Review

Methane Production from Biomass by Thermochemical Conversion: A Review

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Abstract: Methane, the main component of natural gas, is one of the primary sources of energy extensively employed worldwide. However, the utilization of natural gas is limited by reserves and geographical availability. Thus, a thermochemical method of converting biomass to methane is appealing, especially gasification. Important factors affecting methane production are discussed in the review including operating parameters, catalysts of methanation and gas conditioning effects. Low temperature and high pressure are beneficial to promote methanation reaction. Ni-based catalysts are widely used as methanation catalysts, but suffer from deactivation problems due to carbon deposition, sintering and poisoning. The methods of gas conditioning include using water gas shift reaction and adding hydrogen from electrolysis. In addition, environmental and economic views are discussed. Other thermochemical process including hydrothermal gasification, fast pyrolysis and direct methanation at low temperature are also introduced briefly. Based on the above discussion, potential research directions for optimizing methane production are proposed.

Keywords: synthetic nature gas; methanation; gasification; gas conditioning; catalysts

1. Introduction

Natural gas is among the primary sources of energy extensively employed worldwide. The utilizations of fuel and chemical productions have predominantly relied on natural gas in numerous nations. However, as a fossil fuel, not only is its use restricted by reserves and geographical availability, but also the price is highly susceptible to international circumstances. Therefore, the development of synthetic natural gas (SNG) as a substitute for natural gas is crucial.

Methane serves as the primary component of natural gas and SNG, so the increase in methane concentration is the key to producing SNG. Presently, coal is the primary raw material used for SNG production [1]. Due to its relatively abundant reserves compared to natural gas, coal could meet the energy needs [2]. However, the exploitation and the consumption of coal resulted in serious environmental pollution and massive emission of greenhouse gases such as carbon dioxide, which is opposite to achieving carbon neutrality. With the global focus on environmental concerns, methane production from environmentally-friendly biomass sources has become more attractive.

Biomass is defined as biological organics synthesized through photosynthesis, including plants, animals, microorganisms and their associated waste. As a renewable carbon source, biomass possesses the advantages of low price, abundant reserves and minimal pollution. Methane production from biomass could significantly reduce greenhouse gas emissions [3]. According to a life cycle assessment by Pucker et al. [4], greenhouse gas emissions from forest residues via air-steam indirect gasification technology are 80% lower than those of natural gas and 29% lower than those of burning wood chips. Additionally, compared to hydrogen, the other gaseous fuel from biomass, methane, does not migrate through the metal lattice of most materials in gas transportation pipeline, allowing it to use existing natural gas infrastructure and replace natural gas. As a result, the cost of transportation and distribution of methane is cheaper than that of hydrogen [5,6]. Moreover,

high energy efficiency could also be obtained from conversion of biomass to methane. Feng et al. [7] reported that the energy efficiency of Bio-SNG production process using interconnected fluidized beds (IFB) and fluidized bed methanation (FBMR) technology was more than 64%, which was higher than that of hydrogen and diesel production from biomass.

Methane production from biomass can be achieved through biochemical and thermochemical conversion. Anaerobic digestion represents the main method of biochemical conversion, which results in biogas. The technology of anaerobic digestion is more established compared to thermochemical conversion, resulting in lower production costs [8,9]. However, biochemical conversion could not completely convert biomass to methane, resulting in low energy efficiency between 25% and 35%. The long retention time (days, weeks or even months) also occurs in biochemical processes. Based on above reasons, a method of thermochemical conversion with high efficiency and short retention time is attractive [7,10,11].

Gasification is the prime route of methane production by thermochemical conversion from biomass. For the gasification route rather than the gasification reaction stage, this paper will focus on the gas conditioning and methanation stage, which plays key roles in increasing methane concentrations. This review will describe the methanation reaction, catalysts, the reasons and methods of gas conditioning, and summarize environmental and economic assessments. Finally, hydrothermal gasification, fast pyrolysis and direct methanation at low temperature will also be exposited briefly. On the basis of understanding these factors, we will try to discuss further research directions for enhancing methane production through thermochemical conversion of biomass.
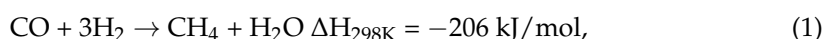
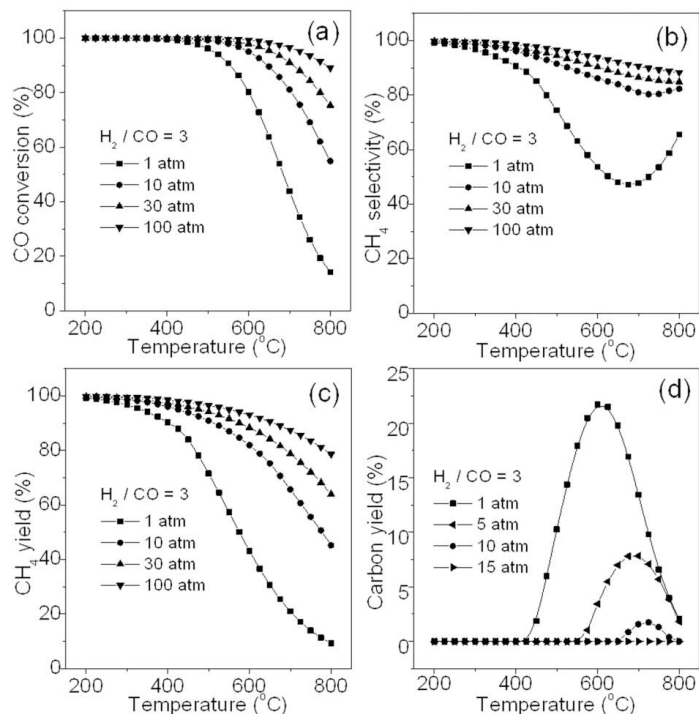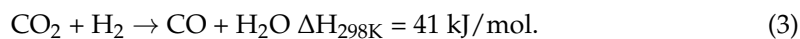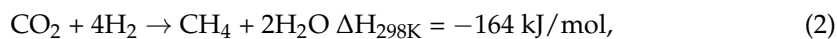## 2. The Route of Gasification for SNG Production and Its Methanation Reaction

Figure 1 shows the process chain of SNG production through biomass gasification. Firstly, the syngas is produced from biomass via gasification, which includes H_2, CO, CO_2, water, methane, tar and other impurities such as sulfur and chlorine. Biomass gasification is influenced by process parameters including reactor, gasification agent, temperature, pressure, etc. Then, the syngas needs to be cleaned to remove tar and impurities [2,12]. Gas conditioning stage is described in Section 3. The route is a common framework, and some of the more complex processes can be grouped into it. Similar gasification route has been applied in some demonstration projects, such as 1-MW Bio-SNG demonstration plant in Güssing (Austria) [13] and 12 MW Bio-SNG demonstration in the Netherlands [14].
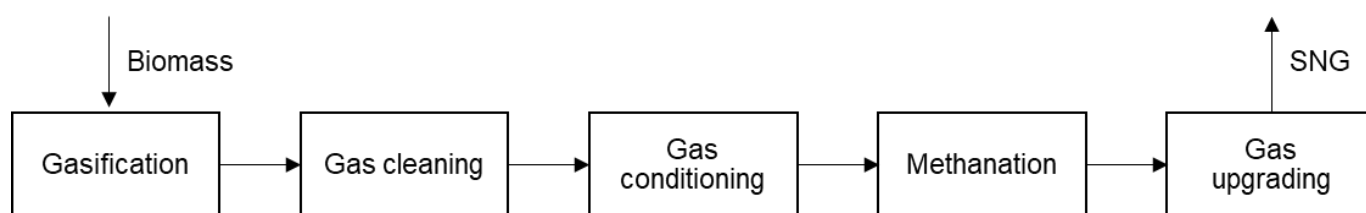

Figure 1. The process chain of SNG production through biomass gasification [1,2,6].

The methanation stage involves two main reactions: CO methanation (Equation (1)) and CO_2 methanation (Equation (2)). The CO_2 methanation (Equation (2)) is a linear combination of CO methanation (Equation (1)) and reverse water gas shift reaction (Equation (3)) [15–17]. Both Equations (1) and (2) are characterized by the release of heat and a significant volume contraction of the reacting gases. Gas volume contraction is stronger for CO methanation (50% volume reduction) than that for CO_2 methanation (40% volume reduction). From the thermodynamic point of view, methanation is promoted at low temperatures and high pressures. Figures 2 and 3 show the influence of temperature and pressure on CO methanation and CO_2 methanation, respectively, and the results are consistent with the thermodynamic judgment. In addition, catalysts designed for methanation are generally active for both reactions [17].

$$CO + 3H_2 \rightarrow CH_4 + H_2O \ \Delta H_{298K} = -206 \text{ kJ/mol}, \tag{1}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \ \Delta H_{298K} = -164 \text{ kJ/mol}, \tag{2}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \ \Delta H_{298K} = 41 \text{ kJ/mol}. \tag{3}$$

Figure 2. Effects of pressure and temperature on CO conversion (**a**), CH$_4$ selectivity (**b**) CH$_4$ yield (**c**), and carbon yield (**d**). Reprinted from [18].
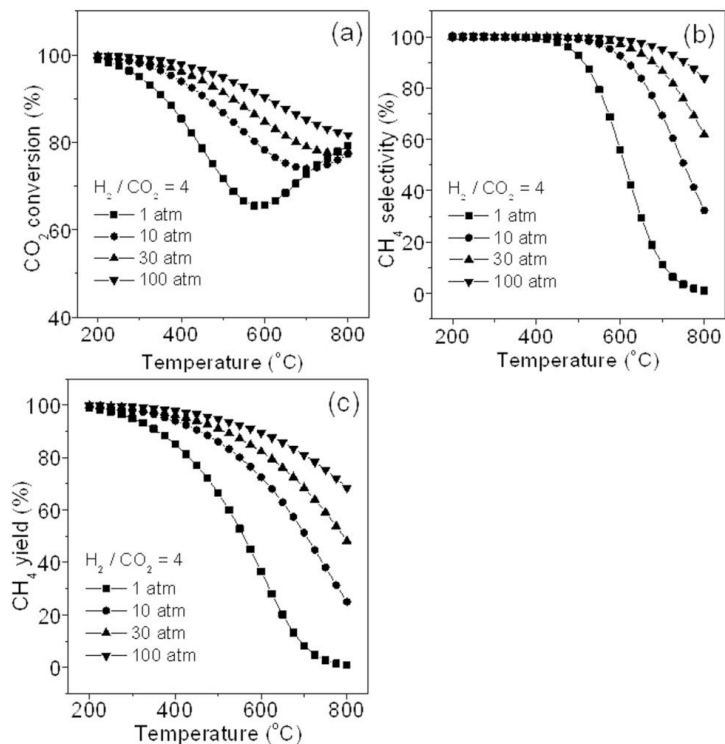
Figure 3. Effects of pressure and temperature on CO$_2$ methanation: (**a**) CO$_2$ conversion, (**b**) CH$_4$ selectivity, and (**c**) CH$_4$ yield. Reprinted from [18].

However, when CO methanation is active, the conversion of CO_2 is limited because the adsorption capacity of CO on the catalyst surface is stronger than that of CO_2. The CO_2 methanation only becomes active with the low content of carbon monoxide [18,19]. Therefore, the CO methanation is the main reaction of producing methane from biomass. However, it has also been suggested that the methanati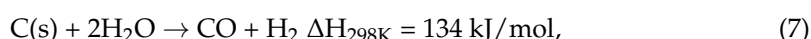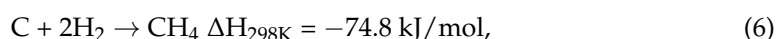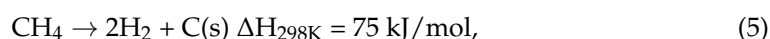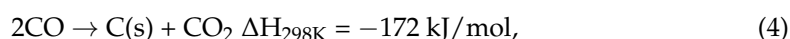on rate of CO and CO_2 in the co-methanation process is still higher than those of the individual reactions in spite of the preferential reaction of CO in the co-methanation process [20].

During the process of methanation, unwanted side reactions can also occur. Coke is one of the reasons for catalyst deactivation, which is mainly formed due to the Boudouard reaction (Equation (4)). At high temperature (500–800 °C), methane decomposition may lead to carbon deposition (Equation (5)). After that, the generated carbon can react with hydrogen and water to form gaseous compounds again (Equations (6) and (7)). Besides carbon monoxide and carbon dioxide, other hydrocarbons such as methane, ethylene, ethane, acetylene, benzene, naphthalene, toluene may be present in syngas. For example, the ethylene reactions could occur including Equations (8)–(10) [1,6,21,22].

$$2CO \rightarrow C(s) + CO_2 \ \Delta H_{298K} = -172 \ \text{kJ/mol}, \tag{4}$$

$$CH_4 \rightarrow 2H_2 + C(s) \ \Delta H_{298K} = 75 \ \text{kJ/mol}, \tag{5}$$

$$C + 2H_2 \rightarrow CH_4 \ \Delta H_{298K} = -74.8 \ \text{kJ/mol}, \tag{6}$$

$$C(s) + 2H_2O \rightarrow CO + H_2 \ \Delta H_{298K} = 134 \ \text{kJ/mol}, \tag{7}$$

$$C_2H_4 + 2H_2 \rightarrow 2CH_4 \ \Delta H_{298K} = -202 \ \text{kJ/mol}, \tag{8}$$

$$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2 \ \Delta H_{298K} = 289 \ \text{kJ/mol}, \tag{9}$$

$$C_2H_4 + 2CO_2 \rightarrow 4\,CO + 2\,H_2 \ \Delta H_{298K} = 292 \ \text{kJ/mol}. \tag{10}$$
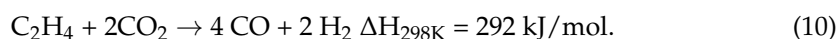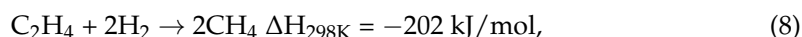
Finally, all impurities such as water and carbon dioxide are removed in the gas upgrading stage to meet the quality specifications of the gas grid or fuel [2,6]. Water is removed by gas cooling and subsequent condensation. Carbon dioxide can be removed through many methods including physical adsorption, pressure swing adsorption and membrane separation [6,23].

3. Methanation Catalysts

Catalysts are usually added to promote methanation. Methanation catalysts typically consist of active metal particles dispersed on a metal oxide carrier. Many transition metals such as Ni, Co, Fe as well as noble metals such as Pt, Ru, Rh are used as active catalysts in methanation reactions [17]. Nowadays, the commercial catalyst for methanation is mainly based on Ni due to the best methanation activity per unit cost [24]. Some noble metals such as Ru have higher activity [25], but the price limits the application. Jaffar et al. [22] investigated the optimization of different operating parameters and different catalysts for methane production in a two-stage pyrolysis-catalytic hydrogenation reactor. The rank of decline in methane production is Ni > Co > Mo > Fe. Higher calcination temperatures for Ni/Al_2O_3 catalyst preparation reduced the methane yield, which was explained by lower catalyst surface area and increased sintering of Ni metal crystals at higher temperatures. When the catalyst loading is added from 5 wt% to 10 wt%, the methane yield increases. However, the yield decreases with further increase in metal loading to 15%. According to SEM-EDXS and XRD, the increase in metal loading leads to sintering of Ni particles and non-uniform distribution of metal Ni, which results in a decrease in catalytic activity. The optimized process results in the highest methane yield of 7.4 mmol/g biomass and 75.5 vol% of methane in the output gas mixture.

Ni-based catalysts may be deactivated due to carbon deposition, sintering and sulfur poisoning. Among them, carbon deposition is the primary challenge. When methane is present as the only hydrocarbon, no surface carbon is formed at low temperature [26]. The main source of carbon deposition is carbon monoxide and higher hydrocarbons such as tar [18,26]. Pyrolytic, encapsulating and whisker carbon are three formations of carbon deposition. Figure 4 shows the electron microscopy images of three formations. The pyrolytic carbon is formed from high hydrocarbons at high temperatures, which mainly cover on the reactor tube and is not related to catalyst deactivation. The encapsulating carbon is composed of a CH_x film or several layers of graphite covered with nickel particle, which would encapsulate the active site directly leading to deactivation. The whisker carbon has low adhesion to the catalyst surface and a loose structure that does not hamper diffusion of reactant gases to the catalyst surface, so the carbon formation has little effect on the methanation activity. However, the accumulation of whisker carbon could block reactors [26–28].
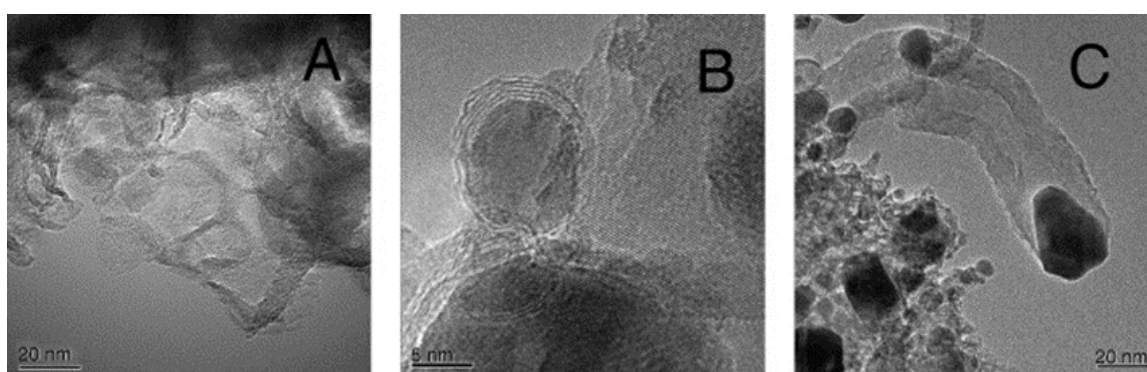
Figure 4. Electron microscopy images (Philips CM200 FEG TEM) of pyrolytic carbon on a $MgAl_2O_4$ carrier (**A**), encapsulating carbon (**B**), and whisker carbon (**C**) on $Ni/MgAl_2O_4$ reforming catalysts. Reprinted from [27].

Sintering is a process of small particles growing in size from heterogeneous catalysts. This growth reduces the surface area of Ni, resulting in decreased catalytic activity and a diminished ability to withstand coke and sulfur. Sulfur poisoning is associated with sulfur-containing components in synthesis gas such as H_2S. The sulfur atom from H_2S is strongly adsorbed on the nickel surface, which blocks the active site as well as accelerates the sintering and oxidation of Ni_0 particles. A sulfur-poisoned nickel catalyst has essentially no activity below 700 °C [17,27,29].

The selection of a suitable preparation method and support can enhance the activity and resistance to deactivation of the catalyst. Xing et al. [30] investigated the methanation of biomass gasification syngas over Ni/Al_2O_3 catalysts prepared by dipping method ($DIP-Ni/Al_2O_3$) and sol–gel method ($SG-Ni/Al_2O_3$) with cordierite honeycomb ceramics as the substrate. The methanation performance of $DIP-Ni/Al_2O_3$ was better than that of $SG-Ni/Al_2O_3$. In addition, $DIP-Ni/Al_2O_3$ had better resistance to carbon deposition and sintering. Under the optimum operating conditions, the CO conversion and methane selectivity of $DIP-Ni/Al_2O_3$ were 98.6% and 90.9%, respectively. Additionally, the methanation performance of $DIP-Ni/Al_2O_3$ is relatively stable. In the experiment WHSV range, carbon monoxide conversion rate and methane selectivity remained basically around 90%. Shinde et al. [31] reported a Ni/TiO_2 catalyst synthesized by sonication for CO methanation. The catalyst synthesized by ultrasonic method had higher methanation activity and stability than the catalyst synthesized by the conventional wet impregnation method. The main reason could be partial substitution of Ni in TiO_2 lattice-created oxide vacancies to promote hydrogen adsorption and spillover from nickel to support. Strong interactions of metal and support also provided high resistance to carbon.

Kamata et al. [32] reported a catalyst called $Ni\#mSiO_2$ consisting of highly dispersed Ni nanoparticles encapsulated in a mesoporous silica ($mSiO_2$) matrix. The catalyst has a Ni

loading of up to 40 wt%. Compared to traditional catalyst, the Ni#mSiO$_2$ was stable over 500 h under clean conditions and has a higher tolerance to sintering, coking and sulfur poisoning. The key factor is the highly stable small Ni particles from the protection of the mesoporous silica matrix resulting in the high dispersion of Ni.

Adding promoters is another effective method. Ding et al. [33,34] developed a CeO$_2$ modified Ni/Al$_2$O$_3$ catalyst for bio-syngas methanation. The Ni/CeO$_2$-Al$_2$O$_3$ catalyst with 60% CeO$_2$ showed excellent bio-syngas methanation performance (91.6% CO conversion and 92% methane selectivity) at low temperatures (350 °C). With the increase in concentration of CeO$_2$, carbon deposition on the surface of Ni/Al$_2$O$_3$–CeO$_2$ was inhibited. The main reason was that the combination of CeO$_2$ and Al$_2$O$_3$ inhibited the entry of Ni species into the interior resulting in promoting the dispersion of nickel monoxide on the Al$_2$O$_3$-CeO$_2$ surface. In addition, the CeO$_2$ over Ni/Al$_2$O$_3$ promoted the separation of NiO from NiAl$_2$O$_4$ by enhancing the NiO-CeO$_2$ interaction and weakening the interaction between Ni and Al$_2$O$_3$, which facilitated the reduction in NiO and the formation of active metal Ni.

Mg and Ru are also commonly used as promoters. Yuan et al. [29] investigated the long-term stability and sulfur resistance of Ni and NiRu catalysts over SiO$_2$ in methanation reactions. Compared to Ru additive catalysts, the stronger adsorption of S on Ni/SiO$_2$ catalysts leads to their rapid deactivation. NiRu/SiO$_2$ catalyst synthesized through polyethylene glycol (PEG)-additive method operated stably for 127 h in the methanation reaction with gas containing H$_2$S, which is longer than individual Ru and Ni catalyst and NiRu/SiO$_2$ catalyst synthesized through PEG-free method. It could be explained by the fact that the formation of small Ni-Ru particles in the NiRu/SiO$_2$ catalyst prepared by the PEG-additive method prevented particle sintering and reduced the deposition of carbon. In addition, the presence of Ru increased the CO-Ni$_0$ interaction, and the S adsorption was reduced when S bound with both Ni and Ru simultaneously. Baidya et al. [35] reported methanation activity and stability of catalyst consisting of Ni, Ru and MgO. The Mg-Ni catalyst activity (93% CO conversion at 375 °C) was higher than that of pure Ni catalyst (80% CO conversion at 475 °C). The addition of Ru to the Mg-Ni catalyst did not change the CO conversion, but the methane yield was slightly increased. In the stability test, the deactivation of the Mg-Ni catalyst was significant, with CO conversion decreasing from 90% to less than 15% after 11 h. The CO conversion activity was stable with the addition of Ru and increased with increasing Ru content. After 11 h of operation on Mg-NiRu05 (0.5% Ru) catalyst and Mg-NiRu10 (1.0% Ru) catalyst, the conversion of CO is 86% and 90%, respectively. These results indicated that Mg is positive to increasing catalyst activity and Ru has an obvious effect on increasing catalyst stability.

4. Gas Conditioning

According to Equation (1), an H$_2$/CO ratio of 3:1 is required to ensure a high CO conversion in the methanation process. As exhibited in Figure 5, increasing in the H$_2$/CO ratio can promote the CO conversion, increase CH$_4$ selectivity and yield, and reduce carbon deposition. Unfortunately, the H$_2$/CO ratio of the syngas from biomass gasification is usually between 0.3 and 2. Thus, the H$_2$/CO ratio must be increased by suitable methods during the gas conditioning stage [1,2,36].

One method is based on water gas shift reaction (WGS, Equation (11)).

$$CO + H_2O \rightarrow H_2 + CO_2 \quad \triangle H_{298K} = -42 \text{ kJ/mol.} \tag{11}$$
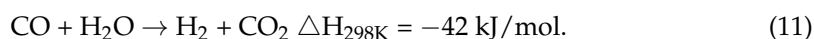
Similar to methanation, catalysts can be used to promote WGS, such as Ni, Fe, and noble metals [37–39]. Especially sorption enhanced reforming (SER) is often used in the production of SNG, where solid sorbents capture carbon dioxide to promote WGS reaction. Martínez et al. [40] investigated a flexible adsorption to enhance an indirect gasification process. The CaO-based material circulated between gasifier and combustor reactors to obtain the syngas composition required for the downstream fuel synthesis process. Finally, the production efficiency was up to 62% (based on LHV) for the production of SNG with

the methane content of 98%. Bartik et al. [41] compared methanation of syngas from conventional gasification with that from SER. The experiment result showed that the higher methane yields and the higher conversions of H_2, CO and CO_2 were obtained from SER. In addition, the SNG was allowed to be injected into the grid without CO_2 separation. Besides promoting WGS reaction, the in situ adsorption of CO_2 on CaO promoted the shift in methanation temperature range to high temperature region, which exceeded the thermodynamic limit to realize high methane selectivity at high temperature required for biomass pyrolysis and tar cracking, as reported by Ding et al. [42].
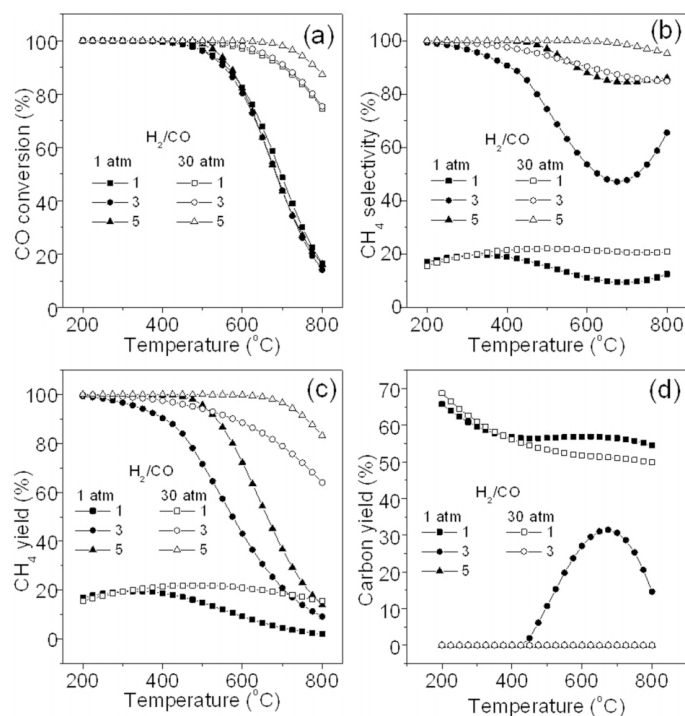
Figure 5. Effect of H_2/CO ratio on CO conversion (**a**), CH_4 selectivity (**b**), CH_4 yield (**c**), and carbon yield (**d**). Reprinted from [18].

WGS reaction can occur in a separate unit or be integrated in gasification (biomass steam gasification) or methanation unit [43–46]. Compressing the WGS reaction and methanation into one unit performs convenient operability, ideal stability and low maintenance cost for the whole system [45]. Moreover, the addition of steam in the reaction phase can largely avoid carbon formation in methanation catalysts [18,47]. However, other researchers reported that steam could induce Ni_2^+-doped alumina phase, forming a certain degree of nickel crystallite agglomeration, which would accelerate the decrease in nickel surface area and the loss of active sites [48]. In the integration unit, the catalyst needs to be active in both WGS reaction and methanation reaction. Dong et al. [45] investigated the synergistic effect of Ni-M (M = Mo, Me, Co or Cr) bimetallic catalysts on the coupling of WGS and partial methanation with gas of low H_2/CO ratio. The experiment result showed that Mn was more suitable than other elements for smaller carbon deposition and wider adaptability to various H_2/CO and H_2O/CO conditions. It could be explained by the fact that the stronger synergistic effect with Ni led to an increased proportion of reducible NiO particles, promoting the dispersion of Ni nanoparticles and enhancing the chemisorption of H_2. A nearly 100 h life test and start/stop cycle test further showed that 15% Ni-3% Mn was stable for industrial applications. The result indicated that it was possible to develop a WGS reaction methanation catalyst with high catalytic activity and stability.

An alternative method is the addition of extra hydrogen. It is reported that the addition of hydrogen to the syngas from biomass gasification can double SNG production compared to the method of using the syngas alone [49]. In addition, SNG production with hydrogen derived from the electrolysis of water can accommodate a large amount

of excess power and utilize intermittent renewable energy [46,49,50]. This can be called Power-to-Gas technology.

The WGS reaction is often combined with the addition of hydrogen to reduce additional introduced hydrogen. Bareschino et al. [46] proposed and researched a creative layout of methane production process to promote the integration of water electrolysis and biomass gasification. The core of this layout was the integration of experimental fluidized bed steam gasification system using spruce wood ball over Fe/Al_2O_3 catalyst and conceptual methanation unit. The results showed that adding steam into air as gasification agent would increase H_2/CO ratio and reduce the concentration of CO_2 in the product gas. This meant not only a reduced supply of H_2 per unit of product produced, but also a lower amount of carbon lost from the biomass as CO_2, thus improving the carbon conversion efficiency of the process.

Giglio et al. [51] performed an energy system analysis of an integrated process for the SNG from biomass. Biomass gasification, solid oxide electrolysis (SOEC) and catalytic reactor for methane synthesis were integrated into two configurations. In the first configuration (CONF1), the electrolysis unit was sized to meet the H_2 content requirement for methanation. In the second configuration (CONF2), the electrolysis supplied the required oxygen to the gasifier, as well as a WGS reactor and a carbon capture/isolation unit was used to adjust the composition of the reaction gas ensuring proper stoichiometry of the methanation process. The process efficiencies of 71.7% and 66.8% for CONF1 and CONF2, respectively, were higher than those of only biomass gasification.

5. Environmental and Economic Assessment

The main method of assessing the environmental burden of methane production is life cycle assessment (LCA). Kolb et al. [3] summarized and compared 30 LCA studies on the greenhouse gas emissions of renewable gases. The result is shown in Figure 6. Generally, greenhouse gas emissions from renewable energy pathways tend to be lower than those from natural gas. Biomethane from anaerobic digestion with manure as a feedstock performed especially well in reducing emissions, which is mainly due to avoided emissions from waste management. For bio-SNG, wood as feedstocks shows low greenhouse gas emissions. A high variance was obtained from straw or waste, because different sources of electricity were used in different studies. When the power of electrolysis was sourced from wind or photovoltaic, the impact was positive for the environment. However, if electricity is sourced from coal, greenhouse gas emissions may exceed those of natural gas.
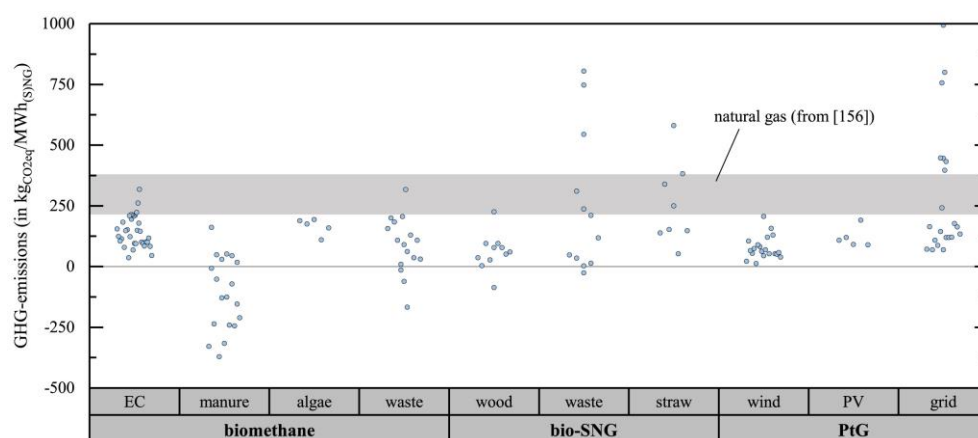
Figure 6. Graphical comparison of the greenhouse gas (GHG) emissions of biomethane from anaerobic digestion and bio−SNG with different feedstock and Power−to−Gas with different electricity sources. The grey area indicates estimates for the CO_2eq emissions of nature gas from Ref. [52]. All values refer to a time horizon of 100 years and are indicated in kg of CO_2eq per MWh of SNG (resp. nature gas). EC = energy crops; SNG = Synthetic Natural Gas; PtG = Power−to−Gas. Reprinted from [3].

Skorek-Osikowska [53] compared the carbon footprint of three systems for methane production, including methanation from syngas, methanation of biogas and biogas upgrading. If biogas was obtained from manure and the emissions were avoided from conventional waste management, biogas upgrading showed the lowest greenhouse gas emissions (at around −60 g CO_2 per MJ of SNG). However, without considering emissions from waste management, methanation from syngas exhibited the lowest environmental impact. Bargiacchi et al. [54] assessed different layouts for SNG production with electrolytic hydrogen in the methodology of LCA. Global Warming Potential (GWP), non-Cumulative Energy Demand (CEDnr) and Acidification Potential (AP) were used as indicators for analysis. SNG produced from biomass and renewable electricity results in lower GWP and CEDnr compared to conventional nature gas, although it has a higher AP. Based on the above studies, SNG from biomass gasification exhibits a smaller environmental burden compared to natural gas, and also performs better than biogas when environmental credits are not accounted for. Hydrogen production through clean electricity is favorable, while electricity derived from fossil fuels may have a negative impact on the environment.

Methane production projects also need to be commercially viable. Song et al. [55] reported a techno-economic assessment of SNG production from agriculture residuals in China. With assumption on price of biomass including transportation of 250 RMB/t, the unit cost of bio-SNG is equivalent to that by coal. Sensitivity analysis shows that the unit cost of bio-SNG increases linearly with increasing biomass price. Billig et al. [9] evaluated the technical and economic aspects of different biomass conversion technologies for methane. Figure 7 showed net value of different technologies on the basis of capacity range. The evaluation exhibited that the costs of biomethane from biochemical conversion and bio-SNG from thermochemical conversion are in the same range. The cost of biomethane is lower than the cost of bio-SNG; however, higher net value was obtained from thermochemical conversion when both used straw as feedstock. This may be due to the high lignin content of straw resulting in low efficiency of biochemical conversion.
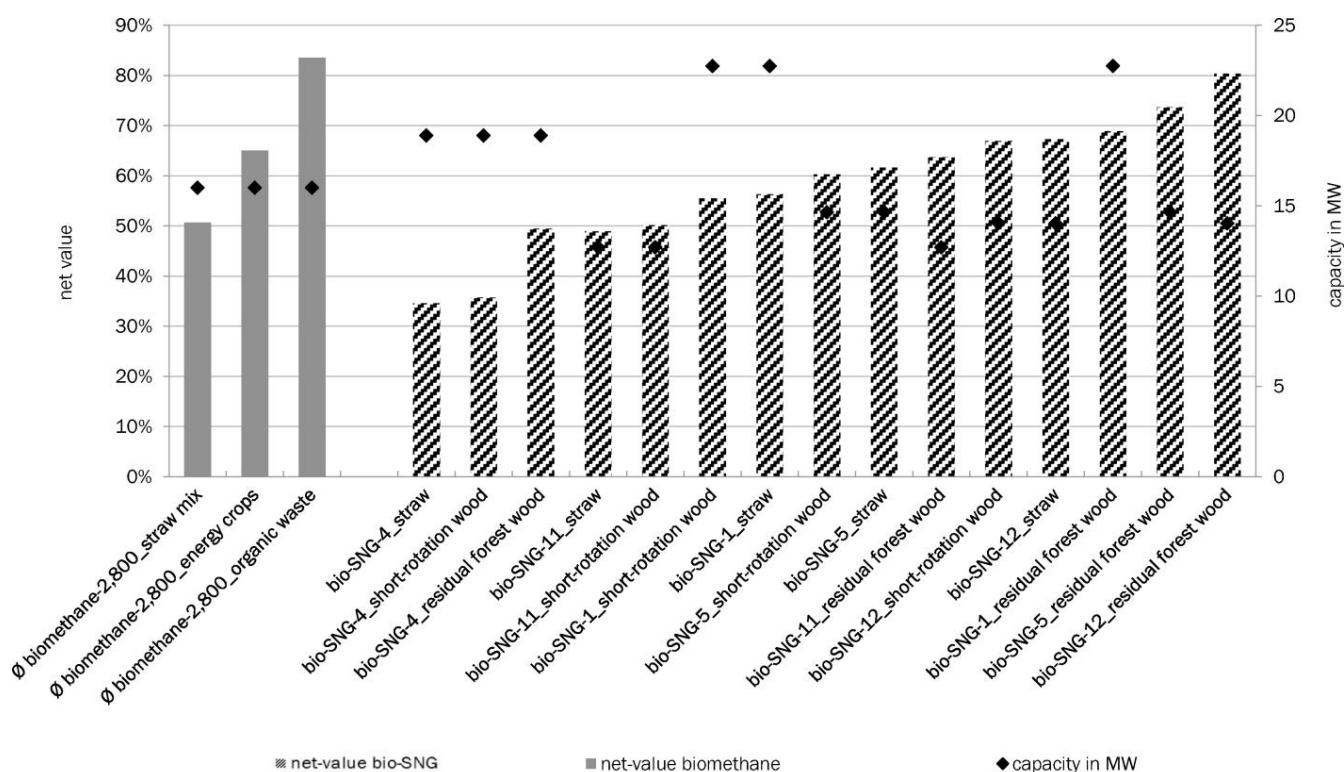
Figure 7. Biochemical conversion and thermochemical conversion net value comparison on the basis of capacity range. Reprinted from [9].

Sarić et al. [49] evaluated the business case of Power-to-Gas in methane production from biomass gasification via three future cumulative tariff curves. Solid oxide electrolyser (SOE) and Proton exchange membrane (PEM) systems were used. The results showed that the case is economically positive only if the price curve is based on a large amount of low-priced intermittent electricity. Only SOE-PG system could generate higher profits than the reference case (without Power-to-Gas), which was due to ability to switch to fuel assisted mode at high electricity prices. The projected room for investment available for a PEM electrolyser is lower because of its lower efficiency and resulting higher operating costs. In the case of large capacity of intermittent electricity, the projected room for investment of an SOE electrolyser is 650 €/kW, and for a PEM electrolyser, it is 350 €/kW. There is still a need for technological progress to reduce costs and improve profits.

6. Other Thermochemical Methods

Some other thermochemical methods are also reported to produce methane. Hydrothermal gasification has received a great deal of attention. Hydrothermal gasification can be defined as the conversion of organic matter to fuel gas in high pressure water, where the pressure is high enough to keep the water in a liquid or supercritical state. This process usually happens at temperatures near or above the critical point for pure water (Pc = 22.1 MPa, Tc = 374 °C), including aqueous phase reforming, supercritical water gasification and near-critical gasification [56–58]. In the gasification route, the biomass feedstock is first decomposed by gasification and then the H_2/CO rich gas is synthesized into methane and carbon dioxide. Gasification occurs at high temperatures, typically 700–1000 °C [12,59,60]. Contrary to gasification configuration, the hydrothermal gasification route does not have an individual methanation unit, and the goal is converting the diluted biomass directly into methane at 300–400 °C [61–63]. The main idea of hydrothermal biomass gasification is based on the special properties of near-supercritical water and supercritical water as a solvent and a reaction partner. The relatively fast hydrolysis of biomass in subaqueous and supercritical water leads to rapid degradation of biomass polymer structure [58,64]. Compared with solid macromolecule, hydrolyzed biomass is allowed to contact with catalyst effectively [61].
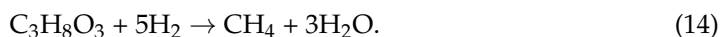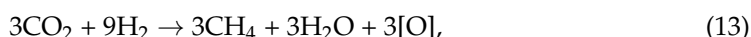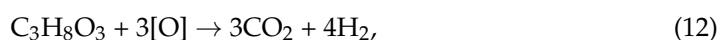
Methane and hydrogen are both produced in hydrothermal gasification. In general, the choice of processing temperature and pressure allows the selection of the main product methane or hydrogen. Similar to methanation reaction, lower temperature and higher pressure is in favor of the production of methane according to thermodynamic principle [64,65]. Cengiz et al. [66] investigated the effect of temperature and pressure on hydrogen and methane yields during hydrothermal gasification of wood residues. The maximum hydrogen yields were 27.0 mol/kg for pine tree sawdust and 24.7 mol/kg for fir tree sawdust at reaction pressures of 20.5 MPa and 20.3 MPa as well as temperature of 600 °C. The maximum yields of methane were 11.7 mol/kg for pine tree sawdust and 11.2 mol/kg for fir tree sawdust at 600 °C and 43.0 MPa.

Supercritical gasification to produce methane exhibits high energy efficiency. Gassner et al. [67] reported the total chemical efficiency of producing SNG from wood-based materials in supercritical water is 70–77%. Ondze et al. [68] studied the energy efficiency of biomass supercritical gasification in three cases: hydrogen production, methane production, heat and electricity cogeneration. Methane production under isothermal or adiabatic conditions was the best in terms of overall energy optimization, with optimal energy efficiencies of 94% and 91%, respectively. The main reason could be that no significant phase change occurs when the system pressure is higher than 22.1 MPa and the enthalpy change is smaller than that for evaporating and superheating the water to the same temperature at a subcritical pressure [64]. Moreover, feedstocks with high water content such as microalgae and sludge can be used to avoid significant energy loss during the drying [61,67].

Catalyst in hydrothermal gasification can be classified as homogeneous and heterogeneous catalyst. Homogeneous catalysts are mainly alkali compounds, such as NaOH and Na_2CO_3. Similar to methanation catalyst, multiphase catalysts have been studied mainly for Ru, Ni and their compounds. Activated carbon is considered effective [63,65]. Because of the lower temperature, hydrothermal gasification to produce methane highly requires more of a multiphase catalyst with high activity to achieve complete conversion and chemical equilibrium [56]. Catalyst deactivation can also occur through sintering and sulfur poisoning in hydrothermal gasification [62,63,65]. However, unlike in methanation, little carbon deposition is observed in hydrothermal gasification [69]. Waldner et al. [57] investigated the SNG production by catalyzed hydrothermal process from wood with high feedstock concentration (10–30%) using Raney nickel as catalyst. The maximum methane yield was 0.33 g/g wood and the product gas contained 49% methane. Under supercritical condition, the remaining liquid phase was always tar-free, colorless and contained less than 2 wt% of feed carbon. Analysis of the waste catalyst shows a slight increase in carbon deposition on the surface (15 atom% for the spent catalyst and 10 atom% for the fresh catalyst). This is mainly due to the fact that the high solubility of biomass intermediates in the reaction medium. The active material from the biomass is "diluted" by the solventization in water, thus the reaction rate of polymerization into unwanted products such as tar and coke is reduced [58].

Several papers have proposed methane production via fast pyrolysis of biomass. In contrast to the gas synthesis in the gasification route, methane is formed directly in fast pyrolysis through the cracking of hydrocarbon chains. Görling et al. [70] performed an overall system analysis of a high-yield device producing methane and biochar by fast pyrolysis. The total energy efficiency of the process was estimated to be 89% (HHV) and the methane yield was 83% (HHV), which is higher than those in the gasification route. Yun et al. [71] prepared methane by pyrolysis-direct methylation over a conventional nickel calcium aluminate catalyst. Acetic acid was used as a single compound bio-oil substitute. Under optimal operating conditions, 81.9% conversion of fuel carbon to gas was achieved, with a methane yield of 15.7% of feed. The researchers also proposed a plant design for the production of high-purity methane from drippy palm empty fruit bunch by fast pyrolysis. Based on simulations of the autothermal plant, the final gas product is predicted to be 99.2% methane and 0.8% H_2. In addition, the thermal efficiency of the plant is 80.6%.

Recently, a new method of converting biomass to methane directly has been proposed. Zhou et al. [72] creatively proposed an oxygen-vacancy (V_O)-mediated catalytic system for direct biomass methanation. Using V_O-mediated catalysis over Ru/TiO_2, biomass feedstocks were oxidized by TiO_2 to form carbon dioxide and V_O (Equation (13), [O] represents the lattice oxygen, glycerol as a model). Then, CO_2 was converted in situ to methane at the Ru site, recovering the consumed lattice oxygen and removing V_O (Equation (14)). Equation (15) was the total reaction. Various biomass resources were converted to methane at 200 °C with yields of 82–99%. This method achieved direct conversion of biomass to methane below 200 °C and provided a new way of methane production.

$$C_3H_8O_3 + 3[O] \rightarrow 3CO_2 + 4H_2, \tag{12}$$

$$3CO_2 + 9H_2 \rightarrow 3CH_4 + 3H_2O + 3[O], \tag{13}$$

$$C_3H_8O_3 + 5H_2 \rightarrow CH_4 + 3H_2O. \tag{14}$$

7. Summary and Perspective

Methane is the main component of natural gas occupying an important position in the area of world energy resources. Biomass has the advantage of low price, rich reserves, environmental friendliness and renewability. Thermochemical method results in high energy efficiency and short residence time, so converting biomass to methane through the thermochemical method is potential. Table 1 lists the advantages and disadvantages of the

mentioned conversion technologies in this review. The gasification route is the predominant production method by thermochemical conversion. The core stage of it includes gasification, gas conditioning and methanation. In addition, methane production is mainly regulated directly by the gas conditioning and methanation stages, with gasification mainly providing the syngas feedstock.

Table 1. Advantages and disadvantages of biomass-to-methane technology [8–11,41,49,50,58,65,73,74].

Technology *		Advantage	Disadvantage
Anaerobic digestion		Mature technology Low cost More types of feeds	Low energy efficiency Long retention time
Gasification		High energy efficiency Short retention time	High gasification temperature Challenges for catalyst selection and stability
	Sorption enhanced reforming	High methane yield CO_2 absorption	Need for suitable adsorbent
	Power-to-Gas	Very high methane yield Accommodating excess power and intermittent renewable energy	High investment Limited by electricity prices and sources Complex systems
Hydrothermal gasification		High energy efficiency Low conversion temperature Less tar and coke Process wet biomass	High pressure High investment Corrosion of reactor Challenges for catalyst selection and stability

* Fast pyrolysis and direct conversion to methane are not listed due to few studies.

Factors affecting the methane production via biomass gasification include operating parameters such as temperature and pressure, catalysts of methanation and gas conditioning methods. The primary reaction in the methanation stage is CO methanation. Low temperature and high pressure are beneficial to promote methanation reaction, and a catalyst is also necessary for the reaction. Currently, Ni-based catalysts are the most popular due to their high activity per unit price, but are subject to deactivation due to carbon deposition, sintering and sulfur poisoning. In terms of catalyst improvement, the researches in the future will be carried out in two main aspects. One is to study the interaction of the support and the active metal. The type and morphology will influence the stability of catalysts. The distribution of metal also plays a role. The research of the interaction of the metal and the support will help to determine the most suitable support. The other aspect is to study the functions of more active metal promoters. More work is needed to determine the specific effects and rationale for the addition of different metal promoters on the activity and stability of Ni-based catalysts (e.g., Mg improves catalytic activity, Ru improves sulfur resistance). In addition to bimetallic catalysts, catalysts containing more active metals need to be investigated. Moreover, both research ideas can be combined and future studies can focus on the complex interaction of multi-metallic catalysts with different supports.

The gas conditioning aims to enhance the H_2/CO ratio, mainly by the WGS reaction or by adding hydrogen. The integration of the WGS reaction with the methanation unit still requires further research to choose suitable catalyst and understand the catalyst deactivation in both methanation and WGS reaction. Additional hydrogen can originate from intermittent renewable power generation such as wind and solar. Researches in the future will focus on ways to combine methane production and renewable energy power generation, realizing efficient utilization of electric power.

Methane from biomass gasification leads to less environmental burden compared to natural gas, but the electricity used for hydrogen production needs to be produced from clean energy. The economics of the project are closely related to the price of biomass. Power prices and electrolyzer costs also need to be focused on for Power-to-Gas technique.

Currently, most projects may be difficult to make a profit. Technological advances such as the reduction in electrolyzer costs are necessary. Increased coordination with the power system can also help boost economic returns.

Finally, other thermochemical methods also have potential. Hydrogen production via hydrothermal gasification has been heavily studied, but methane has received less attention. Fast pyrolysis has rarely been used for methane production, and direct methanation of biomass at low temperatures is a new approach. These areas will need to be supplemented by substantial research in the future.

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