthinathan G, Karthikeyan OP, Banu JR (2020) Bioconversion of marine waste biomass for biofuel and value-added products recovery. In: Kumar RP, Gnansounou E, Raman JK, Baskar G (eds) Refining biomass residues for sustainable energy and bioproducts. Elsevier, Amsterdam, pp 481–507. https://doi.org/10.1016/b978-0-12-818996-2.00022-3
- Fu SF, Xiao Hui Xu, Dai M, Yuan XZ, Guo RB (2017) Hydrogen and methane production from vinasse using two-stage anaerobic digestion. Process Saf Environ Prot 107(April):81–86. https://doi. org/10.1016/j.psep.2017.01.024
- GrandviewResearch (2020) Global hydrogen generation market size | industry report, 2027. https://www.grandviewresearch.com/indus try-analysis/hydrogen-generation-market
- Gujer W, Zehnder AJB (1983) Conversion processes in anaerobic digestion. Water Sci Technol 15:127–167
- Han J, Mintz M, Wang M (2011) Waste-to-wheel analysis of anaerobicdigestion-based renewable natural gas pathways with the GREET model. Argonne, IL (United States). https://doi.org/10.2172/10360 91
- Hashem Nehrir M, Wang C (2015) Fuel cells. In: Rashid MH (ed) Electric renewable energy systems. Elsevier, Amsterdam, pp 92–113. https://doi.org/10.1016/B978-0-12-804448-3.00006-2
- Hassan An, Nelson BK (2012) Invited review: anaerobic fermentation of dairy food wastewater. J Dairy Sci 95:6188–6203. https://doi. org/10.3168/jds.2012-5732
- Henis JMS, Tripodi MK (1977) United States Patent (19) Henis et al. 54 Multicomponent membranes for gas separations (75) inventors
- Hignett TP (1985) Production of ammonia. In: UN Industrial Development Organization (ed) Fertilizer manual. Springer, Dordrecht, pp 49–72. https://doi.org/10.1007/978-94-017-1538-6\_6
- Houf WG, Evans GH, Ekoto IW, Merilo EG, Groethe MA (2013) Hydrogen fuel-cell forklift vehicle releases in enclosed spaces. Int J Hydrog Energy 38(19):8179–8189. https://doi.org/10.1016/j. ijhydene.2012.05.115
- Humenik F, Martin J, Rice M, Roos K (2011) Anaerobic digestion of animal manure the history and current needs. (Presentation, NC State)
- Ibeh B, Gardner C, Ternan M (2007) Separation of hydrogen from a hydrogen/methane mixture using a PEM fuel cell. Int J Hydrog Energy 32(7):908–914. https://doi.org/10.1016/j.ijhyd ene.2006.11.017
- IEA (2020) The future of hydrogen—analysis: IEA. https://www.iea. org/reports/the-future-of-hydrogen
- IndustryARC (2020) Hydrogen market share, size and industry growth analysis 2019–2025. https://www.industryarc.com/Research/ Hydrogen-Market-Research-501664
- Jarvie ME (2018) Anaerobic digestion | chemical process | britannica. https://www.britannica.com/science/anaerobic-digestion
- Jolly WL (2020) Hydrogen: production and applications of hydrogen | britannica. https://www.britannica.com/science/hydrogen/Produ ction-and-applications-of-hydrogen
- Khan I (2020) Waste to biogas through anaerobic digestion: hydrogen production potential in the developing world—a case of Bangladesh. Int J Hydrog Energy 45(32):15951–15962. https://doi. org/10.1016/j.ijhydene.2020.04.038
- Kikuchi E (2000) Membrane reactor application to hydrogen production. Catal Today 56(1–3):97–101. https://doi.org/10.1016/S0920 -5861(99)00256-4
- Kim S, Choi K, Kim JO, Chung J (2013) Biological hydrogen production by anaerobic digestion of food waste and sewage sludge

treated using various pretreatment technologies. Biodegradation 24(6):753–764. https://doi.org/10.1007/s10532-013-9623-8

- Kiran EU, Stamatelatou K, Antonopoulou G, Lyberatos G (2016) Production of biogas via anaerobic digestion. In: Luque R, Lin CS, Wilson K, Clark J (eds) Handbook of biofuels production: processes and technologies, 2nd edn. Elsevier, Amsterdam, pp 259–301. https://doi.org/10.1016/B978-0-08-100455-5.00010-2
- Kyazze G, Dinsdale R, Guwy AJ, Hawkes FR, Premier GC, Hawkes DL (2007) Performance characteristics of a two-stage dark fermentative system producing hydrogen and methane continuously. Biotechnol Bioeng 97(4):759–770. https://doi.org/10.1002/ bit.21297
- Lamb KE, Dolan MD, Kennedy DF (2019) Ammonia for hydrogen storage; a review of catalytic ammonia decomposition and hydrogen separation and purification. Int J Hydrog Energy. https://doi. org/10.1016/j.ijhydene.2018.12.024
- Lim XZ (2019) Turning organic waste into hydrogen. C&EN Glob. Enterprise 97(14):26–29. https://doi.org/10.1021/cen-09714-featu re3
- Linville JL, Yanwen S, Wu MM, Urgun-Demirtas M (2015) Current state of anaerobic digestion of organic wastes in North America. Current Sustain. Renew. Energy Rep. 2:136–144. https://doi. org/10.1007/s40518-015-0039-4
- Lu GQ, Diniz da Costa JC, Duke M, Giessler S, Socolow R, Williams RH, Kreutz T (2007) Inorganic membranes for hydrogen production and purification: a critical review and perspective. J Colloids Interface Sci 314(2):589–603. https://doi.org/10.1016/j. jcis.2007.05.067
- Manoharan Y, Hosseini SE, Butler B, Alzhahrani H, Senior BTF, Ashuri T, Krohn J (2019) Hydrogen fuel cell vehicles; current status and future prospect. Appl Sci 9(11):2296. https://doi. org/10.3390/app9112296
- Markets&Markets (2020) Hydrogen generation market by generation and technology, forecast to 2023 | COVID-19 impact analysis | MarketsandMarkets. https://www.marketsandmarkets.com/Marke t-Reports/hydrogen-generation-market-494.html
- Mcwhorter S, Read C, Ordaz G, Stetson N (2011) Materials-based hydrogen storage: attributes for near-term, early market PEM fuel cells. Curr Opin Solid State Mater Sci 15:29–38. https://doi. org/10.1016/j.cossms.2011.02.001
- Mohanty MK, Das DM (2019) Industrial applications of anaerobic digestion. https://www.researchgate.net/publication/335321355\_ Industrial\_Applications\_of\_Anaerobic\_Digestion
- Moriarty K (2013) Feasibility study of anaerobic digestion of food waste in St. Bernard, Louisiana a study prepared in partnership with the environmental protection agency for the RE-powering America's land initiative: siting renewable energy on potentially contaminated land and mine sites. www.nrel.gov
- Moser M, Mattocks R, Gettier S, Roos K (1998) Benefits, costs and operating experience at seven new agricutural anaerobic digesters. https://19january2017snapshot.epa.gov/sites/production/files /2014-12/documents/lib-ben.pdf
- Muthudineshkumar R, Anand R (2019) Anaerobic digestion of various feedstocks for second-generation biofuel production. In: Azad AK (ed) Advances in eco-fuels for a sustainable environment. Elsevier, Amsterdam, pp 157–185. https://doi.org/10.1016/b978-0-08-102728-8.00006-1
- Nasr N, Elbeshbishy E, Hafez H, Nakhla G, El Naggar MH (2012) Comparative assessment of single-stage and two-stage anaerobic digestion for the treatment of thin stillage. Bioresour Technol 111:122–126. https://doi.org/10.1016/j.biortech.2012.02.019
- Obi FO, Ugwuishiwu BO, Nwakaire JN (2016) Agricultural waste concept, generation, utilization and management. Nigerian J Technol. https://doi.org/10.4314/njt.v35i4.34
- OIPAD (2020) Feedstocks | anaerobic digestion. http://www.bioga s-info.co.uk/about/feedstocks/



- Opus (2017) The illustrated step-by-step guide to anaerobic digestion | Opus energy. https://www.opusenergy.com/blog/illustrated-stepby-step-guide-to-anaerobic-digestion/
- Patterson HBW (2011) Hydrogenation. In: List GR, King JW (eds) Hydrogenation of fats and oils: theory and practice, 2nd edn. Elsevier, Amsterdam, pp 149–158
- Peña Muñoz K, Steinmetz H (2012) Evaluation of pre-treatment on the first stage of an anaerobic digester for enhancing bio-hydrogen production and its associated energy balance. Energy Procedia. https://doi.org/10.1016/j.egypro.2012.09.055

Pinto A (1978) Steam-hydrocarbon process

- Rigby H, Smith SR (2011) New markets for digestate from anaerobic digestion 1 executive summary. www.wrap.org.uk
- Rivière D, Desvignes V, Pelletier E, Chaussonnerie S, Guermazi S, Weissenbach J, Li T, Camacho P, Sghir A (2009) Towards the definition of a core of microorganisms involved in anaerobic digestion of sludge. ISME J 3(6):700–714. https://doi.org/10.1038/ ismej.2009.2
- Rostrup-Nielsen JR (1984) Catalytic steam reforming. In: Anderson JR, Boudart M (eds) Catalysis science and technology. Springer, New York, pp 1–117. https://doi.org/10.1007/978-3-642-93247-2\_1
- Santos DMF, Sequeira CAC, Figueiredo JL (2013) Hydrogen production by alkaline water electrolysis. Quim Nova 36(8):1176–1193. https://doi.org/10.1590/S0100-40422013000800017
- Saur G, Milbrandt A (2014) Renewable hydrogen potential from biogas in the United States. www.nrel.gov/publications
- Sbarciog M, Giovannini G, Chamy R, Vande Wouwer A (2018) Control and estimation of anaerobic digestion processes using hydrogen and volatile fatty acids measurements. Water Sci Technol 78(10):2027–2035. https://doi.org/10.2166/wst.2018.465
- Shirasaki Y, Yasuda I (2013) Membrane reactor for hydrogen production from natural gas at the tokyo gas company: a case study. In: Basile A (ed) Handbook of membrane reactors, vol 2. Elsevier, Amsterdam, pp 487–507. https://doi.org/10.1533/9780857097 347.2.487
- Shiva Kumar S, Himabindu V (2019) Hydrogen production by PEM water electrolysis: a review. Mater Sci Energy Technol 2(3):442– 454. https://doi.org/10.1016/j.mset.2019.03.002
- Siyavula (2011) Organic macromolecules: biological macromolecules. https://cnx.org/contents/dDWDbEU-@1/Organic-Macromolecules-Biological-macromolecules

- UCAR (2012) Methane | UCAR Center for Science Education. https:// scied.ucar.edu/methane
- University of Michigan (2019) Life cycle impacts life cycle impact of wastewater treatment systems 1
- USDA (2008) Farm-based anaerobic digesters as an energy and odor control technology background and policy issues
- USDA (2020) Food Waste FAQs | USDA. https://www.usda.gov/foodw aste/faqs
- Van DP, Takeshi F, Minh GH, Phu ST (2019) Comparison between single and two-stage anaerobic digestion of vegetable waste: kinetics of methanogenesis and carbon flow. Waste Biomass Valorization. https://doi.org/10.1007/s12649-019-00861-0
- Van DP, Fujiwara T, Tho BL, Toan PPS, Minh GH (2020) A review of anaerobic digestion systems for biodegradable waste: configurations, operating parameters, and current trends. Environ Eng Res 25:1–17. https://doi.org/10.4491/eer.2018.334
- Volkov VV (2012) Hydrogen selective membranes. In: Drioli E, Giorno L (eds) Encyclopedia of membranes. Springer, Berlin, pp 1–2
- Wilkie AC (2005) Anaerobic digestion: biology and benefits. In: Natural resource, agriculture, and engineering service. Dairy Manure Management: Treatment, Handling, and Community Relations NRAES-176. Cornell University, Ithaca, NY, pp 63–72
- Xu F, Khalaf A, Sheets J, Ge X, Keener H, Li Y (2018) Phosphorus removal and recovery from anaerobic digestion residues. In: Li Y, Ge X (eds) Advances in bioenergy, vol 3. Elsevier, Amsterdam, pp 77–136. https://doi.org/10.1016/bs.aibe.2018.02.003
- Yin H, Yip ACK (2017) A review on the production and purification of biomass-derived hydrogen using emerging membrane technologies. Catalysts 7(10):297. https://doi.org/10.3390/catal7100297
- Zhang Y, Banks CJ, Heaven S (2012) Anaerobic digestion of two biodegradable municipal waste streams. J Environ Manag 104(August):166–174. https://doi.org/10.1016/j.jenvm an.2012.03.043
- Zhu H, Stadnyk A, Béland M, Seto P (2008) Co-production of hydrogen and methane from potato waste using a two-stage anaerobic digestion process. Bioresour Technol 99(11):5078–5084. https:// doi.org/10.1016/j.biortech.2007.08.083
- Ziemiński K (2012) Methane fermentation process as anaerobic digestion of biomass: transformations, stages and microorganisms. Afr J Biotechnol. https://doi.org/10.5897/ajbx11.054