

A Review on Optimization Production and Upgrading Biogas Through CO₂ Removal Using Various Techniques

Dian Andriani · Arini Wresta · Tinton Dwi Atmaja ·
Aep Saepudin

Received: 10 June 2013 / Accepted: 18 November 2013 /
Published online: 30 November 2013
© Springer Science+Business Media New York 2013

Abstract Biogas from anaerobic digestion of organic materials is a renewable energy resource that consists mainly of CH₄ and CO₂. Trace components that are often present in biogas are water vapor, hydrogen sulfide, siloxanes, hydrocarbons, ammonia, oxygen, carbon monoxide, and nitrogen. Considering the biogas is a clean and renewable form of energy that could well substitute the conventional source of energy (fossil fuels), the optimization of this type of energy becomes substantial. Various optimization techniques in biogas production process had been developed, including pretreatment, biotechnological approaches, co-digestion as well as the use of serial digester. For some application, the certain purity degree of biogas is needed. The presence of CO₂ and other trace components in biogas could affect engine performance adversely. Reducing CO₂ content will significantly upgrade the quality of biogas and enhancing the calorific value. Upgrading is generally performed in order to meet the standards for use as vehicle fuel or for injection in the natural gas grid. Different methods for biogas upgrading are used. They differ in functioning, the necessary quality conditions of the incoming gas, and the efficiency. Biogas can be purified from CO₂ using pressure swing adsorption, membrane separation, physical or chemical CO₂ absorption. This paper reviews the various techniques, which could be used to optimize the biogas production as well as to upgrade the biogas quality.

Keywords Biogas · CO₂ · Production · Optimization · Upgrading

Introduction

The problem caused by the availability of fossil fuels and the presence of global warming due to carbon dioxide (CO₂) released from burning fossil fuels attracts more public attention in development and utilization of alternative, non-petroleum-based renewable sources of energy.

D. Andriani (✉) · A. Wresta · T. D. Atmaja · A. Saepudin
Research Center for Electrical Power and Mechatronics, Indonesian Institute of Sciences (LIPI), Komplek
LIPI, Jl. Cisitu No. 21/154D, Bandung 40135, Indonesia
e-mail: deal401@yahoo.com

D. Andriani
Research Center for Biotechnology, Indonesian Institute of Sciences (LIPI), Jl. Raya Bogor Km. 46,
Bogor 16911, Indonesia

This problem can partially be circumvented by the production of biogas from organic materials in a biological process [1–3]. Biogas production from the variety of biological wastes through fermentation technology is growing worldwide and is considered as a solution in current scenario. This technology is considered economical, environment friendly, and known as the most efficient as compared to all other technologies of energy production through biological or thermo-chemical routes of energy conversion processes [4]. Biogas is produced during anaerobic digestion of organic substrates, such as cattle or pig manure, sewage sludge, agricultural waste, and municipal wastes. Anaerobic digestion is a complex biological process that converts organic materials to methane through three major steps: hydrolysis, acetogenesis, and methanogenesis. Biogas is comprised of mainly of methane (CH_4) 40–75 % and carbon dioxide (CO_2) 15–60 %. Trace amounts of other components such as water (H_2O) 5–10 %, hydrogen sulfide (H_2S) 0.005–2 %, siloxanes 0–0.02 %, halogenated hydrocarbons (VOC) < 0.6 %, ammonia (NH_3) < 1 %, oxygen (O_2) 0–1 %, carbon monoxide (CO) < 0.6 %, and nitrogen (N_2) 0–2 % can be present and might be inconvenient when not removed [5–7]. The biogas has different applications, such as a source for heat, steam, and electricity, household fuel for cooking, fuel cell, and can be further upgraded to vehicle fuel, or for production of chemicals. Taking all these aspects into account, biogas becomes a well-established technology for generating bioenergy and considered as one of the most environmentally beneficial processes for replacing fossil fuels [8, 9].

Production and utilization of biogas has several environmental advantages, such as: (1) it is a renewable energy source, (2) it reduces the release of methane to the environment, (3) it can be used as a substitute for fossil fuels [10], and (4) it reduces the emission of CO_2 from combustion. Methane as flammable compounds in biogas contains four atoms of hydrogen and only contains one carbon atom, so that the combustion gases contain more H_2O than CO_2 , which will reduce the risk of gas emissions causing the greenhouse effect. To enhance biogas production, various techniques can be applied, such as pretreatments (chemical, thermal, enzymatic) and/or the substrate (manure, sewage sludge) can be co-digested with other wastes to achieve synergetic effects that make the anaerobic digestion process more profitable [11]. Co-digestion with other wastes, whether industrial (glycerin), agricultural (fruit and vegetable wastes), or domestic (municipal solid waste) is a suitable option for improving biogas production [11–13]. Serial digester also can be used to optimize the biogas production. Serial digester configuration which consists of main digester with long retention time and post-digester with short retention time could improve biogas production and achieve better effluent quality in terms of VFA (volatile fatty acids) concentration compared to a single reactor [14].

Biogas produced from organic materials can be used directly to generate power, but the large volume of CO_2 reduce its heating value, and limiting economic feasibility to use. Therefore, depending on the end use, different biogas treatment steps are necessary. For some applications, such as vehicle fuel or grid injection, where it is important to have high energy content in the biogas, the biogas needs to be upgraded [10]. It is important to have an optimized upgrading process in terms of low energy consumption and high efficiency giving high methane content in the upgraded biogas. The basic gas cleaning steps including: (1) water vapor removal, (2) H_2S removal, (3) CO_2 removal, and (4) siloxane and trace gas removal. This paper will emphasize the biogas cleaning by removal CO_2 . This review paper briefly discuss the techniques for optimization biogas production as well as the techniques for removing CO_2 in order to upgrade the biogas for certain uses.

Optimization Techniques for Biogas Production

The biogas production technology offers many attractive routes to utilize certain categories of organic materials to meet partial energy needs. The proper functioning of biogas system can

provide multiple benefits to the users and environment resulting in resource conservation and environmental protection [3]. Biogas can be produced from most types of organic materials. There were different technologies for the biogas production and various aspects affect the composition of the raw gas produced, such as the substrate, the production technology, and the collection of gas. It was important to optimize the biogas production technology, since the substantial role of the biogas in substituting the conventional energy sources (fossil fuels, oil). The most common technologies for optimizing the biogas production discussed in this review paper such as pretreatment of the substrates, biological approaches, co-digestion a substrates with other wastes, and the use of serial digesters.

Pretreatment Solid Substrates

The methane-rich biogas from lignocellulosic materials comes mostly from hemicellulose and cellulose. Lignin fraction in lignocelluloses causes slower degradation rate [15]. The production of biogas from lignocellulosic materials was dependent on the performance, cost effectiveness, and product generation of pretreatment process. Hence, the methane yield per wastes volume can be further improved.

In using the lignocellulosic materials, the biodegradability of the substrate was a key factor in what percentage of the theoretical yield can be achieved [16]. Due to its complexity, the organic compounds in lignocellulosic material were not fully degraded during the process [17, 18]. Hydrolysis can be the rate-limiting step for anaerobic digestion process in cases that the substrate was in particulate form [19]. Therefore in this step, physical, chemical, and biological pretreatment of lignocellulosic materials were required to break down high molecular mass organic compounds into the simple and more susceptible monomers for biodegradation. Pretreatment of substrate were known to optimize digestion process and increases the methane yield [3].

Various pretreatments had been done to optimize biogas production. Maceration of biomass to produce particle sizes below 0.35 mm has, in one study on manure, increased biogas yield by 15–20 % [20]. Thermal treatment of sewage sludge has been shown to increase the biogas yield by 50 and 80 % after heating to 70 and 170 °C, respectively [21]. Alkaline treatment of sewage sludge had been observed to increase the speed of biogas production and to cause an initial rate increase of 150 % [22]. Pretreatment using *N*-methylmorpholine-*N*-oxide (NMMO or NMO) had been done by Teghammar et al. [16]. This pretreatment had improved the methane yield by 400–1,200 % compared to untreated materials. Ozone oxidation of sewage sludge had resulted in an initial biogas yield increase of 200 % [23], while wet oxidation produced a 35 % methane yield increase. Ultrasound and microwave treatments of sewage sludge had been shown to increase initial gas production by 20–50 % [24]. Extrusion as pretreatment had been observed by Hjorth et al. and it had shown 18–70 % increment of biogas yield after 28 days [17]. Biological pretreatment could also be an effective method for optimizing biodegradability and enhancing the highly efficient biological conversion of lignocellulosic wastes into biogas. Zong et al. was used corn straw at ambient temperature (about 20 °C) treated by new complex microbial agents to improve anaerobic biogas production [25]. These treatment conditions resulted in 33.07 % more total biogas yield, 75.57 % more methane yield, and 34.6 % shorter technical digestion time compared with the untreated sample. The pretreatment methods classification is provided in Fig. 1.

Biological Approaches

Anaerobic digestion was a complex biological process operated by various functional groups of microorganisms that convert organic matter to methane through three major steps, including

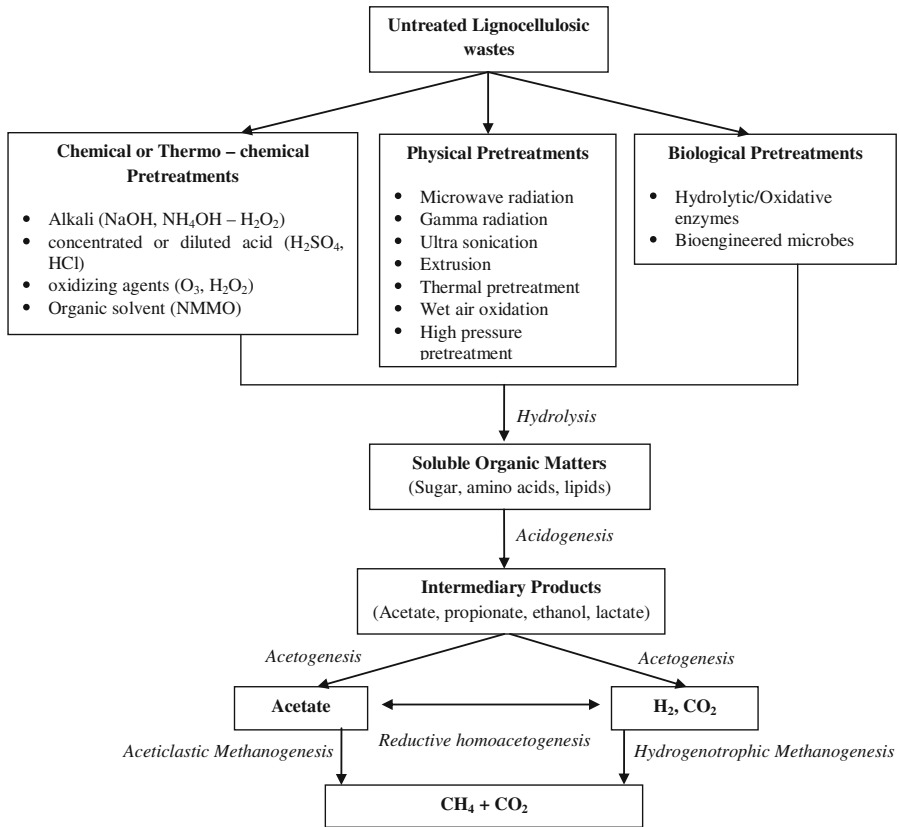


Fig. 1 Pretreatment methods classification for biogas production [modified from references 16–24]

hydrolysis/acidogenesis, acetogenesis, and methanogenesis. Biogas formation was a catabolic process that is exothermic. Energy was made available during anaerobic respiration and makes chemical, transport, and mechanical work possible [26].

Hydrolysis, acidogenesis, and acetogenesis were conducted by members of the *Eubacteria*. The hydrolysis step was conducted mainly by *Clostridia* and *Bacilli* to produce sugar intermediates [1]. Sugar intermediates were fermented to organic acids (acidogenesis) which was converted to acetate, CO_2 , and H_2 by bacteria performing secondary fermentations [27, 28]. The final methanogenesis step was conducted by *Archaea* which were restricted to a limited spectrum of input substrates (acetate, CO_2 , and H_2) that can be used for methane formation [29].

Various approaches had been developed for biogas optimization, including involving biological system. Research on diversity of these microbial communities was needed for the optimization of biogas production technologies and to improve the economic viability of this technology [30, 31]. ACS et al. had found the positive correlation between the intensification of biogas production and the presence of an added hydrogen-producing strain in a natural biogas-generating system [32]. Introducing a hydrogen-producing new member into the natural consortia was more challenging than altering the composition of microbial consortia [32]. *Caldicellulosiruptor saccharolyticus* was a good hydrogen producer and the beneficial effect of adding this strain to biogas generating system had been demonstrated [33]. The existence of

hydrogen-producing strains will increase the amount of hydrogen in the system which was then with the hydrogen methanogenic microorganisms processed into methane, which in turn increases the production of methane, then lowers the amount of CO₂, and increases the purity of the biogas produced.

Using the same strain, *C. saccharolyticus*, Acs Norberthas developed a method for quantitative identification of a single bacterium in the biogas generating microbial population that invokes Real-Time PCR [34]. Two unique genes, which code for proteins characteristic of this organism were selected. These were Ech (similar to *Escherichia coli* hydrogenase-3), and the Cel (cellulase) [34]. He also found that T-RFLP in capillary gel electrophoresis, combined with the conventional cloning sequencing was a promising way for quantitative and qualitative monitoring of the biogas-producing consortia.

Various molecular biological techniques also have been developed to optimize biogas production. Klocke et al. had utilized 16S-rDNA clone libraries and subsequent sequencing of 16S-rDNA amplicons to determine the composition of biogas-producing microbial communities [35]. Moreover, Chachkhiani et al. used polymerase chain reaction single-strand conformation polymorphism (PCR-SSCP) followed by sequencing of obtained DNA-molecules to elucidate community structures in biogas reactors [36]. Andreas et al. had analysed the composition and gene content of a biogas-producing microbial community from the production-scale biogas plant fed with renewable primary products using the ultrafast 454-pyrosequencing technology [1]. They identified the putative key organism involved in intermediate steps of bio-methanogenesis and found that the syntrophic associations with methanogens seem to be of importance, i.e. metabolites produced by some secondary fermenters potentially feed methanogenic Archaea. Furthermore, molecular biological approaches provide the basis for a rational approach to improve the biotechnological process of biogas production.

Serial Digestion System

Anaerobic digestion for biogas production was commonly practiced in continuously stirred tank reactor (CSTR) [37, 38]. Conventional one-step CSTR was simple to operate but less efficient in terms of the effluent quality compared to other reactor configurations such as two-phase reactor system [37, 39]. Jeihanipour et al. investigated the efficacy of a two-phase CSTR, modified as stirred batch reactor (SBR) and up flow anaerobic sludge blanket bed (UASB) process in producing biogas from pre-treated and untreated jeans textiles [8]. However, although the two-phase system had widely been suggested for enhancing digestion performance, it was also sensitive to the substrate with high easily degradable organic load, and in that case the biogas yield by two-phase system is nearly the same as the single CSTR [40]. The main disadvantage of using two-phase system is the separation of acidogenic and methanogenic step can disrupt the syntrophic relationship between bacteria and methanogens, which can cause product inhibition in the acidogenic reactor [40, 41].

An alternative approach to overcome the problems with one-step CSTR and two-phase system is to operate two methanogenic reactors connected in series (serial digestion system) [37]. Some researches in biogas production using serial digestion have been done. Boe has demonstrated that serial digestion, with percent volume distributions of 90/10 or 80/20 between the two methanogenic reactors, improved biogas production by 11 % compared to a traditional one-step CSTR process [42]. Boe and batstone confirmed that the longer the retention time in the post-digester (second reactor of serial process), the higher the methane recovery of the overall serial digestion [43]. Kaparaju et al. examined the possibility of optimizing biogas production from manure in a bench scale cascade of two methanogenic

serial CSTR at mesophilic conditions operated at 55 °C with 15 days HRT [37]. Results showed that serial digestion improved biogas production from manure, as compared to one-step process, and that the best volume distribution was 70/30 and 50/50 %. Ge et al. achieved 44 % volatile solid (VS) reduction in a bench scale system of working volume of 4.6 L, the dual mesophilic digestion of primary sludge with HRTs 2 and 14 days for first and second stage respectively [44]. Thus, serial digestion can be considered a method to improve conversion efficiency. However, the extra installation costs and process complexity in executing serial digestion concept should be evaluated with the economic gain achieved due to extra biogas produced. The schematic of serial digester can be seen in Fig. 2.

Co-digestion Techniques

An interesting option for optimizing biogas production yields was by using co-digestion technique [45]. This technique can be defined as the combined anaerobic treatment of several substrates with complementary characteristics. The benefits of using co-digestion techniques including dilution of potential toxic compounds, improved balance nutrients, synergistic effect of microorganism, increased load of biodegradable organic matter and higher biogas yield [46]. As a result, biogas and organic matter removal yields were enhanced. The increase in biogas production was mainly due to a better carbon and nutrient balance and in consequence to the increase in organic loading rate [47]. According to Mata-Alvarez et al., digestion of more than one substrate in the same digester can establish positive synergism and the added nutrients can support microbial growth [48].

Various co-digestion techniques had been done by mixing the substrate for biogas production with compound such as glycerol, agricultural wastes, and food wastes. Astals et al. did the comparison of biogas production using reference digester, and co-digester [49]. The daily biogas production, at standard temperature and pressure (STP) conditions, biogas production from reference digester was approximately 1.2 L day⁻¹ while co-digester produced approximately 5.6 L L day⁻¹, which represents an increase in biogas production of 380 %. It has to be highlighted that an increase of 380 % represents the highest biogas increase among the studies that had used glycerol as co-substrate, where the average increase vary from 100 to 200 % [12, 50]. The benefits of using mixing animal manure and glycerol were (1) the elevated content of water in manure acts as solvent for glycerol; (2) the high alkalinity of manure gives a buffering capacity for the temporary accumulation of volatile fatty acids; (3) the wide range of macro- and micro-nutrients present in the manure were essential for bacterial growth; and (4) glycerol supplies rapidly biodegradable matter [48]. Misi and Forster found that batch co-digestion, at

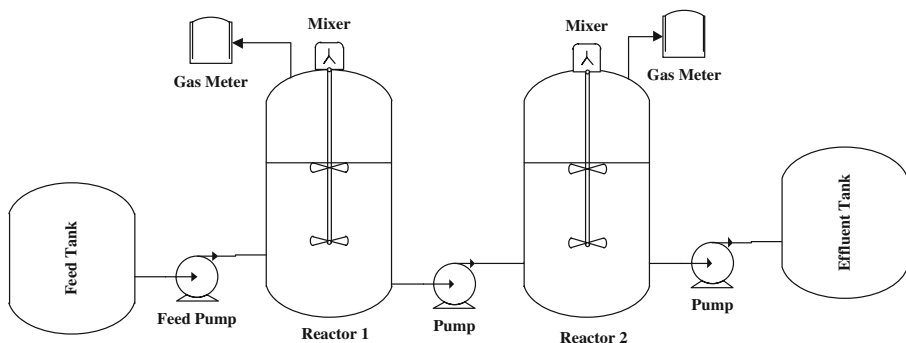


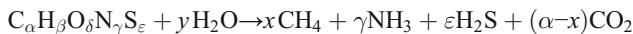
Fig. 2 Schematic of serial digester for biogas upgrading [modified from references 40–43]

35 °C, of cattle manure with molasses (50 % on dry weight basis) increased the biogas yield approximately 380 %, from 60 to 230 L/kg VS [51, 52]. Hamed and Ruihong had investigated biogas production from co-digestion of dairy manure and food waste [53]. After 30 days of digestion, the biogas yield using 48 % food waste and 52 % dairy manure was 531 L/kg VS which were significantly higher than that of unscreened manure alone (59 L/kg VS). This result mainly might due to the high biodegradability of food waste as a desirable material to co-digest with dairy manure [54]. Using different substrates, during mesophilic anaerobic co-digestion of cattle manure and fruit and vegetable wastes (FVW) in a continuous stirred tank reactor (CSTR) at 35 °C, Callaghan et al. found that increasing the percentage of FVW from 20 to 50 % increased the methane yield from 230 to 450 L/kg VS added [45]. Xiao Liu et al. using food waste, fruit vegetable waste, and dewatered sewage sludge to be co-digested in a continuous stirred-tank reactor for biogas production with HRT of 20 days [52]. The system had a biogas production rate of 4.25 m³ (m³ d)⁻¹ and a biogas yield of 0.72 m³ kg VS⁻¹ added, which was 10–20 % higher than the reported biogas yield for co-digestion of organic fraction of MSW (OFMSW) and dewatered sewage sludge (DSS) [55, 56]. Co-digestion with other wastes, whether industrial (glycerin), agricultural (fruit and vegetable wastes), or domestic (municipal solid waste) was also a suitable option for improving biogas production [12, 13].

Upgrading Biogas with CO₂ Removal

On the formation of biogas, CO₂ produced in large amounts from the acetogenesis and methanogenesis while the H₂ produced with very small quantities from acetogenesis process. Approximately 70 % CH₄ in biogas produced from acetate, and 30 % CH₄ produced from CO₂ and H₂ [57].

Biogas formation reaction was a chemical reaction that occurs with the help of an enzyme as a catalyst. Composition of the product gas produced will depend on the type of organic compound in the substrate described by anaerobic microorganisms. The theoretical or stoichiometric production of methane in anaerobic digestion can be calculated according to [15]:



In which $x = (4\alpha + \beta - 2\delta - 3\gamma - 2\varepsilon)/8$ and

$$y = (4\alpha - \beta - 2\delta + 3\gamma + 2\varepsilon)/4$$

Based on those stoichiometric equations, it can be estimated the levels of methane produced from the decomposition of some type of substrates. Levels of methane from the decomposition of fat was estimated to about 70 %, about 63 % from protein decomposition, and about 50 % from cellulose decomposition [58]. Levels of methane from decomposition of different substrates ranging were from 50 to 70 %, and the level of CO₂, the main constituent of biogas after methane [59], was about 30–50 %. Large amount of CO₂ significantly lower heating value of biogas, which in turn lowers combustion efficiency, effectiveness and economic value of biogas equipment generated.

Removing CO₂ from biogas resulting in the remaining gas, often called biomethane that had the properties of purified gas and can be utilized in every applications such as transportation fuel, raw materials for chemical industry, or in fuel cells which convert it to electricity with high efficiency [60]. Depending on the end use, different biogas upgrading methods are necessary. The presences of CO₂ in biogas often affect biogas combustion efficiency, and the

effectiveness of internal combustion engines. It causes the need of greater gas flow to produce a certain amount of energy than if the fuel is only use methane, and it also require a larger combustion chamber, which further adds to the costs required to meet both land area and installation of equipments.

The upgrading of biogas was needed since the energy content of biogas is in direct proportion to the methane concentration and by removing CO₂ in the upgrading process the energy content of the gas is increased [10]. Various techniques have been developed to purify biogas from CO₂ contamination. This review of existing biogas upgrading techniques was carried out to identify the most promising option for biogas application. The existing biogas upgrading techniques, especially CO₂ removal techniques were summarized below.

Absorption Techniques

In the upgrading of biogas using the absorption technique, the principle was that the CO₂ was more soluble than methane. The raw biogas meets a counter flow of a liquid (water, chemical solution) in the specific column. The liquid will thus contain increased concentration of CO₂ and leaving the column, while the upgraded gas that leaving the column will have an increased concentration of methane [10]. The most common absorption techniques used for biogas upgrading are water scrubbing, chemical scrubbing, and physical scrubbing. The difference in these techniques relies on the types of used absorbents in the column.

Water Scrubbing

Water scrubbing considered as a simple process to remove CO₂ since CO₂ has a higher solubility in water than methane [10]. The biogas consist mostly methane and CO₂ will be mixed with the water in the packed scrubber column. Biogas was compressed and added to scrubber column from the bottom side, typically at a pressure of 1,000–2,000 kPa [5]. The column was then filled with the water using high pressure water pump. Based on Henry's law constant that linked methane partial pressure in gas phase with mol fraction of methane in water at 25 °C as much as 36,600 atm [61], and the modification of CO₂ solubility in water at 25 °C as much as 0.608×10^{-3} [61], thus obtained Henry's law constant that linked CO₂ partial pressure in gas phase and CO₂ mol fraction in liquid phase as much as 1,644.74 atm. The value of Henry's law constant of methane was 22 times higher than CO₂ Henry's law constant, which shown less solubility of methane in water compare to CO₂. Due to the difference in the solubility of CH₄ and CO₂, if the biogas mixture was passed into the water stream, then the CO₂ will dissolve into the water and CH₄ would remain in the gas phase, so that the CO₂ can be separated from the methane in the biogas. The concentration of CO₂ decrease during the flow through water as the clean gas becomes more concentrated with methane [5, 10, 62, 63]. The process performance was dependent on factors such as the scrubbing column, composition of raw gas, water flow rates, and the purity of used water [64].

To enhance the solubility of CO₂ in water, the higher pressure about 1,000–2,000 kPa was needed in the water scrubbing process [5]. CO₂ had a low solubility in water, the diffusivity of CO₂ in water was very small as 0.138 cm²/s [61], showing the slow process of mass transfer of CO₂ from the gas phase into the water. This low diffusivity values lead to a slow absorption process of CO₂ by water in the biogas, so the water purification using gas scrubber takes a long retention time in the column, and as a result a large column volume required to obtain biogas with high methane levels.

The other disadvantage of using water scrubber is if the fresh water is the only source of water. In this case, the fresh water can be a major expenditure when using water scrubbing in

biogas upgrading. For this reason water recycling was an economically attractive choice [62]. The water which exits the scrubber column with absorbed CO_2 can be regenerated and re-circulate back to the scrubber column. Regeneration the water can be accomplished by depressuring or by stripping the water with air in the similar type of column [63]. The use of cheap water can be considered as another alternative, for example outlet water from a sewage treatment plant [63]. When the cheap water was used, it is not recommended to re-circulate the water.

Lantela et al. had observed the landfill gas upgrading with pilot-scale water scrubber [62]. They used the water recycling without adding new water to the system. The process parameters were defined by a previous study made with this pilot system. The effect of pressure (20–25 bar), temperature (10–25 °C), and water flow speed (5.5–11 L/min) on the upgrading performance, trace compounds (siloxanes, halogenated compounds) and water quality were investigated. In this work, the highest CO_2 removal efficiency 88.9 % was achieved at 25 bar, 11 L/min and 10–15 °C. In the terms of comparative economic analysis, Boateng and Kwofie had compared the capital, annual operational, and maintenance cost of water scrubber to that of the chemical absorption and biological method of purifying biogas [65]. The result was shown that the water scrubber was more efficient and eco-friendly compared to other methods. The proposed designed biogas water scrubber was able to remove 93 %v/v of CO_2 present in raw biogas. The loss of methane in this method was relatively small (less than 2 %) because of the large difference in solubility of CO_2 and methane in water [5]. The schematic of water scrubbing technique can be seen in the Fig. 3.

Chemical and Organic Physical Scrubbing

Chemical scrubbing using amine solution or alkali solution relies on the same underlying mechanism as water scrubbing. Two types of amine compounds that commonly used were mono ethanol amine (MEA) and di-methyl ethanol amine (DMEA) [10]. Alkali solutions that generally employed are sodium, potassium, and calcium hydroxides [63, 66]. The chemical

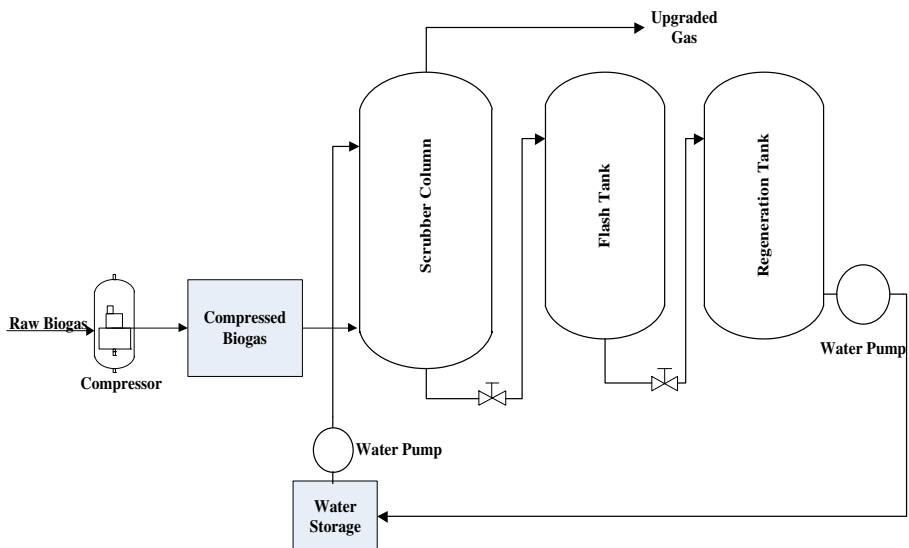
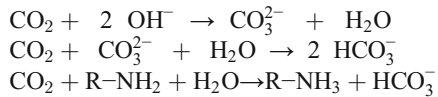


Fig. 3 Schematic of water scrubbing technology for biogas upgrading [modified from references 5, 10, 63]

scrubbing involved formation of reversible chemical bond between the solute (CO_2) and the solvent. Chemical absorption was an efficient technology for the removal of CO_2 from gas mixture. In an absorption column, the CO_2 was transferred from the gas to the gas/liquid interface, and then to the bulk of the liquid phase, CO_2 was then reacting with the chemical substance in the column where reactions take place. In the case of CO_2 absorption, the following reactions take place [67]:



After the reaction, the chemical was regenerated with steam or heat and CO_2 can possibly be recovered. The advantages of using chemical scrubbing were high efficiency and higher reaction rates compared to water scrubbing, and the ability to operate at low pressure [64]. Because of based on acid–base reaction, the chemical absorption process run rapidly, thus the retention time in the column becomes shorter and the column volume becomes smaller. The use of MEA solution as a solvent has the advantage of being able to regenerate; this solution can be completely regenerated by boiling for about 5 min. The other disadvantage was large amount of chemicals are required to obtained high purity of CH_4 -enriched gas [5, 64].

Tippayawong and Thanompongcharhave investigated chemical absorption of CO_2 in a package column using sodium hydroxide, calcium hydroxide, and MEA [64]. Test results revealed that the aqueous solutions used were effective in reacting with CO_2 in biogas (over 90 % removal efficiency), creating CH_4 -enriched fuel. Absorption capability was transient in nature. Saturation was reached in about 50 min for $\text{Ca}(\text{OH})_2$, and 100 min for NaOH and MEA, respectively.

Instead of water and chemical compounds, CO_2 removal can be done through physical absorption, in which the separation was based on differences in physical solubility of CO_2 and methane in a solvent. CO_2 was very soluble in the solvent, while methane was not/slightly soluble in the solvent, so that when biogas was passed into the solvent, the CO_2 will be carried over into the solvent, and in the gas phase lags the methane that have separate from CO_2 (gas with high methane content). Solvent regeneration was usually done by distillation and required a higher energy than the regeneration of solvents on chemical absorption. Polyethylene glycol (Selexol™) with a physical absorption process can also be used [10, 63]. The CO_2 was known to be more soluble in PEG which results in a lower solvent demand and less pumping. The PEG can also be regenerated by heating and/or depressurizing. The schematic of chemical/physical scrubbing was described in Fig. 4.

Pressure Swing Adsorption

Pressure swing adsorption (PSA) was a method to separate certain gas from a gas mixture based on its affinity to an adsorbent material [63]. In the case of biogas purification, PSA use a package column filled by adsorbent material as a molecular sieve such as zeolite, active carbon, or silica gel for differential adsorption of gas (CO_2) and letting the methane pass through [68, 69]. Commonly, the PSA unit consists of series vessels, each working on a different stadium: adsorption, depressurization, desorption, and pressurization [70]. The PSA process relied on the fact that under pressure, gases tend to be attracted to adsorbent. The higher pressure, the more gas was adsorbed [63]. The advantages of using PSA technique are more than 97 % methane enrichment, low power demand, and low emission. The PSA process also requires dry gas so the crude biogas is dried before it enters the process [5].

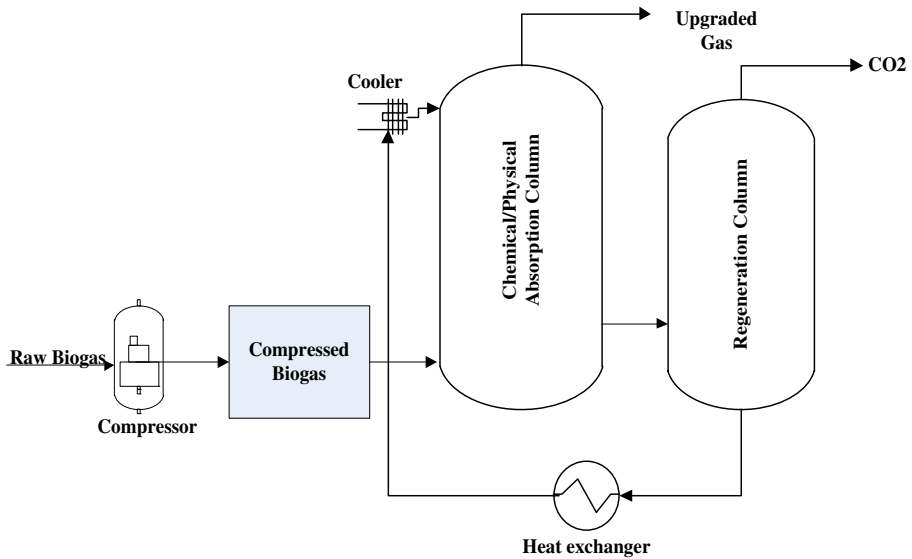


Fig. 4 Schematic of chemicals/physicals scrubbing technology for biogas upgrading [modified from references 5, 10, 63]

PSA can be operated either on the basis of equilibrium or kinetic selectivity, depending on the residence time in the column. For separation based on equilibrium selectivity, the stronger adsorbed components in a gas mixture are retained within the column, while the effluent contains the less strongly adsorbed species. In the case of separation based on kinetic selectivity, the faster diffusing species are retained by the adsorbent and the high pressure product was concentrated in slower diffusing components [71].

Montanari et al. had investigated the use of 4A and 13X zeolite adsorbent [72]. They found that 13X and 4A molecular sieves were able to adsorb selectively carbon dioxide from biogases, allowing their upgrading to pure methane or to enrich them in methane. 13X zeolites show a definitely larger capacity for adsorption of CO₂ than 4A zeolite, although regeneration by purging nitrogen at room temperature is much slower on 13X than on 4A. The schematic of PSA technique was describe in Fig. 5.

Membrane-Based Techniques

The principle of membrane separation technique was that some components of raw biogas are transported through a membrane while others were retained [63]. The membrane can be constructed as hollow fiber modules, spiral wound modules, and envelope type modules [73]. Typical operating pressure was in the range of 25–40 bars. Due to high packing density, the application of hollow fiber and spiral wound modules was more common [73]. Usually the process was often performed in two stages. Before the gas enters the hollow fibers, it passed through a filter remains water and oil droplet and aerosols, which would otherwise negatively affect the membrane performance [10].

There are two membrane separation techniques: (1) high-pressure gas separation or gas–gas separation and (2) gas–liquid adsorption membrane [5]. In both techniques, multiple stages might be required and as a consequence an increase of methane loss is obtained. In gas–gas separation, pressurized gas ranging from 2,000 to 3,600 kPa was first used to remove H₂S and

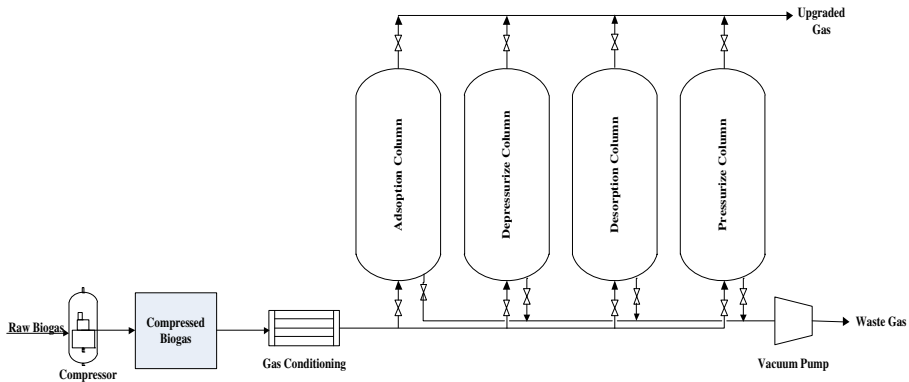


Fig. 5 Schematic of pressure swing adsorption (PSA) technology for biogas upgrading [modified from references 5, 10, 63]

oil vapors. The raw biogas can be purified up to 94 % CH_4 in one-stage performance. The purity can be enhanced up to 96 % CH_4 when two- or three-stage performance was used [9]. In gas–liquid separation, a micro porous hydrophobic membrane separates the gaseous from the liquid phase. The molecules from the gas stream, flowing in one direction, which were able to diffuse through the membrane, will be absorbed on the other side by the liquid flowing in counter current [5]. Liquid was prevented from flowing to the gas side due to slight pressurization of the gas. The absorption membranes work at approximately atmospheric pressure (100 kPa) [5]. In this process, the raw biogas can be upgraded to more than 96 % CH_4 in one step.

Membrane technology has many advantages, such as low cost, high energy efficiency, ease of processing, excellent reliability and small footprint [74–76]. However, the potential application of membrane technology largely depends on the ability of membrane materials to exhibit high separation performance. Polymeric membranes dominate traditional gas separations because they are (1) much cheaper than inorganic membranes, (2) able to be easily fabricated into commercially viable hollow fibers or flat sheets that can be processed into hollow fiber or spiral wound modules, (3) in advanced stage of development, (4) stable at high pressures, and (5) easily scalable [74, 77, 78]. Basu et al. analysed the membrane materials for biogas upgrading as mentioned in Table 1 [74].

Table 1 Membrane materials for biogas upgrading [74]

Organic polymers materials	Non-polymeric materials
Polysulfane (PSf), polyethersulfone (PES)	Carbon molecular sieves (CMS)
Cellulose acetate (CA), cellulose triacetate (CTA)	Non-porous carbon
Polyimide (PI), polyetherimide (PEI)	Zeolites and non-zeolitic molecular sieves
Polyamide (PA)	Ultramicroporous amorphous silica
Polycarbonate (PC)	Palladium alloys
Polyphenyleneoxide (PPO)	Mixed conducting perovskites
Polymethylpentene (PMP)	
Polydimethylsiloxane (PDMS)	
Polyvinyltrimethylsilane (PVTS)	

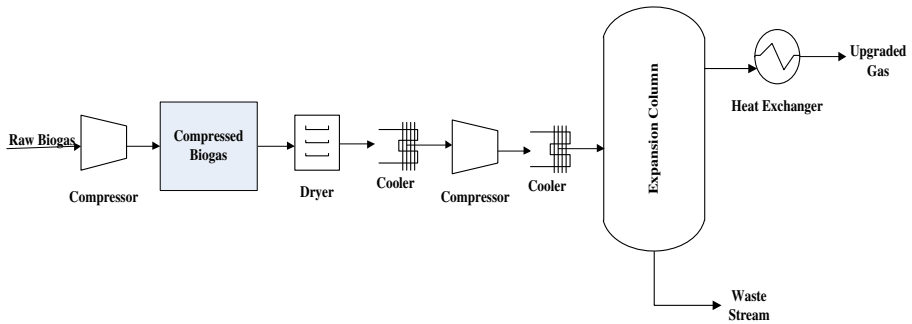


Fig. 6 Schematic of cryogenic separation for biogas upgrading [modified from references 5, 10, 63]

Biological Techniques

The biological technique can be alternative way to upgrade the biogas. This biological system can effectively remove CO_2 while approximately doubling the original CH_4 mass. Because chemical used in this technique was limited, this process was considered economical and environmentally friendly. The use of chemotrophic, heterotrophic, and autotrophic bacteria to upgrade biogas was well established. Microalgae culture also can be considered as appropriate option. Chemotrophic thiobacteria can purify CO_2 in both aerobic and anaerobic pathways. Most thiobacteria were autotrophic, consuming CO_2 and generating chemical energy from the oxidation of reduced inorganic compounds. Biogas, which contains around 30 % CO_2 , was a good source of inorganic carbon, rendering it more suitable for autotrophic bacteria.

Strevett et al. investigated the mechanism and kinetics of chemo-autotrophic biogas upgrading [79]. In this experiment, different methanogens using only CO_2 as a carbon source and H_2 as an energy source were examined. The selection between mesophilic and thermophilic operation temperatures was typically based on whether the completion of reaction or the rate of reaction is of primary concern. Thermophilic methanogens exhibit rapid methanogenesis, while mesophilic bacteria give more complete conversion of the available CO_2 [79].

Ya Kao et al. [80] had investigated the use of culture system with outdoor microalgae-incorporating photo-bioreactors to upgrade biogas produced from the anaerobic digestion of swine wastewater. Using ethyl methane sulfonate (EMS) random mutagenesis, they isolated a mutant strain of microalga, *Chlorella* sp. MB-9, which was tolerant to high CH_4 and CO_2 . In the field study of outdoor operation, 70 % of the CO_2 in desulfurized biogas could be captured by the *Chlorella* sp. MB-9 cultures. The CH_4 concentration in the effluent biogas from the *Chlorella* cultures increased from its original 70 % up to 85–90 %. The established outdoor microalgae-incorporating culture system with a gas cycle-switching operation could be efficiently used as a CO_2 capture model for biogas upgrading [80].

The advantages of biological techniques were low energy requirement, mild conditions, and the elemental sulfur byproduct can be re-used for the production of sulfuric acid or agricultural application [81, 82]. The disadvantages of using these techniques are additional nutrients were required for growing the bacteria or microalgae, and a small amount of O_2 and N_2 were left in treated biogas [63].

Cryogenic Separation

Cryogenic separation was based on the principle that different gases liquefy at different temperature-pressure domains, it was possible to produce biomethane by cooling and

Table 2 Summary of advantages and disadvantages of techniques for CO₂ removal [5, 10, 63]

Techniques	Advantages	Disadvantages
Water scrubbing	<ul style="list-style-type: none"> • Simple process, remove both H₂S and CO₂ using a water stream • No special chemicals required • Good methane content at outlet (more than 97 %) • Low CH₄ losses (< 2 %) • Low cost to operate and maintain 	<ul style="list-style-type: none"> • High pressure, need higher energy to press the gas and to pump the water • Based on physical solubility (physical process), thus the process is slow • Need a larger column volume compare to chemical absorption • Difficulty in recovery of CO₂ • Requires a lot of water even with regeneration • Corrosion problem due to H₂S • Clogging due to bacterial growth
Chemical scrubbing/ chemical absorption	<ul style="list-style-type: none"> • High CH₄ purities (>95 %) and low CH₄ losses (<0.1 %) • More CO₂ dissolved per unit of volume (compared to water) • Very low CH₄ losses (<0.1 %) • The process is faster than water scrubbing • The column volume is smaller than water scrubbing • Chemical solvent is easier to regenerated 	<ul style="list-style-type: none"> • Energy intensive, as steam has to be supplied to regenerate the chemical solution • Solvent difficult to handle • Corrosion problems • Waste chemical may require treatment
Physical scrubbing/ physical absorption	<ul style="list-style-type: none"> • Higher absorption rather than water • High CH₄ purities (>95 %) and low CH₄ losses 	<ul style="list-style-type: none"> • Solvent regeneration is complex if H₂S is not removed first • Need higher energy to regenerate the solvent • Solvent is expensive and difficult to handle
Pressure swing Adsorption (PSA)	<ul style="list-style-type: none"> • Economy in production with comparatively high purity. • Capital cost share moderate. • Relatively quick installation and start up 	<ul style="list-style-type: none"> • High capital cost (affected by number of column in PSA unit) • Incomplete scrubbing (other treatments are needed before and afterward) • CH₄ losses when malfunctioning of valves
Membrane based techniques	<ul style="list-style-type: none"> • Fast installation and startup. • Production output is flexible. • Purity and flow rate can vary • Low energy required • High CH₄ purities (>96 %) 	<ul style="list-style-type: none"> • Low membrane selectivity • Notsuitableforhighpurityneeds. • Consumes relatively more electricity per unit of gas produced • Often yields lower methane concentration though high purity is possible • High cost membrane
Biological techniques	<ul style="list-style-type: none"> • Low energy requirements • No unwanted end products • Enrichment of CH₄ 	<ul style="list-style-type: none"> • Additional nutrients are required for bacterial growth • Small amount of O₂ and N₂ are left in treated biogas • Low cost process
Cryogenic separation	<ul style="list-style-type: none"> • High CH₄ purities (90–98 %) • Produce CO₂ in marketable form, such as can be used as dry ice • Liquid methane reduces gas volume, thus can be packaged in the tube and can be easily distributed 	<ul style="list-style-type: none"> • Uses lots of process equipment, mainly compressor, heat exchanger and cooler • High operating and maintenance cost

Table 3 Energy requirement (in kilowatt hour per cubic metre) of upgraded biogas [83–85]

Techniques	Persson, 2009	Beil, 2009	Berndt, 2006
PSA	0.5–0.6	0.24	0.335
Water scrubbing	0.3	0.2	0.43
Chemical scrubbing	0.15	0.12	0.646
Physical scrubbing	0.4	–	0.49
Membrane based	–	0.19	0.769
Cryogenic separation	–	–	–

compressing the biogas. Boiling point of methane at a pressure of 1 atm as much as $-161.5\text{ }^{\circ}\text{C}$ [61] was lower than the boiling point of CO_2 which is $-78.2\text{ }^{\circ}\text{C}$ [5a], thus allowing the separation of CO_2 from methane by liquefying CO_2 at very low temperatures. Operating pressure then increased so that disbursements can be performed at higher temperatures. Based on the data of CO_2 and methane boiling point, the critical pressure data and the critical temperature of CO_2 at 7.383 MPa or 72.86 atm and 304.21 K or $31.21\text{ }^{\circ}\text{C}$ [61], also the pressure data and the critical temperature of methane at 4.599 MPa or 45.3886 atm and 190.564 K or $82.436\text{ }^{\circ}\text{C}$ [61], CO_2 and methane gas was very difficult to thaw. Cryogenic separation demands significant energy inputs to operate at very low temperatures and at high pressure [5]. Even though this process can produce the high purity of the upgraded biogas (about 99 % CH_4) as well as the large quantities of raw biogas that can be efficiently processed, this separation requires the use of process equipment mainly compressor, turbine, heat exchanger, and cooler [5]. The raw biogas was compressed until 1,000–8,000 kPa. Compression was done in different stadia with interim refrigeration. The compressed gas needs to be dried in advance to prevent freezing in the following cooling steps. The dried and compressed biogas was eventually cooled till $-25\text{ }^{\circ}\text{C}$ up to $45\text{ }^{\circ}\text{C}$ depending on the system used. The condensed CO_2 was removed and treated in a next step to recover the remnant CH_4 ; in this case, the calorific value is raised. The biogas is cooled further to $-55\text{ }^{\circ}\text{C}$ and the remaining gas streaming was further expanded to 800–1,000 kPa in an expansion tank, reaching a temperature of about $-110\text{ }^{\circ}\text{C}$. In these conditions, there was a gas–solid phase balance, with the solid phase being CO_2 and the gaseous phase containing more than 97 % CH_4 . The CH_4 gas stream was collected and heated before leaving the installation [5]. This process was of specific value when the final product is liquid biomethane (LBM), equivalent to liquid natural gas (LNG). In this case, cooling for purification is synergic to further cooling to produce LBM [68]. The schematic of cryogenic separation for biogas upgrading is described in Fig. 6.

Table 4 The summary of cost estimates of and maintenance costs of upgrading technologies [83, 86]

Techniques	Maintenance cost (€/year)	Cost per m^3 (€/m ³)
PSA	56,000	0.26
Water scrubbing	15,000	0.15
Chemical scrubbing	59,000	–
Physical scrubbing	39,000	–
Membrane based	25,000	0.22
Cryogenic separation	–	0.40

The summary of advantages and disadvantages of techniques for CO₂ removal was provided in Table 2. When selecting the upgrading process, the amount of energy needed to upgrade raw biogas became a significant factor. The lower amount of energy is used for upgrading, the more net energy is available for final use [83]. The summary of energy requirement (in kilowatt hour per cubic metre) of upgraded biogas was provided in Table 3 [84–86]. The summary of cost estimates of and maintenance costs of upgrading technologies was available at Table 4 [83, 86].

Conclusion

Optimizing of biogas production as well as the upgrading biogas quality is important in order to meet the requirement of biogas as an alternative energy source substituting the conventional fossil fuels. The enhancement in technology for optimizing and upgrading biogas in the future is expected. Although the production of biogas is a mature technology that is established worldwide, but the commercial utilization is still limited as the gas need to be purified before on-site use. Although various upgrading technologies have been developed, a technology can be chosen according to the highest achievable methane content and the type of technique that is implemented depends on desired product, economical and possibly ecological issues. When the desired product in the form of gas, the chemical absorption considered as the recommended process due to a rapid process, easiness of regeneration, and low cost. The cryogenic separation is a recommended process if the desired product in the form of liquid. The presence or the absence of supplier for the technology in the particular country could also determine the possibility of chosen technique.

Acknowledgements The writers would like to thank all researchers in Research Centre for Electrical Power and Mechatronics, Indonesian Institute of Sciences.

References

1. Schlüter, A., Bekel, T., Narytzka, N. D., Michael, D., Rudolf, E., Gartemann, K. H., Irene, K., Lutz, K., Holger, K., Olaf, K., Mussgnugd, J. H., Heiko, N., Karsten, N., Alfred, P., Kai, J. R., Rafael, S., Andreas, T., Alexandra, T., Prisca, V., & Alexander, G. (2008). The metagenome of a biogas-producing microbial community of a production-scale biogas plant fermenter analysed by the 454-pyrosequencing technology. *Journal of Biotechnology*, 136, 77–90.
2. Angelidaki, I., & Ellegaard, L. (2003). Codigestion of manure and organic wastes in centralized biogas plants: status and future trends. *Applied Biochemistry and Biotechnology*, 109, 95–105.
3. Yadavika, S., Sreekrishnan, T. R., Kohli, S., & Rana, V. (2004). Enhancement of biogas production from solid substrates using different techniques—a review. *Bioresource Technology*, 95, 1–10.
4. Chandra, R., Tekeuchi, H., Hasegawa, T., & Kumar, R. (2012). Improving biodegradability and biogas production of wheat straw substrates using sodium hydroxide and hydrothermal pretreatments. *Energy*, 43, 273–282.
5. Ryckebosch, E., Drouillon, M., & Vervaeren, H. (2011). Techniques for transformation of biogas to biomethane. *Biomass and Bioenergy*, 35, 1633–1645.
6. Wellinger, A., & Lindberg, A. (2002). Biogas upgrading and utilisation. IEA Bioenergy Task 24: Energy From Biological Conversion of Organic Waste. http://www.biogasmax.eu/media/biogas_upgrading_and_utilisation_018031200_1011_24042007.pdf. Accessed 8 March 2013.

7. Wheless, E., & Pierce, J. (2004). Siloxanes in landfill and digester gasupdate. Whittier (Canada) and Long Beach (California): Los Angeles County Sanitation Districts and SCS Energy. http://www.scsengineers.com/Papers/Pierce_2004Siloxanes_Update_Paper.pdf. Accessed 8 March 2013.
8. Jeihani pour, A., Aslanzadeh, S., Rajendran, K., Balasubramanian, G., & Taherzadeh, M. J. (2013). High-rate biogas production from waste textiles using two-stage process. *Renewable Energy*, *52*, 128–135.
9. Weiland, P. (2010). Biogas production: current state and perspectives. *Applied Microbiology and Biotechnology*, *85*, 849–860.
10. Petersson, A., & Wellinger, A. (2009). Biogas upgrading technologies—developments and innovations. IEA Bioenergy.
11. Marañón, E., Castrillón, L., Quiroga, G., Fernández-Nava, Y., Gómez, L., & García, M. M. (2012). Co-digestion of cattle manure with food waste and sludge to increase biogas production. *Waste Management*, *32*, 1821–1825.
12. Amon, T., Amon, B., Kryvoruchko, V., Bodiroza, V., Pötsch, E., & Zollitsch, W. (2006). Optimising methane yield from anaerobic digestion of manure: effects of dairy systems and of glycerin supplementation. *International Congress Series*, *1293*, 217–220.
13. Macias-Corral, M., Samani, Z., Hanson, A., Smith, G., Funk, P., Yu, H., & Longworth, J. (2008). Anaerobic digestion of municipal solid waste and agricultural waste and the effect of co-digestion with dairy cow manure. *Bioresource Technology*, *99*(17), 8288–8293.
14. Boe, K., Karakashev, D., Trably, E., & Angelidaki, I. (2009). Effect of post-digestion temperature on serial CSTR biogas reactor performance. *Water research*, *43*, 669–676.
15. Deublein, D., & Steinhauser, A. (2008). *Biogas from waste and renewableresources. An introduction*. Weinheim: Wiley.
16. Teghammar, A., Yngvesson, J., Lundin, M., Taherzadeh, M. J., & Sarvari, H. I. (2010). Pretreatment of paper tube residuals for improved biogas production. *BioresourTechnol*, *101*, 1206.
17. Hjorth, M., Christensen, K. V., Christensen, M. L., & Sommer, S. G. (2010). Solid–liquid separation of animal slurry in theory and practice. a review. *Agron. Sustain. Dev.*, *3*, 153–180.
18. Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., & Ladisch, M. (2005). Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, *96*, 673–686.
19. Davidsson, Å. (2007). Increase of biogas production at wastewater treatment plants. Ph.D. thesis, Lund University, Lund, Sweden
20. Angelidaki, I., & Ahring, B. K. (2000). Methods for increasing the biogas potential from the recalcitrant organic matter contained in manure. *Water Science and Technology*, *41*, 189–194.
21. Bougrier, C., Delgenès, J. P., & Carrere, H. (2006). Combination of thermal treatments and anaerobic digestion to reduce sewage sludge quantity and improve biogas yield. *Process Safety and Environment Protection*, *84*, 280–284.
22. Lin, J. G., Chang, C. N., & Chang, S. C. (1997). Enhancement of anaerobic digestion of waste activated sludge by alkaline solubilization. *Bioresource Technology*, *62*, 85–90.
23. Bougrier, C., Battimelli, A., Delgenès, J. P., & Carrere, H. (2007). Combined ozone pretreatment and anaerobic digestion for the reduction of biological sludge production in wastewater treatment. *Ozone Science and Engineering*, *29*, 201–206.
24. Xie, R., Xing, Y., Ghani, Y. A., Ooi, K. E., & Ng, S. W. (2007). Full-scale demonstration of an ultrasonic disintegration technology in enhancing anaerobic digestion of mixed primary and thickened secondary sewage sludge. *Journal of Environmental Engineering and Science*, *6*, 533–541.
25. Zeng, X., Ma, Y., & Ma, L. (2007). Utilization of straw in biomass energy in China. *Renewable and Sustainable Energy Reviews*, *11*(5), 976–987.
26. Willey, J. M., Sherwood, L. M., & Woolverton, C. S. (2009). *Prescott's Principles of Microbiology*. New York: McGraw-Hill.
27. Drake, H. L., Kuse, I. K., & Matthies, C. (2002). Ecological consequences of the phylogenetic and physiological diversities of acetogens. *Antonie Van Leeuwenhoek*, *81*, 203–213.
28. Myint, M., Nirmalakhandan, N., & Speece, R. E. (2007). Anaerobic fermentation of cattle manure: modeling of hydrolysis and acidogenesis. *Water Research*, *41*, 323–332.
29. Deppenmeier, U., Muller, V., & Gottschalk, G. (1996). Pathways of energy conservation in methanogenicarchaea. *Archives of Microbiology*, *165*, 149–163.
30. Hofman-Bang, J., Zheng, D., Westermann, P., Ahring, B. K., & Raskin, L. (2003). Molecular ecology of anaerobic reactor systems. *Advances in Biochemical Engineering/Biotechnology*, *81*, 151–203.
31. Nettmann, E., Bergmann, I., Mundt, K., Linke, B., & Klocke, M. (2008). Archaea diversity within a commercial biogas plant utilizing herbal biomass determined by 16S rDNA and mcrA analysis. *Journal of Applied Microbiology*, *105*(6), 1835–1850.

32. Ács, N., Bagi, Z., Rakhely, G., Kovács, E., Wirth, R., & Kovács, K. L. (2011). *Improvement of biogas production by biotechnological manipulation of the microbial population* (3rd IEEE International Symposium on Exploitation of Renewable Energy Sources). Serbia: Subotica.
33. Bagi, Z., Ács, N., Bálint, B., Horváth, L., Dobó, K., Perei, K. R., Rakhely, G., & Kovács, K. L. (2007). Biotechnological intensification of biogas production. *Applied Microbiology and Biotechnology*, *76*, 473–482.
34. Ács, N. (2010). Monitoring the biogas producing microbes. *Act Biologica Szegediensis*, *54*(1), 59–73.
35. Klocke, M., Máhnert, P., Mundt, K., Souidi, K., & Linke, B. (2007). Microbial community analysis of a biogas-producing completely stirred tank reactor fed continuously with fodder beet silage as mono-substrate. *Systematic and Applied Microbiology*, *30*, 139–151.
36. Chachkhiani, M., Dabert, P., Abzianidze, T., Partskhaladze, G., Tsiklauri, L., Dudaui, T., & Godon, J. J. (2004). 16S rDNA characterisation of bacterial and archaeal communities during start-up of anaerobic thermophilic digestion of cattle manure. *Bioresource Technology*, *93*, 227–232.
37. Kaparaju, P., Ellegaard, L., & Angelidaki, I. (2009). Optimization of biogas production from manure through serial digestion: lab-scale and pilot-scale studies. *Bioresource Technology*, *100*, 701–709.
38. Wilkie, A. C., Castro, H. F., Cubisnki, K. R., Owens, J. M., & Yan, S. C. (2004). Fixed-film anaerobic digestion of flushed dairy manure after primary treatment: wastewater production and characterisation. *Biosystems Eng.*, *89*(4), 457–471.
39. Speece, R. E., Duran, M., Demirel, G., Zhang, H., & DiStefano, T. (1997). The role of process configuration in the performance of anaerobic systems. *Water Science Technology*, *36*, 539–547.
40. Boe, K., & Angelidaki, I. (2009). Serial CSTR digester configuration for improving biogas production from manure. *Water research*, *43*(1), 166–172.
41. Smith, D. P., & McCarty, P. L. (1989). Reduced product formation following perturbation of ethanol- and propionate-fed methanogenic CSTRs. *Biotechnology and Bioengineering*, *34*(7), 885–895.
42. Boe, K. (2006). Online monitoring and control of the biogas process, Ph.D. Thesis, Technical University of Denmark.
43. Boe, K., & Batstone, D. J. (2005). Optimisation of serial CSTR biogas reactors using modeling by ADM1. In: Proceedings of the First International Workshop on the IWA Anaerobic Digestion Model No. 1 (ADM1), 2–4 September 2005, Lyngby, Denmark: 219–221.
44. Ge, H. Q., Jensen, P. D., & Batstone, D. J. (2011). Increased temperature in the thermophilic stage in temperature phased anaerobic digestion (TPAD) improves degradability of waste activated sludge. *Journal of Hazardous Materials*, *187*, 355–361.
45. Callaghan, F. J., Wase, D. A. J., Thayanithy, K., & Foster, C. F. (1999). Co-digestion of waste organic solids: batch studies. *Bioresource Technology*, *67*, 117–122.
46. Akgdag, O. N., & Sponza, D. L. (2007). Co-digestion of mixed industrial sludge with municipal solid wastes in anaerobic simulated landfilling bioreactors. *Journal of Hazardous Materials*, *140*, 75–85.
47. Mshandete, A., Kivaisi, A., Rubindamayugi, M., & Mattiasson, B. (2004). Anaerobic batch co-digestion of sisal pulp and fish wastes. *Bioresource Technology*, *95*(1), 19–24.
48. Mata-Alvarez, J., Macé, S., & Llabrés, P. (2000). Anaerobic digestion of organic solid wastes: an overview of research achievements and perspectives. *Bioresource Technology*, *74*(1), 3–16.
49. Astals, S., Ariso, M., Galí, A., & Mata-Alvarez, J. (2011). Co-digestion of pig manure and glycerine: experimental and modelling study. *Journal of Environmental Management*, *92*(4), 1091–1096.
50. Fountoulakis, M. S., & Manios, T. (2009). Enhanced methane and hydrogen production from municipal solid waste and agro-industrial by-products co-digested with crude glycerol. *Bioresource Technology*, *100*, 3043–3047.
51. Misi, S. N., & Forster, C. F. (2001). Batch co-digestion of multi-component agro-wastes. *Bioresource Technology*, *80*(1), 19–28.
52. Xiao, L., Xingbao, G., Wei, W., Lei, Z., Yingjun, Z., & Yifei, S. (2012). Pilot-scale anaerobic co-digestion of municipal biomass waste: focusing on biogas production and GHG reduction. *Renewable energy*, *44*, 463–468.
53. Hamed, M. M., & Ruihong, Z. (2010). Biogas production from co-digestion of dairy manure and food waste. *Bioresource Technology*, *101*, 4021–4028.
54. Zhang, R., El-Mashad, H. M., Hartman, K., Wang, F., Liu, G., Choate, C., & Gamble, P. (2006). Characterization of food waste as feedstock for anaerobic digestion. *Bioresource Technology*, *98*(4), 929–935.
55. Sosnowski, P., Wieczorek, A., & Ledakowicz, S. (2003). Anaerobic co-digestion of sewage sludge and organic fraction of municipal solid wastes. *Advances in Environmental Research*, *7*, 609–616.
56. Capela, I., Rodrigues, A., Silva, F., Nadais, H., & Arroja, L. (2008). Impact of industrial sludge and cattle manure on anaerobic digestion of the OFMSW under mesophilic conditions. *Biomass and Bioenergy*, *32*, 245–251.

57. Ritchie, D. A., Edwards, C., Mc Donald, I. R., & Murrell, J. C. (1997). Detection of metanogen and metanotrophs in natural environment. *Global Change Biology*, 3, 339–350.
58. Ward, A. J. (2010). *Biogas potential of fish wax with cattle manure*. Internal Report-Animal Science: Department of Biosystems Engineering, Faculty of Agricultural Sciences, University of Aarhus.
59. Tortora, G. J., Funke, B. R., & Case, C. L. (2010). *Microbiology, an introduction* (10th ed.). Redwood City: Benjamin Cummings.
60. Ahring, B. K. (2003). Perspectives for anaerobic digestion. *Advances in Biochemical Engineering/Biotechnology*, 81, 1–30.
61. Green, D. W., & Perry, R. H. (2008). *Perry's chemical engineers' hand book* (8th ed.). New York: McGraw-Hill Companies Inc.
62. Läntelä, J., Rasi, S., Lehtinen, J., & Rintala, J. (2012). Landfill gas upgrading with pilot-scale water scrubber: performance assessment with absorption water recycling. *Applied energy*, 92, 307–314.
63. Zhao, Q., Leonhardt, E., MacConnell, C., Frear, C., & Chen, S. (2010). Purification technologies for biogas generated by anaerobic digestion. CSANR Research Report.
64. Tippayawong, N., & Thanompongchart, P. (2010). Biogas quality upgrade by simultaneous removal CO₂ and H₂S in a packed column reactor. *Energy*, 35, 4531–4535.
65. Ofori-Boateng, C., & Kwofie, E. M. (2009). Water scrubbing: a better option for biogas purification for effective storage. *World Applied Science Journal*, 5, 122–125.
66. Baciocchi, R., Carnevale, E., Corti, A., Costa, G., Lombardi, L., Olivieri, T., Zanchi, L., & Zingaretti, D. (2012). Innovative process for biogas upgrading with CO₂ storage: results from pilot plant operation. *Biomass and Bioenergy*, 1–10.
67. Georgiou, D., Petrolekas, P. D., Hatzixanthis, S., & Aivasidis, A. (2007). Absorption of carbon dioxide by raw and treated dye-bath effluents. *J Hazardous Mater*, 144, 369–376.
68. Krich, K., Augenstein, A., Batmale, J., Benemann, J., Rutledge, B., & Salour, D. (2005). Upgrading dairy biogas to biomethane and other fuels. In K. Andrews (Ed.), *Biomethane from dairy waste—a sourcebook for the production and use of renewable natural gas in California* (pp. 47–69). Clear Concepts: California.
69. Bourque, H. (2006). Use of liquefied biogas in transport sector. Conférencesur les crédits CO₂ et la valorisation du biogas. www.apcas.qc.ca. Accessed 21 February 2013.
70. Persson, M. (2003). Evaluation of upgrading techniques for biogas [Internet] Lund. School of Environmental Engineering. Available from: <http://www.sgc.se/dokument/Evaluation.pdf>. Accessed 20 February 2013.
71. Gomes, V. G., & Hassan, M. M. (2001). Coalseam methane recovery by vacuum swing adsorption. *SeparPurifTechn*, 24, 189–196.
72. Montanari, T., Finocchio, E., Salvatore, E., Garuti, G., Giordano, A., Pistarino, C., & Busca, G. (2011). CO₂ separation and landfill biogas upgrading: a comparison of 4A and 13X zeolite adsorbents. *Energy*, 36, 314–319.
73. Scholz, M., Melin, T., & Wessling, M. (2013). Transforming biogas into biomethane using membrane technology. *Renewable and Sustainable Energy Reviews*, 17, 199–212.
74. Basu, S., Asim, L. K., Angels, C. O., Chunqing, L., & Ivo, F. J. V. (2009). Membrane-based technologies for biogas separations. *Chemical Society reviews*. doi:10.1039/b817050a.
75. Stern, S. A. (1994). Polymers for gas separation: the next decade. *Journal of Membrane Science*, 94, 1–65.
76. Lai, Z. P., Bonilla, G., Diaz, I., Nery, J. G., Sujaoti, K., Amat, M. A., Kokkoli, E., Terasaki, O., Thompson, R. W., Tsapatsis, M., & Vlachos, D. G. (2003). Microstructural optimization of a zeolite membrane for organic vapor separation. *Science*, 300, 456–460.
77. Henis, J. M. S., & Tripodi, M. K. (1983). The developing technology of gas separating membranes. *Sciences*, 220, 11.
78. Merkel, T. C., Freeman, B. D., Spontak, R. J., He, Z., Pinnau, I., Meakin, P., & Hill, A. J. (2002). Ultrapermselective, reverse-selective nanocomposite membranes. *Science*, 296, 519–522.
79. Strevett, K. A., Vieth, R. F., & Grasso, D. (1995). Chemo-autotrophic biogas purification for methane enrichment: mechanism and kinetics. *ChemEng J BiochemEng J*, 58, 71–79.
80. Chien-Ya, K., Sheng-Yi, C., Tzu-Ting, H., Le, D., Ling-Kang, H., & Chih-Sheng, L. (2012). Ability of mutant strain of microalgae *Chlorella* sp. To capture carbon dioxide for biogas upgrading. *Applied energy*, 93, 176–183.
81. Kim, S., & Kim, H. T. (2004). Optimization of CO₂ absorption process with MEA solution. *Carbon Dioxide Utilization for Global Sustainability*, 153, 429–434.
82. Vannini, C., Munz, G., Mori, G., Lubello, C., Verni, F., & Petroni, G. (2008). Sulphide oxidation to elemental sulphur in a membrane bioreactor: performance and characterization of the selected microbial sulphur-oxidizing community. *Systematic and Applied Microbiology*, 31, 461–473.
83. Beil, M. (2009). Overview on (biogas) upgrading technologies. “European Biomethane Fuel Conference”, Göteborg/Sweden, 2009-09-09. http://www.biogasmax.co.uk/media/3t3_overview_on_upgrading_iset_062510600_0654_30092009.pdf. Accessed 8 Mar 2013.

84. Persson, M. (2007). Persson, M., (2003). Evaluation of upgrading techniques for biogas. Lund Institute of technology. http://cdm.unfccc.int/filestorage/E/6/T/E6TUR2NNQW9O83ET10CX8HTE4WXR2O/Evaluation%20of%20Upgrading%20Techniques%20for%20Biogas.pdf?t=THd8bXd4Ym1xfDA2DYK9aB2Opw27r_iwL_Ux. Accessed 27 Nov 2013.
85. Berndt, A. (2006). Carbo Tech Engineering GmbH, Intelligent Utilisation of Biogas—Upgrading and Adding to the Grid.Jonkoping. http://biogas-infoboard.de/pdf/presentation_CarboTech%20Engineering%20GmbH.pdf. Accessed 8 Mar 2013.
86. De Hullu, J., Maassen, J. I. W., van Meel, P. A., Shazad, S., Vaessen, J. M. P. (2008). Comparing different biogas upgrading techniques. Eindhoven University of Technology, The Netherlands. <http://students.chem.tue.nl/ifp24/BiogasPublic.pdf>. Accessed 8 Mar 2013.