Chapter

Steam Explosion Pretreatment: Biomass Waste Utilization for Methane Production

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Abstract

Lignocellulosic biomass as a second-generation biofuel resource such as waste from agricultural, forester industry, and unutilized wood and non-wood biomass was widely reported to use it as feedstock for methane production. As the carbon-neutral resources, biomass waste conversion for biofuel is in line with the SDGs 7 and 15 goal that can meet the needs and qualify to the standard of sustainable consumption and production pattern, and increasing the renewable energy. The wood and non-wood unutilized biomass and biomass waste are commonly faced with the recalcitrant character of the lignocellulose complex (LCC) which impacted the digestion process of the methane fermentation. Steam explosion pretreatment was enhanced the methane production by breaking the LCC into cellulose, hemicellulose, and lignin-derived product generated from the pretreatment process. Those steam-exploded products were reported effective in the conversion process into methane. The combination of steam explosion pretreatment which is an environmentally friendly pretreatment, and the use of carbon-neutral resources will provide the green biofuel which helps decrease the greenhouse gasses from the biomass waste dumping process and convert it into sustainable biofuel i.e. methane. This chapter will describe the steam explosion system development on the utilization of biomass for methane production, and the action of methane production enhancement.

Keywords: biomass conversion, biomass waste, biomass utilization, biofuel, biogas, methane, steam explosion, environmentally friendly, second-generation biofuel

1. Introduction

The carbon neutrality or the net-zero carbon dioxide emission could be fulfilled by the way to used energy and fuel from biomass resources. The plant from the agricultural and forestry sector could help the achievement of balancing the carbon dioxide from the utilization of biomass waste produced from its process. Other than that, the utilization of biomass waste could counter the production of greenhouses gas (GHG) produced from the biomass waste dumping process. The conversion from the biomass waste into methane through anaerobic digestion could maintain the GHG release from biomass waste. The use of biomass waste as carbon neutral resources can be through biomass conversion by steam explosion pretreatment, anaerobic digestion where the biogas could use for LNG substitution for household use, for power generation fuel which produces the electricity that could fulfill the self-sufficient off-grid and for the on-grid electricity system. The biogas also could convert into hydrogen for transportation fuel and other utilization. The compressed biogas with methanerich (CH₄) and hydrogen (H₂) was potentially utilized as secondary energy, which is widely introduced in several sectors such as public transportation, household application, and other application (**Figure 1**).

The steam explosion pretreatment was commonly used for biomass treatment to break the recalcitrant of lignin carbohydrate complex (LCC) or lignin-carbohydrate polymer which is the main structure of biomass in addition to other content such as resin that makes biomass known as a substrate that is difficult to convert into biofuel through the digestion process or as a source of lignin and cellulose base of biomaterials. The steam explosion also generated the cellulose and low molecular lignin that could be utilized as a biomaterial, where the low molecular lignin could be separated by an extraction process using various types of solvents such as epoxy resin and thermosetting resin by converting low molecular lignin into lignin-epoxy resin or using it directly as a curing agent [1–6]. The steam-exploded lignocellulosic biomass also could be utilized as an antioxidant resource which is rich in polyphenol content [7–11], and its cellulose content also could utilize as cellulose-nanofiber (CNF) resource that is widely used for sustainable biomaterials [12–14].

As the psychochemical pretreatment, the steam explosion could break the LCC and also change the chemical content as a derivative product of the content of cellulose, hemicellulose, lignin, and other specific contents that differ from one biomass to another. The steam explosion pretreatment which is based on the hydrothermal pretreatment method with high pressure and short retention time then suddenly depressurized to make the explosion effect from the pressure differences between the pressure of the steaming chamber and the normal pressure of the explosion chamber [15]. The explosion effect disrupts the structure of LCC fibrils which break



Figure 1.

Carbon neutral biomass waste and unutilized biomass anaerobic digestion scheme via steam explosion pretreatment.

its polymer chain and become small particle size that could facilitate the digestion process easily [16]. Other than that, the chemical content from the LCC could change become derived product such as cellulose that could continuedly to be degraded into cellobiose-glucose-HMF(5-(hydroxymethyl)furfural)-levulinic acid; hemicellulose that could degrade into the pentoses (xylose, arabinose) and could continuedly be degraded into furfural and formic acid, the hexoses (mannose, glucose, galactose) that could continue to degrade into HMF and continue into formic acid or levulinic acid, and hemicellulose also could produce acetyl and continue to degrade into acetic acid; the lignin content could degrade into the lignin precursors such as sinapyl alcohol, p-coumaryl alcohol, and coniferyl alcohol, those compound could continuedly degrade into phenolic compounds such as catechol, guaiacol, vanillin, syringaldehyde, 4-hydroxybenzaldehyde, 4-hydroxybenzoic acid, and vanillic acid. The compounds degradation from steam explosion pretreatment was influenced by the temperature, pressure, and steaming time. That condition was influenced by the degree of severity factor (R_0 or S_0 SF) which caused from the temperature condition and residence time [17]. The other factor i.e., pH condition was also affected the physiochemical products such as the acid addition as a catalysator, which knownly as combined severity factor (CSF) [18]. Since the severity factor could not faithfully describe the steam explosion disregard the effect of the explosion condition, Yu et al., [19] added a comprehensive factor which quantified the explosion severity that could better describing the steam explosion severity condition by explosion power density (EPD). The severity factor, combined severity factor, and explosion power density could be calculated with the equations:

$$R_0 = t x e^{[(T_r - 100)/14.75]}$$
(1)

Where T_r represent the temperature reaction (°C), and *t* represent the resident time (minutes) [20].

$$S_{0} = \log \int_{0}^{t} \exp\left(\frac{T[^{\circ}C] - 100^{\circ}C}{14.75}\right) dt$$
 (2)

The time integral of S_0 was described the process of non-isothermal heating character [20, 21].

$$CSF = \log(R_0) - pH \tag{3}$$

Where the $Log(R_0)$ as a severity factor value and pH represent the pH level after the acid was added [18].

$$P_e = \frac{\Delta H_s + \Delta H_1 + \Delta H_m}{(t \ x \ V)} \tag{4}$$

Where the ΔH represent as the enthalpy drop from the steam (*s*), liquid water (1), and biomass (*m*), *t* represent the duration of the explosion, and *V* represent the volume of reactor [19].

The derived product from cellulose, hemicellulose, and lignin could affect the fermentation process on the anaerobic digestion as the fermentation inhibitors,

nevertheless, it can be controlled by adjusting the inhibitor threshold. On the other hand, the inhibitor from physicochemical pretreatment product could be handled by detoxification process through biological, physical, or chemical. The biological detoxification via hired the microorganism that could produce enzymes that change the chemical structures of the fermentation inhibitor compounds which present in the biomass hydroxylate [22–24]. The physical detoxification could remove the inhibitor compounds without changing the chemical structure such as using activated charcoal or activated carbon for neutralizing the hydrolysate, and also by an extraction process using trialkyl amine as an alkali detoxication, n-octanol, and kerosene [25–27]. The chemical detoxification was treated by adding the modified pH such as water extraction, sodium hydroxide, and reductive substance [16, 23, 28, 29]. The potential compounds that could be converted into methane from steam-exploded biomass fraction, is not only cellulose, hemicellulose, and monosaccharides compound, the steam-exploded aromatic lignin fraction and its derived product such as syringaldehyde and vanillin also could be converted into methane by the anaerobic digestion process [15, 30–36].

The use of methane as secondary energy has been widely used, such as a substitute for liquified natural gas (LNG) for household networks and as a fuel for transportation. In addition, methane can also be converted into other secondary energy such as hydrogen by separating its carbon and is included in a cheap hydrogen source similar to LNG [37], compared to other hydrogen sources. Other than that, the methane produced from biomass waste and unutilized biomass has several advantages such as renewable, sustainable, and carbon-neutral compared with LNG which included depleted natural resources that cannot be renewable. The common hydrogen conversion system from the methane can be done in several ways such as steam reforming methane (SRM), dry-reforming methane (DRM), catalytic decomposition methane (CDM), and partial-oxidation methane (POM), those systems were widely introduced in laboratory-scale or existing technology industrial used.

In this chapter, we will try to delineate state the art of methane conversion and its derived products from biomass waste and fast-growing unutilized biomass by steam explosion pretreatment. The combination of carbon-neutral resources and environmentally friendly pretreatment could give the alternative perception from only combustion utilization to the system that vaporization the biomass waste and unutilized biomass into more potentially produces more product from one system.

2. Potential biomass waste and unutilized wood and non-wood biomass

The agriculture and forestry industries were producing sustainable and renewable biomass waste which included carbon-neutral resources that could be converted into methane by an anaerobic digestion process. The utilization of biomass waste from this sector also could help to reduce land-use change from the biomass that is mainly used only for the biofuel feedstock. The conversion of the biomass waste into methane is free from quality problems of biomass as combustion fuel that need specific calorimetry and density that could not be fulfilled by all the biomass waste. **Table 1** showed the agricultural commodity that produces biomass waste with minimum utilization such as palm oil, barley, corn, rice, sorghum, wheat, and sugarcane. Other than that, the forestry industry such as pulp and paper mills, and unutilized fast-growing biomass such as reed and grassland are potentially utilized for methane conversion.

Commodity	World production (1000 MT)	Production share top 10 country	Potential biomass waste
Palm oil	76.538	Indonesia 58%, Malaysia 26%, Thailand 4%, Colombia 2%, Nigeria 2%, Guatemala 1%, Honduras 1%, Papua New Guinea 1%, Equator 1%, Brazil 1%	Empty Fruit Bunches, Kernel Fibbers, Kernel Shell, Midrib, Trunk
Barley	145–511	EU 36%, Russia 12%, Australia 9%, Ukraine 7%, UK, Canada 5%, Argentina 3%, Turkey 3%, Morocco 2%, Iran 2%	Barley straw, Brewer Spent Grain
Corn	1.208.734	US 32%, China 23%, Brazil 10%, EU 6%, Argentina 5%, Ukraine 3%, India 3%, Mexico 2%, South Africa 1%, Russia 1%	Stem, Leave, Cobs
Rice	510.776	China 29%, India 24%, Bangladesh 7%, Indonesia 7%, Vietnam 5%, Thailand 4%, Burma 2%, Philippines 2%, Pakistan 2%, Brazil 2%	Rice Husk, Rice Straw
Sorghum	66.301	US 18%, Nigeria 10%, Ethiopia 8%, Sudan 8%, Mexico 7%, India 7%, Argentina 6%, China 5%, Brazil 4% Burkina Faso 3%	Stem, Leave, Sorghum Grain Waste
Wheat	777.890	EU 18%, China 18%, India 14%, Russia 10%, US 4%, Ukraine 4%, Pakistan 3%, Canada 3%, Argentina 3%	Straw
Sugarcane	181.082	Brazil 19%, India 18%, EU 9%, China 6%, Thailand 5%, US 5%, Pakistan 4%, Russia 4%, Mexico 4%, Australia 2%,	Sugarcane Bagasse

Table 1.

World production agricultural potential commodity with minimum biomass waste utilization [38].

3. Steam explosion pretreatment

The steam explosion pretreatment for lignocellulosic biomass that was used for methane conversion was widely reported in several studies with various experiment conditions and biomass feedstock. The steam explosion pretreatment was reported as stand-alone pretreatment for lignocellulosic biomass for methane production feedstock. Kobayashi et al., [39] used the abundant and fast-growing such as bamboo as a feedstock for methane production by an anaerobic fermentation process which operated in mesophilic condition (37°C), where the steam explosion was set in 3.53 MPa (243°C) for 0,1, 3, 5, 10, and 20 minutes of steaming time. The 5 minutes steaming time was produced the higher methane with 215 ml/g, that amount was 80% from the methane amount prediction that calculated from cellulose and hemicellulose amount from 1 gram of steam-exploded bamboo. Wu et al. [40] was used palm oil mill waste such as empty fruit bunches and palm oil fronds to convert it by steam explosion treatment at 1.5 MPa for 1 minute of steaming time. They concluded that steam explosion pretreatment enhanced the biogas production, and improved the energy values (gross energy, digestible energy, metabolic energy, net energy for maintenance, and net energy for lactation) from palm oil frond and empty fruit bunches. Lizasoain et al. [41] were used reed biomass for methane conversion using various steam explosion conditions from 160 to 220°C with 5, 10, 15, and 20 minutes of steaming time resulted in the severity factor from 2.47 to 4.83. That study has resulted in the 89% enhancement compared to untreated feedstock from steam explosion condition at 200°C for 15 minutes. Theuretzbacher et al. [42] reported utilizing wheat straw as a methane production feedstock by steam explosion pretreatment at 140, 160, and 178°C with 30, 60, and 120 minutes of steaming time which resulted in various severity factors from 2.7 to 4.4 SF Log (R_0). The highest methane production was from 140°C for 60 minutes steaming time at 3.0 SF Log (R_0) which produced 286 l_n kgVS-1. Steinbach et al. [43] were used steam explosion for rice straw to produce biogas by various severity factor 3.05 to 5.29 (S_0) from 162 to 240°C for 12 to 30 minutes steaming time. They concluded the moderate severity increases the methane production whereas severe condition dramatically drops the methane production caused by an inhibitor that formed in high severity condition. Those were similar conditions to the report from Lizasoain et al. [41]. Vivekanand et al. [44] was used the rape straw steam-exploded with emphasizing in chemical composition changes under various severity (3.5 to 5) that could impact the methane production under mesophilic conditions for 81 days. The steam-exploded rape straw was treated under 190 to 230°C with 5, 10, and 15 minutes. They concluded that the formation of the inhibitor compounds does not impact methane production. The other report explained the compounds that could be formed from biomass steam-exploded were known as an inhibitor such as HMF and furfural, also the other lignin-derived products in form of phenol and polyphenol as lignin polymers and/or lignin oligomers such as vanillin and syringaldehyde could also convert into methane. They resulted that the HMF could produce methane 450 ml CH₄/gMV, furfural 430 ml CH₄/gMV, syringaldehyde 453 ml CH₄/gMV, vanillin 105 ml CH₄/gMV. This study also reported examining the various lignin polymers such as, organosoly, lignosulfonates, and kraft lignins that could produce 14 to 46 ml CH₄/gMV. They concluded that a higher syringyl/guaiacyl ratio that generated the syringaldehyde and vanillin by partial depolymerization of lignin polymer, and lower molecular weight of lignin polymer could conduct high methane production [36]. The steam explosion pretreatment was reported to generate the low molecular lignin in line with the increased degree of the SF values [1, 5, 45–47].

The comparation between steam-explosion pretreatment and other pretreatment was reported in several studies. Take et al. [48] reported examined the Japanese cedar chip *Cryptomeria japonica* as methane production feedstock by comparation psychochemical pretreatment using steam explosion at various pressure conditions at 3.53 MPa (243°C) and 4.51 MPa (258°C) for 5 minutes steaming, steaming pretreatment at 170°C for 30 minutes, and biological pretreatment using Ischnoderma resinosum, Fomitella fraxinea, Mycoleptodonoides aitchisonii, Trichaptum abietinum, Cyathus stercoreus, and Trametes hirsute. The result from the steam explosion pretreatment could produce the highest methane with 180 ml/g with less energy use, compare with steam treatment and biological pretreatment from *Cyathus stercoreus* which only produces methane in 45 and 43 ml/g, respectively. The combination pretreatment between the steam explosion and other treatments for methane production feedstock was reported in several studies. Sholahuddin et al. [16] reported to utilize agricultural biomass waste i.e., rice husk which was treated using steam explosion at 2.53 MPa (224°C) for 5 and 7 minutes steaming time followed by water extraction for methane production, and without water extraction. The water extraction as a dilution treatment to lower the pH condition that increased due to acid formation of psychochemical effect and reduce the concentration of fermentation inhibitor produced from the physicochemical pretreatment into under the threshold. The anaerobic digestion was operated in mesophilic condition (37°C) by using activated

cow dung for the inoculum which is naturally rich in cellulolytic microflora resulted produced 199 ml/g methane from 41% cellulose content, that amount was reached 96.1% of methane conversion from the prediction, compared to without water extraction which only 28 ml/g of methane from the same steam explosion condition i.e., 7 minutes of steaming time. Theuretzbacher et al. [49] reported to use a wheat straw for methane production by combination pretreatment using biological using Scheffersomyces stipitis and thermo-mechanical using steam explosion at 180, 200, and 220°C, those combinations was examined to reduce the thermal energy input where the biological condition could facilitate the steam explosion to break the LCC in low-temperature condition. The highest methane production from the combination of biological pretreatment and steam explosion 250 and 252 l_n kg VS-1 with no significance from 180 and 200°C, respectively. Bauer et al. [50] used late-harvested hay that pretreated using steam explosion at 160 to 220°C for 5, 10, and 15 minutes steaming time followed by enzymatic hydrolysis using b ß-glucosidases and hemicellulases that resulted in high yield glucose from 220°C for 15 minutes, xylose 175°C for 10 minutes. Those combinations resulted in 15.9% methane enhancement compared to the untreated. The anaerobic digestion. The anaerobic digestion. Matsakas et al. [51] reported to used hybrid pretreatment which combines the steam explosion and organosolv where the 99,8% ethanol with 1:2 ratio between biomass chips: ethanol, and heated in 200°C (1.519 MPa) with 15, 30, and 60 minutes of steaming time. The organosolv-steam-exploded products were filtrated using vacuum filtration, and the solid residue was washed using ethanol and dried and continued to the anaerobic digestion process. Weber et al. [52] used steam explosion with temperature setting 142, 164, and 179°C (0,38, 0,68, and 0,98 MPa), after that the solid reside of steamexploded was separated by centrifuge. The methane production was prepared by a 2:1 ratio between inoculum and substrate. Li et al. [53] used corn stover by sequent pretreatment using potassium hydroxide (KOH) 0.5 and 1.5% and steam explosion under 1.2 MPa for 10 minutes steaming time. Those combinations were applied to improve the digestion ability of biomass which resulted in 80% improvement from untreated corn stover with 258 ml/gvs from 1.5% KOH and 1.2 MPa for 10 minutes steaming time, where the only steam exploded and KOH treatment in the same condition was only produced 143.8 and 208.6 ml/ g_{vs} , respectively.

4. Methane production enhancement

The steam explosion pretreatment that disintegrated the LCC impacted the higher accessibility of the digestion process to convert the cellulose, hemicellulose, and lignin and its derived products into biogas [15]. Those pretreatments were simplified the hydrolysis process, however, to gain the economical factor is necessary to improve the production rate, solid retention time, and hydraulic retention time. The conversion of steam-exploded lignocellulosic biomass into methane was counted heavily on cellulose and hemicellulose as the main conversion source, even though the conversion of lignin-derived products from psychochemical pretreatment also contribute to the amount of methane production. **Figure 2** was described the methane production from lignocellulosic biomass was produced through the simultaneous system from saccharolytic and hydrolytic processes to convert the cellulose and hemicellulose into oligomers and monomers, hydrolytic and dissipotrophic organism as primary anaerobe process, the syntrophic process, acetogenic process initiates the biopolymers



Figure 2.

Potential enhancement and low emission of lignocellulosic biomass conversion into methane.

degradation of polysaccharides such as cellulose and hemicellulose, starch, glycogen, and chitin, also the other common content such as protein, lipids, and nucleic acid. The saccharolytic and hydrolytic degraded those content into oligomers and monomers such as cellobiose, glucose, amino acids, purines, pyrimidines, fatty acids, and glycerol [56]. The cellulose and hemicellulose are commonly converted by cellulolytic microflora from the phylum of Firmicutes commonly Ruminococcaceae and Clostridiaceae families 17 such as from genus Clostridium, Ruminococcus, Cellobacterium, Butyrivibrio, Fibrobacter, and Acetivibrio [57–59]. The starch could be degraded by the genus Thermoanaerobacterium, Succinimonas, Ruminobacter, Bacteroides, Prevotella, Bacteroides, Clostridium, and Butyrivibrio. The protein and amino acid are commonly degraded by genus Syntrophomanas, Bacteroides, Clostridium, Peptostreptococcus Acidaminococcus, Selenomonas, and Fusobacterium. The xylan and pectin are commonly degraded by genus Ruminococcus, Lachnospira Bacteroides, Butyrivibrio, Prevotella, and Clostridium. The species from those genera also could degrade the other polymer such as lignin and its derived products especially the species from Lysinibacillus and Paenibacillus. The hydrolytic and dissipotrops as primary anaerobes process digest the cellobiose, glucose, amino acids, purines, pyrimidines, fatty acids, and glycerol and produce organic acid such as butyrate, succinate, lactate, pyruvate acetate, propionate, and lactate; aromatic compounds; the alcohol form such as ethanol, propanol, butanol, and methanol; carbon dioxide; hydrogen; and also produced volatile fatty acids (VFAs) [59] which dominate the degradation of cellulose. The alcohol form, VFAs, lactate, and succinate continued to degrade into single carbon compounds and hydrogen and acetate through the syntrophic process. The single carbon also could into acetate via homoacetogens process and also could directly form the methane through the hydrogenotrophic methanogens. The methane from acetate formed through the acetoclastic methanogens, however, those process was inactivated in low concentration of acetate and in hightemperature condition, other than that, acetoclastic methanogens could be blocked by the presence of high ammonia and VFAs concentration. That simultaneous system condition directly influences the SRT and HRT that affected the time consumed and energy that affected the production cost.

4.1 Enhancement: Saccharolytic and hydrolytic pathway

The methane production enhancement could be done by enhancing the simultaneous system from each process such as saccharolytic and hydrolytic, hydrolytic and dissipotrophic, syntrophic, acetogenic, and methanogenic processes. The enhancement process commonly used Biological augmentation by the addition of archaea or bacterial cultures that get high-rate of degradation time and thermophilic condition which could speed up the production rate. The bioaugmentation of the saccharolytic hydrolytic process that converts the cellulose becomes oligomers and monomers was reported in several studies. The bioaugmentation using cellulolytic bacterium from genus *Caldicellulosiruptor* that operate in thermophilic condition i.e., Caldicellulosiruptor bescii which focuses on the improvement of hydrolysis process that degraded the carbohydrate content from steam-exploded biomass such as cellulose, hemicellulose, and other lignocellulosic content, and fermented the C5 and C6 sugar on the simultaneous process. The C. bescii has a special characteristic that is quite different from other cellulolytic bacteria which has the enzymatic system in a multi-modular pathway, which secreted the individual cellulases and could bind and catalyze multiplied, wherein, this condition will support the indigenous primary anaerobes bacteria synergically [60]. Mulat et al. [61] were applied bioaugmentation for steam-exploded lignocellulosic biomass converted into methane which operated in 62°C, the C. bescii was added as bioaugmentation where steamexplosion pretreatment itself enhanced 118% the methane production, and the combination of steam-exploded pretreatment and bioaugmentation was enhanced 140% methane production improvement. The other species cellulolytic microflora from the genus Clostridium such as *Clostridium thermocellum* which operated in a thermophilic condition also has the capability to continuedly form ethanol directly from cellulose, and also accelerates the hydrolysis process and could produce higher H₂ that supports the hydrogenotrophic methanogens to produce more methane [62–65]. Other than that, C. thermocellum has the special capability to reform non-growth state into sporulation stage and L-phase in stress conditions [66]. The steam explosion and bioaugmentation using *C. thermocellum* were reported to be compared where the steam explosion was enhanced 62% methane production and bioaugmentation was enhanced 12% of methane production [64]. The other report from *C. thermocellum* enhanced the anaerobic digestion of lignocellulosic agricultural residue which resulted in an increase of 39% of methane production [67]. Tsapekos et al. [68] was used C. thermocellum and Melioribacter roseus as bioaugmentation for lignocellulosic agricultural residue conversion into methane by continuously stirred tank reactor (CSTR) which resulted in 34 and 11% methane production enhancement, respectively. The other species from *Clostridium* such as *Clostridium cellulolyticum* as a bioaugmentation agent for the wheat straw that resulted in 13% of methane production compared to non-bioaugmented [65]. Cetar et al. [69] was reported to trial bioaugmentation agents from various genus such as *Pseudobutyrivibrio* using Pseudobutyrivibrio xylanivorans, Fibrobacter using Fibrobacter succinogenes, Ruminococcus using Ruminococcus, and flavefaciens using Clostridium cellulovorans to enhance the hydrolysis process of brewery spent grain by comparation using two bioaugmentation agent each treatment that impacted to enhance the biogas production with resulted in 17.8% from *P. xylanivorans* alone, 6.9% from a combination of *P. xylanivorans* and *F. succinogenes*, and 4.9% from a combination of *C. cellulovorans* and *F. succinogenes*. The other report was described to examine the bioaugmentation that combined with steam explosion using ruminal fungus such as *Pecoramyces sp.* which isolated from goat rumen to enhance the methane production from steam-exploded corn stover [70].

4.2 Enhancement: Hydrogenotrophic methanogens pathway

The other bioaugmentation pathway is to enhance hydrogenotrophic methanogens which are affected by ammonia inhibition, where the syntrophic acetate oxidation coupled with hydrogenotrophic methanogens are influenced by ammonia inhibition [71]. The bioaugmentation via syntrophic oxidation bacteria that operate in mesophilic and thermophilic conditions such as *Clostridium ultunense* [72], *Syntrophaceticus* [73], Tepidanaerobacter acetatoxydans [74]; and Thermacetogenium phaeum and Thermotoga *lettingae* [75–77], respectively. The syntrophic oxidation bacteria were syntrophic cooperation with hydrogenotrophic methanogens, which could use its ability of acetate digestion into H_2 and CO_2 and surmount the energy barriers [78]. Those systems are based on interspecies hydrogen transfer by reducing the hydrogen partial pressure which purposed H_2 and formate transfer [79]. In this case, formate plays an important role as an electron carrier at the time when the hydrogenotrophic methanogen and oxidizing bacteria have a distance gap through the Wood-Ljungdahl pathway [78, 80]. The bioaugmentation strategy was to present the syntrophic oxidation bacteria and hydrogenotrophic methanogens that could resist high ammonia levels. Tian et al. [72] was used a syntrophic acetate oxidizing bacteria i.e., C. ultunense that resists high ammonia levels with about 7 g NH_4^+ -NL – 1 and significantly increased with high activity in line with *Methanoculleus sp* as a hydrogenotrophic methanogen. Fotidis et al. [81] were used a combination to hire a bioaugmentation agent for syntrophic acetate oxidation association with hydrogenotrophic methanogen i.e., C. ultunense and Methanoculleus bourgensis respectively. That study was operated in mesophilic condition resulted in the increase of growth rate and incubation period of syntrophic acetate oxidation agent with 42 and 33%, respectively. Another bioaugmentation strategy to alleviate the ammonia inhibition under thermophilic conditions using Methanoculleus thermophilu resulted in 45 to 52% VFAs decreasing and 11 to 13% methane production improvement. This condition was described as the condition that the addition *M. thermophilu* could handle the ammonia inhibition which was proven by high activity and positive growth of *T. phaeum* is a syntrophic acetate oxidizing bacterium that stimulated by those additions [82]. The other report that examined the *M. bourgensis* as hydrogenotrophic methanogen bioaugmentation alone, added in CSTR with ammonia concentration at 5 g NH_4^+ -NL – 1 which enhanced 31.3% methane production [83].

5. Feasibility study

Steam explosion pretreatment feasibility study was reported in several studies, Shafei et al. [84] was reported the feasibility of the economic factor from biomass waste as feedstock for biogas by simulating the paper tube residual and wheat straw using steam explosion pretreatment. The result from the simulation was concluded the application of steam explosion pretreatment was increased 13% of the investment cost, however that application was decreased the production cost of methane production by 36% efficiency which brings about 80% total energy efficiency with costing 0.36 and 0.48 Euro/m3 from paper tube residual and wheat straw, respectively. In this simulation, the feedstock is unloaded from the transporter and continued to chopping process to reduce the feedstock size and collected into storage piles. The crushed feedstock continues to pretreatment process through horizontal conveyor belt which continuously processes low-pressure pre-steamer, removing non-condensable gas,

high pressure with a horizontal extruder that uses steam as the driving force. The steam exploded feedstock continues to digestion process which simulated using established solid organic reactor which has 3150 m3 in total volume with 2–4 days retention time and about 20 days of residence time for fully digested by the circulated system by 5:1 ration between the residence feedstock and new feedstock. The final process is dewatering the slurry which fully digested from the digester. Kral et al. [85] was described the life cycle assessment (LCA) from a hypothetical local biogas system by adapting and integrating the steam explosion pretreatment to use unused grassland biomass as co-substrate the existing biogas reactor of Austrian alpine municipality. They used a comparation case study from the status quo of heating oil, wood chips, and grid electricity as reference scenarios for municipal energy resources; and hypothetical local biogas that is also used for municipal energy sources with 500-kWel biogas plant using unused grassland with a steam explosion as the pretreatment. The result was described that the LCA from biogas from biomass and status quo energy resources have significant differences with $\rho < 0.05$ from six categories, where the biogas electricity from steam-exploded grassland has a lower impact than the status quo energy with climate change contribution in 0.367 CO_{2-eq} kWhe-1 from and 0.501 CO_{2-eq} kWhe-1, respectively.

The steam explosion pretreatment was reported to enhance the full-scale biogas plant production which used a wheat straw as co-substrate for pig manure [86]. The result from the study stated that the addition of pretreated wheat straw using liquid hot water-steam explosion produced 24–34% higher methane, this condition was obtained from pretreatment at 165°C and 2.33 MPa for 10 minutes steaming time which break the LCC into low-mass polysaccharides, and at this severity factor (SF) did not generate the HMF and furfural that could inhibit the fermentation process. The steam explosion apparatus that used in this study could daily continuous process 2.300–3800 kg of wheat straw that could use 100-160 m³ recycled water from the biogas plant with ration 20:1 and 23:1 between wheat straw and recycled water. Maroušek et al. [87] was used combination pretreatment for sunflower stalks in existing large-scale biogas reactor by maceration under 75 to 95°C for 20 to 200 seconds and continue to steam explosion pretreatment under 0.8 to 2.2 MPa for 2 to 20 minutes of steaming time, where the pretreatment was used the sole heat waste from the existing system. The optimum production was 99 m³ methane VSt⁻¹ from feedstock that macerated at 95°C for 100 seconds and continue to steam-exploded at 2 MPa for 17 minutes, where the steam explosion pretreatment higher than 2 MPa was impacted to the decreasing of methane production due to the formation of inhibitors such as furan and HMF. Pérez-Elvira et al. [88] were reported the pilotscale feasibility study which demonstrated the hydrolysis process using steam explosion, anaerobic digestion with an energy output of cogeneration unit. This study was used an automatic continuous steam explosion of 10 L which connected to a 200 L mesophilic anaerobic digestion reactor and directly connected to the power generation where the engine exhaust gas was utilized to heat the boiler unit for steamed the hydrolysis reactor (steam explosion). The result from this study was described that the combination of steam explosion as thermal hydrolysis and anaerobic digestion which resulted considered for full-scale application. The residence time was only 40% compared to the conventional digestion and proved that this system was fully self-sufficient energy without additional energy input for all the processes. Those systems were generated 1 MW green electricity which is a 246 kW surplus compared to the conventional system, with could generate 58% less volume of bio-waste from the process.

6. Methane conversion: secondary energy

The methane conversion as secondary energy through the biogas purification to get higher methane content for household, fuel transportation, and the methane conversion into hydrogen. The biogas purification for secondary energy was mandatory to get high content methane and to reduce the carbon dioxide (CO_2) to increase the density and the calorific value, and cleaning out the hydrogen sulfide (H_2S) due to the corrosivity character for the metal part of in all the system such as gas storage tank, piping system, compressor, engine, and also the toxicity that harmful to the environment [89]. The CO₂ removal could be removed through physical absorption by water or organic scrubbing that could be physically bound with CO_2 [90, 91]. The absorption using organic solvent could also remover the H_2S , ammonia (NH₃), hydrogen cyanide (HCN) and also water vapor with low losses of CH₄, and included into regeneration system with low temperature waste, however the operation and technology investment is expensive; chemical absorption by using di-methyl ethanol amine (DMEA) or mono ethanol amine (MEA), and solution of alkali such as NaOH, K2CO₃, KOH, iron hydroxides ($Fe(OH)_3$), and $FeCl_2$ that could actively absorb the CO₂ [92, 93]; pressure swing absorption by sequences process of adsorption, desorption, and pressurization by hiring the synthetic resin, zeolite, activated carbon, silica gel, or activated charcoal which also could separate the N_2 , H_2S and O_2 [94]; cryogenic separation which takes advantage of the different boiling points of CO2 and CH4 by condensation process on gas cooling at elevated pressures that could separate the CO₂ and also the other gas content such as O_2 , N_2 and siloxanes [95]; membrane separation which base on the properties of the selective permeability of the membrane through two system i.e., gas–liquid separation where the liquid absorbs the CO₂ and also the H_2S diffusing via the membrane, gas–gas separation by the gas phase from the both side of membranes [96, 97]; hydrate formation which based on the equilibrium partition of the components between gaseous and hydrate phases, clathrate phase equilibrium for the water-phenol-carbon dioxide system [98, 99]. Other than that, CO_2 and H_2 compounds in biogas also could be utilized via biological conversion by hiring the microbial to convert the CO₂ and H₂ into methane [100, 101]. The H₂S could be removed by physical and chemical absorption by converting H₂S to elemental sulfur or metal sulfide utilizing either water or organic solvent in the physical absorption process or aqueous chemical solutions 98. The water adsorption could generate cheap operation as long as the water is available and easy to get, this system also could remove the H_2S at the same time, however, this system was included in a not-regenerative system and require high-pressure conditions and complex engineering [102]; activated carbon adsorption that catalyzed the H₂S oxidation into metal sulfide or sulfur which usually used impregnated activated carbon and catalyticimpregnated carbon which has highest oxidation rate compare with activated carbon [103, 104]; adsorption by iron oxides (Fe₂O₃), Fe(OH)₃ or zinc oxides (ZnS) that could easily reacted with H_2S and forming the FeS and ZnS from the reaction [105, 106]; biological biofiltration and desulfurization using litautotrophic bacteria that can convert H2S into sulfate and sulfur bases using electron donors from H₂S and carbon sources from CO_2 (Figure 2). Moreover, the content of H_2S in biogas could be prevented by in-situ prevented via dosing the oxygen in the digester system, where the microbiological oxidation converted the H₂S into elemental sulfur [89, 107]. The other in-situ treatment was using iron chloride (FeCl₂) dosing into the digester by forming the iron sulfide (FeS), where the FeS could be easily removed through the solid discharge which is a good content fertilizer nutrient [108]. Other than that, the

other compounds such as nitrogen (N_2) , oxygen (O_2) , volatile organic compounds (VOCs), carbon monoxide (CO), and NH_3 were removed to get the methane purity [109]. Methane as secondary energy was widely applied in several countries.

The hydrogen conversion from the methane commonly through the conversion system such as SRM [37, 110–112], DRM [113, 114], CDM [115, 116], and POM [117, 118]. The SRM was widely used in industrial applications with a high theoretical H_2 /CO ratio and its efficiency with low operational and production costs. The SRM system could SRM could continuedly one system with water gas shift (WGS) which could convert more hydrogen in the process where the steam and CH₄ mixed and produced syngas from hydrocarbon and water reaction [37, 112]:

$$H_2O + CH_4 \rightarrow 3H_2 + CO$$

The WGS process continue to convert the CO by water reaction [37, 112]:

$$H_2O + CO \rightarrow CO_2 + H_2$$

However, the SRM facing the complex system depends on the quality of biogas, high CO_x emission, water demand, and high investment capital [118]. The conversion through the DRM has a good point with CO₂ reduction, however, the still facing with the carbon deposition problem, influenced on CO disproportionate and reverse water gas shift reaction, and carbon deposition problem [119]. The POM was offering high selectivity and conversion rates with short residence time, and is known as a simple system with less desulphurization and not using catalyst during the process [115, 120]. Nevertheless, pure O₂ was required for the process with high CO_x emission and possibility the of producing NO_x emission with soot formation during the process [121]. The CDM was the simplest process with only one step with a single reactant, produced H₂ with high purity by mild reaction condition and no GHG emission during the process. The CDM also could produce nanocarbon material by carbon sequestration which forms a stable solid. Even though it looks promising, the CDM is still in lab level experiment which is necessary for catalyst deactivation, unreacted methane in out-stream with low purity nano-carbon, and the catalyst regeneration produced the secondary emission [114, 116, 121].

7. Conclusion

The utilization of lignocellulosic biomass waste and unitized fast-growing biomass as carbon-neutral resources by methane conversion by steam explosion pretreatment and its secondary energy (compressed biogas, nitrogen, and electric) was potentially to be the solution to fulfill the SDGs requirement which is renewable and environmentally friendly. This chapter has described the state the art, feasibility study in the full-scale application, and the life cycle assessment that could give deliberation to industry and stakeholders that consider applying the system.

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Conflict of interest

The authors declare no conflict of interest.

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