

Review

Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production

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ABSTRACT

Gasification technology has been investigated to effectively and economically convert lowvalue and highly distributed solid biomass to a uniform gaseous mixture mainly including hydrogen (H₂), carbon monoxide (CO), methane (CH₄) and carbon dioxide (CO₂). This gaseous mixture can be further used as an industrial feedstock for heat and power generation, H₂ production and synthesis of liquid fuels. Significant advances have been made in the technology of biomass gasification and syngas utilization. This review was conducted to introduce the recent advances in biomass gasification and syngas utilization. The critical technical issues and perspectives of biomass gasification were discussed.

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1. Introduction

Biomass such as forest, agricultural and organic processing residues can be converted to commercial products via either biological or thermochemical processes [1-3]. Biological conversion of low-value lignocellulosic biomass still faces challenges in low economy and efficiency [1]. Combustion, pyrolysis and gasification are three main thermochemical conversion methods. Biomass is traditionally combusted to supply heat and power in the process industry. The net efficiency for electricity generation from biomass combustion is usually very low, ranging from 20% to 40% [2]. Biomass cofired in existing combustors is usually limited to 5-10% of the total feedstock due to the concern about plugging of existing coal feed systems [3]. Pyrolysis converts biomass to bio-oil in the absence of oxygen (O2). Limited uses and difficulty in downstream processing of bio-oil have restricted the wide application of biomass pyrolysis technology [4].

Gasification converts biomass through partial oxidation into a gaseous mixture of syngas consisting of hydrogen (H₂), carbon monoxide (CO), methane (CH₄) and carbon dioxide (CO_2) [5,6]. The oxidant or gasifying agents can be air, pure O_2 , steam, CO2 or their mixtures. Air, while a cheap and widely used gasifying agent, contains a large amount of nitrogen, which lowers the heating value of the syngas produced. If pure O₂ is used as the gasifying agent, the heating value of syngas will increase but the operating costs will also increase due to the O2 production. Partial combustion of biomass with air or O₂ can provide heat for drying the biomass, raising the biomass temperature and driving the endothermic gasification reactions, and generate water and CO2 for further reduction reactions [7]. The heating value and H₂ content of syngas can be increased if steam is used as the gasifying agent, in which case the heating value of the product gas is about 10–15 MJ N m⁻³ [8,9], compared with 3–6 MJ N m⁻³ for air gasification of biomass [10,11]. The use of CO₂ as the gasifying agent is promising because of its presence in the syngas. CO_2 with a catalyst such as Ni/Al can transform char, tar and CH4 into H₂ and/or CO, thus increasing H₂ and CO contents [12–14]. Pure steam or CO₂ requires an indirect or external heat supply for the endothermic gasification reactions [15-18]. Alternatively, a mixture of steam or CO₂ and air or O2 can be used as the gasifying agent, and the partial combustion of biomass with air/O2 provides the heat required for the gasification [9,19-21].

There are three main types of gasifiers: fixed bed, moving bed and fluidized bed gasifiers [5–7]. Both fixed bed and moving bed gasifiers produce syngas with large quantities of either tar and/or char due to the low and non-uniform heat and mass transfer between solid biomass and gasifying agent. However, they are simple and reliable designs and can be used to gasify very wet biomass economically on a small scale [7]. Fluidized bed gasifiers, which consist of a large percentage of hot inert bed materials such as sand and 1–3% of biomass, have been used widely in biomass gasification [7]. Fluidized bed gasification can achieve a high heating rate, uniform heating and high productivity [22]. The productivity, gas heating value and gasifier efficiency for gasification of rice husk in an industrial-scale circulated fluidized bed gasifier (\emptyset 1.8 m) were 960 kgm⁻²h⁻¹, 4.6–6.3 MJ Nm⁻³ and 65%, compared with 127 kgm⁻²h⁻¹, 3.8–4.6 MJ Nm⁻³ and 47% for gasification of rice husks in a downdraft fixed bed gasifier (\emptyset 2 m) [23].

The syngas can be used to generate heat and power like natural gas [24,25], synthesize other chemicals and liquid fuels [26–35], or produce H₂ [8,36–38]. The application of biomass gasification technology strongly depends on syngas quality control technologies [12,39–43]. Comprehensive information on biomass gasification research, development, demonstration and commercialization has been provided by the International Energy Agency (IEA) Bioenergy (http://www. gastechnology.org/iea) and European Gasification Network (Gasnet at http://www.gasnet.uk.net). Guides to gasification design and operation have been provided by Knoef [5] and Higman and van der Burgt [6]. The objective of this paper was to review the advances of biomass gasification in terms of ash agglomeration mechanism and reduction, syngas quality control and syngas utilizations.

2. Ash agglomeration mechanism and reduction

Ash-related problems including sintering, agglomeration, deposition, erosion and corrosion are the main obstacles to economical and viable applications of biomass gasification technologies [44]. Alkali metals, such as potassium, react readily with silica, even at temperatures far below 900 °C, by breaking the Si–O–Si bond and forming silicates or reacting with sulfur to produce alkali sulfates. The alkali silicates and sulfates have melting points even lower than 700 °C and tend to deposit on the reactor walls and leave a sticky deposit on the surface of the bed particles, causing bed sintering and defluidization [45,46]. Furthermore, the presence of ash such as alkali in syngas can cause problems of deposition, corrosion and erosion for equipment that utilizes syngas such as a gas turbine [10].

Fluidized bed gasification performs better than fixed bed gasification to reduce ash-related problems since the bed temperature of fluidized bed gasification can be kept uniformly below the ash slagging temperature. The low gasification temperature can also reduce the volatilization of ash elements such as sodium and potassium into the syngas, thus improving the quality of syngas [10]. Alkali, as well as char, can be separated from syngas using a cyclone. Gabra et al. [47] found that 80% of the alkali compounds in cane trash separated with the char in a cyclone gasifier. Leaching and fractionation are the two main pretreatments used to reduce ash-related problems [45,46,48]. The efficiency of water leaching on the removal of inorganic elements dependeds on biomass feedstocks. Feedstocks such as wheat straw have poor leaching of alkali metals, chlorine and sulfur possibly because the complex structure of straw retards the extraction of alkali metals from the materials during leaching [45]. Mechanical fractionation could reduce up to 50% of the ash in the biomass but the remaining ash still causes the ashrelated problems at a high temperature [45,46].

3. Syngas quality control and cleaning technology

3.1. Syngas quality

During gasification, part of the biomass is converted to char and tar instead of syngas. Gabra et al. [47] reported an average char yield of 17.5% of the input fuel during bagasse gasification. Herguido et al. [49] found that only 80% of the carbon in the feedstock was converted to syngas during steam-fluidized bed gasification of wood sawdust. Four percent of the carbon was in liquid tar and the remaining carbon was in solid char. Use of syngas as a fuel for internal combustion engines, gas turbines and fuel cells for heat and power generation, and as a feedstock for the synthesis of liquid fuels and chemicals depends mainly on cleaning technologies used to remove particulate dust and condensable tar in the syngas. Reduction and conversion of char and tar can also increase syngas gas yield and overall conversion efficiency.

3.2. Syngas quality control during gasification

Particulate dust and tar removal technologies can broadly be divided into two categories: (1) treatments during gasification and (2) gas cleaning after gasification. Different treatments inside a gasifier for char and tar reduction include (a) gasifier modifications [20,50,51], (b) proper selection of operating parameters [52–55] and (c) use of bed additives/catalysts [8,56]. Devi et al. [12] prepared a comprehensive review on different treatments for char and tar elimination during biomass gasification.

Gasifier design parameters have an effect on char and tar formulation. Low heating rates lead to the formation of coke/ char. One possible reason is that furfurals and other unsaturated compounds in the tar may polymerize with free radicals when the biomass or tar-water mixtures spend sufficient time at a low temperature [52,53]. Therefore, fluidized bed gasification generates less char than fixed bed gasification because it can achieve a high heating rate. However, due to the fluidization of biomass particles in the gasifiers, some fine particles could be entrained above the fluidizing bed and large bubbles may result in gas bypass through the bed, lowering the biomass conversion efficiency. Pan et al. [50] reported that 20% of secondary air injection to the primary air injection above the biomass feeding point in a fluidized bed gasifier reduced 88.7% (wt) of the total tar for the gasification in temperatures from 840 to 880 °C. Alternatively, the circulating fluidized bed gasifiers can recycle solids to

increase the residence time and thus increase biomass conversion efficiency, compared with bubbling fluidized bed gasifiers [23,51].

Operating parameters such as gasification temperature, pressure and the equivalence ratio (ER, the ratio of O_2 required for gasification to O_2 required for full combustion of a given amount of biomass) also have an effect on char and tar formulation. High gasification temperature can achieve a high carbon conversion of the biomass and low tar content in syngas [21]. Narvaez et al. [56] observed a drastic decrease in tar content from 19 gNm^{-3} at 700 °C to 5 gNm^{-3} at 800 °C during bubbling fluidized bed gasification of biomass. However, too high operating temperature decreased the energy efficiency and increased the risk of ash sintering and agglomeration as discussed in Section 2 [12]. Pressurized biomass gasification has also been investigated for the decrease of tar formation [54]. Furthermore, no costly syngas compression will be required for the downstream syntheses of fuels and chemicals from high-pressure syngas [54]. If air or O_2 is used as the gasifying agent, ER is an important operating parameter. Kinoshita et al. [55] and Narvaez et al. [56] reported that the tar content decreased sharply as the ER was increased during biomass gasification because of more availability of O2 to react with volatiles of tar inside the gasifier. However, too high ER may cause low concentrations of H_2 and CO with high CO_2 content in the product gas, resulting in a low heating value of the product gas. The value of ER is usually 0.2-0.4 [10,11,56]. The advantages and technical challenges of different operating conditions of biomass gasification are summarized in Table 1.

3.3. Hot gas cleaning technologies

Several mechanical methods such as cyclones, bag filters, baffle filters, ceramic filters, fabric filters, rotating particle separators, wet electrostatic precipitators and water scrubbers have been used to remove particulate dust and tar from syngas after gasification [57]. Water scrubbing and wet electrostatic precipitation are unattractive due to their economics and the environmental pollution of residue water [37]. Most mechanical methods for gas cleaning, such as fabric filters, rotating particle separators and water scrubbers, can operate only at low temperatures (i.e., <200 °C). Hot gas cleaning could improve energy efficiency and lower operational costs for high-temperature utilizations of syngas such as H₂ production by steam reforming and water-gas shift reactions, and combined heat and power generation by a high-temperature fuel cell [26,40]. Furthermore, the concern about environmental and safety issues related to hot dry gas cleaning systems is generally low [58]. Char and other particles in hot syngas can be removed using ceramic filters, which can be operated up to a temperature of 600 °C. However, ceramic filters are used mainly for particle removal from high-pressure gas because the pressure drop through ceramic filters is high [57]. Hasler and Nussbaumer [57] observed that a 90% particle removal was easier to achieve than a 90% tar removal using the mechanical methods. Therefore, tar separation is a key issue for a successful application of biomass-derived syngas.

	Main advantages	Main technical challenges	Main references
Gasifying agents Air	 Partial combustion for heat supply of gasification Moderate char and tar content 	 Low heating value (3–6 MJN m⁻³) Large amount of N₂ in syngas (e.g., >50% by volume) Difficult determination of ER (usually 0.2–0.4) 	[10,11,56]
Steam	1. High heating value syngas (10–15 MJ N m $^{-3}$) 2. H $_2$ -rich syngas (e.g., $>50\%$ by volume)	 Require indirect or external heat supply for gasification High tar content in syngas Require catalytic tar reforming 	[8,9,15–18]
Carbon dioxide	1. High heating value syngas 2. High H_2 and CO in syngas and low CO_2 in syngas	 Require indirect or external heat supply Required catalytic tar reforming 	[12–14]
Gasifier design Fixed/moving bed	 Simple and reliable design Capacity for wet biomass gasification Favorable economics on a small scale 	 Long residence time Non-uniform temperature distribution in gasifiers High char or/and tar contents Low cold gas energy efficiency Low productivity (e.g., ~5 GJ m⁻² h⁻¹) 	[5–7,80]
Fluidized bed	 Short residence time High productivity (e.g., 20-30 GJ m⁻² h⁻¹) Uniform temperature distribution in gasifiers Low char or/and tar contents High cold gas energy efficiency Reduced ash-related problems 	 High particulate dust in syngas Favorable economics on a medium to large scale 	[5–7,50,80]
Gasifier operation Increase of temperature	 Decreased char and tar content Decreased methane in syngas Increased carbon conversion Increased heating value of syngas 	 Decreased energy efficiency Increased ash-related problems 	[21,56]
Increase of pressure	 Low char and tar content No costly syngas compression required for downstream utilization of syngas 	 Limited design and operational experience Higher costs of a gasifier at a small scale 	[55]
Increase of ER	Low char and tar content	Decreased heating value of syngas	[56,57]

Table 1 – Advantages and technical challenges of different gasifying agents, gasifier designs and operations for syngas production

3.4. Catalytic reforming of tar

Tar can be further converted to gas through the steamreforming reaction. Catalysts are needed to enhance the reaction, which could be a low-temperature reforming reaction (e.g., 350–600 °C) or a high-temperature reforming reaction (e.g., 500–800 °C). Three main groups of catalysts including (1) naturally occurring catalysts such as dolomite and olivine; (2) stable metals such as nickel, and alkali metals; and (3) alkalis such as KOH, KHCO₃ and K₂CO₃ have been evaluated for elimination of tar in the syngas [59]. Char was also used to effectively reform tar. Char can be produced inside a gasifier but it is converted during gasification. Therefore, there is a need for an external continuous supply of char into the gasifier or modification of gasifier design [60,61]. The main catalysts for tar reforming are listed in Table 2.

Naturally occurring dolomite is the most popular catalyst used for tar conversion [8,56,62]. Narvaez et al. [56] reduced tar content by 40% when 3% of calcined dolomite to biomass by mass was added into the gasifier, mostly due to the catalytic steam and dry reforming of tar as

$$\begin{aligned} & \mathsf{C}_{\mathsf{n}}\mathsf{H}_{\mathsf{m}}\;(\mathsf{tar}) + \mathsf{n}\mathsf{H}_{2}\mathsf{O} \leftrightarrow (\mathsf{n} + \frac{\mathsf{m}}{2})\mathsf{H}_{2} + \mathsf{n}\mathsf{C}\mathsf{O} \\ & (\mathsf{tar}\;\mathsf{steam}\text{-reforming}\;\mathsf{reaction}), \end{aligned} \tag{1}$$

$$\begin{array}{l} C_nH_m \ (tar) + nCO_2 \leftrightarrow \frac{m}{2}H_2 + 2nCO \\ (tar \ dry-reforming \ reaction). \end{array}$$

Catalyst typeRepresentative catalystsMain advantageTechnical challengesReferencesNaturally occurring catalystDolomite Olivine Clay ZeoliteCheap1. Moderate reforming efficiency 2. Easily eroded and broken[8,12,56,62-64 2. Easily eroded and brokenAlkali and saltsKOH KHCO3 K2CO31. High reforming efficiency 2. Increased hydrogen in syngasIncreased plugging and deactivation of other metal catalysts at a high temperature[12,65-68]Stable metal with oxide supportNiO/Al2O3 Ni/CeO2/Al2O3 RhCeO2SiO21. High reforming efficiency 2. Increased hydrogen content in syngas1. Stable metals are expensive 2. Metals are easily deactivated by coke, poisoned by H2S and sintered by ash melting 3. Require hot-water-resistant support materials[12,37,70-77]					
Naturally occurring catalyst Dolomite Olivine Clay Zeolite Cheap 1. Moderate reforming efficiency [8,12,56,62–64 Alkali and salts KOH KHCO3 K2CO3 1. High reforming efficiency Increased plugging and deactivation of other metal catalysts at a high temperature [12,65–68] Stable metal with oxide support NiO/Al ₂ O ₃ 1. High reforming efficiency 1. Stable metals are expensive efficiency 1. Stable metals are expensive content in syngas [12,37,70–77] Ni/CeO ₂ /Al ₂ O ₃ 2. Increased hydrogen RhCeO ₂ SiO ₂ 2. Increased hydrogen content in syngas 1. Stable metals are expensive content in syngas [12,37,70–77]	Catalyst type	Representative catalysts	Main advantage	Technical challenges	References
Alkali and salts KOH KHCO3 K2CO3 1. High reforming efficiency Increased plugging and deactivation of other metal catalysts at a high temperature [12,65–68] Stable metal with oxide support NiO/Al ₂ O ₃ 1. High reforming efficiency 1. Stable metals are expensive efficiency 1. Stable metals are expensive efficiency [12,37,70–77] Ni/CeO ₂ /Al ₂ O ₃ 2. Increased hydrogen rhiceO ₂ SiO ₂ 2. Increased hydrogen efficiency 1. Stable metals are expensive efficiency [12,37,70–77] Ni/CeO ₂ /Al ₂ O ₃ 2. Increased hydrogen rhiceO ₂ SiO ₂ 2. Increased hydrogen content in syngas 3. Require hot-water-resistant support materials	Naturally occurring catalyst	Dolomite Olivine Clay Zeolite	Cheap	 Moderate reforming efficiency Easily eroded and broken 	[8,12,56,62–64]
Stable metal with oxide support NiO/Al ₂ O ₃ 1. High reforming efficiency 1. Stable metals are expensive [12,37,70–77] Ni/CeO ₂ /Al ₂ O ₃ 2. Increased hydrogen RhCeO ₂ SiO ₂ 2. Increased hydrogen content in syngas 1. Stable metals are expensive [12,37,70–77] Stable metal with oxide support Ni/CeO ₂ /Al ₂ O ₃ 2. Increased hydrogen content in syngas 1. Stable metals are expensive [12,37,70–77] Stable metals are expensive Stable metals are expensive 1. Stable metals are expensive [12,37,70–77] Stable metals are expensive Stable metals are expensive 1. Stable metals are expensive [12,37,70–77] Stable metals are expensive Stable metals are expensive 1. Stable metals are expensive [12,37,70–77] Stable metals are expensive Stable metals are expensive 1. Stable metals are expensive [12,37,70–77] Ni/CeO ₂ /Al ₂ O ₃ Stable metals are expensive 1. Stable metals are expensive 1. Stable metals are expensive [12,37,70–77]	Alkali and salts	KOH KHCO3 K2CO3	 High reforming efficiency Increased hydrogen in syngas 	Increased plugging and deactivation of other metal catalysts at a high temperature	[12,65–68]
LaNi _{0.3} Fe _{0.7} O ₃	Stable metal with oxide support	NiO/Al ₂ O ₃ Ni/CeO ₂ /Al ₂ O ₃ RhCeO ₂ SiO ₂ LaNi _{0.3} Fe _{0.7} O ₃	 High reforming efficiency Increased hydrogen content in syngas 	 Stable metals are expensive Metals are easily deactivated by coke, poisoned by H₂S and sintered by ash melting Require hot-water-resistant support materials 	[12,37,70–77]

Biomass tar is a light hydrocarbon and phenolic mixture. Naphthalene was the most difficult tar compound to reform [63,64]. Myren et al. [64] found that a layered combined catalyst of dolomite with silica on top gave considerably less naphthalene in tar and a lower amount of total tar than dolomite alone. However, dolomite is soft, and easily eroded and broken by other solid particles in a gasifier. The tar reduction capacity and activity of naturally occurring olivine is comparable to calcined dolomite [8].

Table 2 – Main catalysts for tar reforming

For steam gasification of biomass, addition of alkali metals, especially potassium, can significantly reduce tar and increase H_2 in syngas [65–67]. An addition of 8 wt% K₂CO₃ in a fluidized bed for steam gasification of wood at 750 °C could reduce phenolic tar compounds by a factor of 5 [67]. The addition of salts such KOH, KHCO₃ and K₂CO₃ caused an increase in H_2 and a decrease in CO yield by acceleration of the water–gas shift reaction [65,66]. Therefore, the salts in biomass may increase the H_2 yield and decrease the CO yield [68]. However, it should be noted that alkali and salts in biomass can cause plugging and deactivation of other metal catalysts, depending on the design of the reactor, concentration of the alkali and salts, and gasification temperature [69].

Heterogeneous metal catalysts such as Ni and Rh, with support materials such as silica oxide and alumina oxide (e.g., Ni/Al₂O₃, Ni/CeO₂/Al₂O₃ and Rh/CeO₂/SiO₂), have been used to convert tar to gas through low-temperature catalytic reformation of tar [70-72]. Only a limited number of stable metal catalysts can be used in the steam-reforming process because of the oxidation of the metal in a hot-water environment [65,66]. The traditional support materials of silica and alumina oxides are degraded severely in hot water [73]. Combinations of stable metals such as ruthenium or nickel bimetallics and stable support materials such as titania, zironia and carbon have been developed for lowtemperature steam reforming of tar [74]. Rapagna et al. [37] used a tri-metallic catalyst with a ternary oxide support structure (LaNi_{0.3}Fe_{0.7}O₃) in a fixed bed reactor to reform syngas produced by steam-fluidized bed gasification of olivine. Their results showed that 90% of the tar in the syngas

was converted at 800 $^\circ C$ and a space time of 0.45 s. No coke formation was observed on the catalyst surface.

Although nickel and other stable metal catalysts can almost completely remove tar, they are expensive, easily deactivated by coke formation, poisoned by H_2S and sintered by ash melting at high temperature. Both alkali and dolomite catalysts are cheaper but they cannot remove all tar in the syngas. Swierczynski et al. [75] and Wang et al. [76,77] developed a combined Ni–dolomite catalyst for steam reforming of tar using metallic nickel as an active phase grafted on dolomite. Their results showed that 97% of tar removal was obtained at a reforming temperature of 750 °C and a space velocity of 12,000 h⁻¹ and no obvious deactivation of catalyst was observed in 60 h tests [77].

4. Syngas utilizations

4.1. Combined heat and power generation from syngas

Low heat value syngas from air gasification of biomass can be used in a combustor [78]. Compared with direct biomass combustion, syngas from biomass gasification can increase the biobased fuel percentage used in existing pulverized coal combustors without any concern about plugging of the coalfeeding system during co-firing of biomass coal. Biomass gasification can reduce the potential of ash slugging or other ash-related problems because the gasification temperature is lower than combustion and clean syngas is supplied to the combustor. A gasification process can use a variety of biomasses with large variations in their properties such as moisture content and particle size [78]. However, if syngas is combusted directly to generate steam for power generation via a steam turbine, the electricity efficiency is limited by the theoretical limit of a steam turbine.

High-quality syngas with almost no tar and dust and high heating value can be fed to gas engines directly [79,80] or gas turbines [10,24,47,81] for power generation. Syngas usually is cooled down to increase the energy density for its use in a gas

engine [79,80]. The lower heating value of syngas produced by air gasification of biomass is usually around $5 MJN m^{-3}$ compared with $38 \,\text{MJN}\,\text{m}^{-3}$ for natural gas. However, Sridhar et al. [80] found that the de-rating of a gas engine was not significant if the syngas was used to replace natural gas because the energy density per unit of air and syngas mixture at a stoichiometric air to fuel ratio of 1.2 was only 15-20% lower than an air and natural gas mixture at a stoichiometric ratio of 17. Gas turbines can transform hot syngas to mechanical energy and thus increase the energy efficiency of conversion. A typical biomass integrated gasification combined cycle (BIGCC) involves combustion of the hot syngas from a gasifier in a gas turbine to generate electricity in a topping cycle. The hot exhaust gas from the turbine is used to generate steam through a heat recovery steam generator [24,81,82]. The steam is used in a steam turbine to generate additional electricity in a bottom cycle or used as processing heat. Miccio [81] reported that the overall efficiency of the BIGCC system was 83% and the electrical efficiency was 33%. Rodrigues et al. [24] found that for cofiring of 35–50% of natural gas and syngas produced at a lower heating value of $6 \,\text{MJ}\,\text{N}\,\text{m}^{-3}$ in a BIGCC plant, no de-rating was required for the gas turbines.

A fuel cell uses H_2 and O_2 to produce electricity and the byproduct of heat in the presence of an electrically conductive electrolyte material. Although H_2 is the only electrochemically active fuel in the fuel cell, CH_4 and CO in the syngas can be converted into H_2 using water-reforming and water-gas shift reactions as [83,84]

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO + 292.41 \text{ kJ mol}^{-1}$$
(methane water-reforming reaction), (3)

 $CO + H_2O \leftrightarrow H_2 + CO_2 - 41.98 \text{ kJ mol}^{-1}$ (water-gas shift reaction). (4)

The high-efficiency and high-quality by-product heat of molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs) should make them attractive in combined heat and power (CHP) generation with technical progress and cost reduction [85–87]. The SOFC is more tolerant to H₂ impurities and can run with a mixture of H_2 and CO [88]. A field test showed that the EDB/ELSAM 100 kW SOFC-CHP system developed by Westinghouse produced 109 kW net AC to the utility grid at 46% electrical efficiency and 65 kW at 27.5% of thermal efficiency to the district heating system [89]. A SOFC usually operates at about 1000°C, which may cause the reductions in energy efficiency and stability of the fuel cell [90]. The MCFC normally operates at 600 °C and 0.35-0.40 MPa (gauge) and produces residual heat at around 400 °C. The electrical efficiency of a MCFC was more than 50% [84], while the electrical efficiency by an integrated biomass gasifier and MCFC system was 36-40% [91]. The current cost for a fuel cell power generator ranges from 1100 to 1500 US\$ kW⁻¹, which is about two to three times the cost of gas turbines and internal combustors. Considering the increased energy efficiency, increased power quality and reduced emission, fuel cell systems hold a promising market potential in CHP generation. Under specific operating conditions of the system, fuel cells are expected to have lifetimes of over 40,000 h with the use of state-of-the-art materials [92].

4.2. Hydrogen production

Biomass gasification produces syngas, which is a gaseous mixture of H_2 , CO, CH_4 and CO_2 . Biomass gasification followed by water reforming of CH_4 to H_2 and CO (Eq. (3)), water–gas shift reaction of CO to H_2 and CO_2 (Eq. (4)) with catalysts such as copper–zinc, and CO_2 adsorption using an adsorbent such as CaO given in Eq. (5) can produce pure H_2 [20–23]. Adsorption can remove CO_2 from the gas stream [38]:

$$CaO + CO_2 \leftrightarrow CaCO_3.$$
 (5)

 CO_2 can be removed from the snygas after gasification or adsorbent can be added directly into a gasifier. Besides production of H₂ from syngas using the adsorption technology, it is possible for an adsorbent to sequester CO_2 from syngas [38,82].

4.3. Synthesis of Fischer–Tropsch fuels

A gas mixture of CO and H_2 can be used to produce hydrocarbons of variable chain length via the Fischer–Tropsch (FT) reaction:

$$CO + 2H_2 \rightarrow -CH_2 - +H_2O - 165 \text{ kJ mol}^{-1}$$
. (6)

The $-CH_2$ - is a precursor for long-chain hydrocarbons. Products made by the FT reaction are hydrocarbons of different lengths, which are an alternative to conventional diesel, kerosene and gasoline [93]. Cobalt is usually used as the catalyst for the FT synthesis at pressures from 20 to 40 bar and temperatures between 180 and 250 °C [26]. The FT has been used commercially to produce liquid fuels from coalderived syngas by Sasol in South Africa and natural gasderived syngas by Shell in Malaysia [26]. Tijmensen et al. [26] gave a comprehensive review on the technical feasibility and economics of an integrated biomass gasification and FT process for production of liquid fuels.

One of the technical issues for FT synthesis is the ratio of H₂ to CO, which should be close to 2:1 according to Eq. (6). Different gasification methods can produce a wide range of syngas compositions with H₂ to CO ratios varying between 0.45 and 2. Syngas produced by biomass gasification also contains a large amount of CH₄ and CO₂. A steam-reforming process is required to convert CH₄ to CO and H₂. A water-shift reaction may be necessary to adjust the H₂ to CO ratio by converting part of CO with steam to H₂ for FT synthesis if the ratio is too low. Another technical issue is the reduction of inert gases such as CO₂ and contaminants such as H₂S for the FT synthesis because the inert gases and contaminants can lower catalyst activity due to catalyst poisoning [26]. The production costs of FT fuels are currently higher than those of diesel. However, FT fuels contain little or no contaminants such as sulfur and aromatics compared with gasoline and diesel, which can lower pollutant emissions. Therefore, the long-term perspective for FT fuels is promising [26].

4.4. Synthesis of methanol and dimethyl ether from syngas

Methanol and dimethyl ether (DME) are promising clean liquid fuels because they are storable and would be alternatives to gasoline and diesel fuels [27,28]. Methanol also has been used widely to react with triacylglycerols for the production of biodiesel. Syngas is a mixture of H_2 , CO, CO₂ and CH₄, which can be used as a feedstock to synthesize methanol and DME. Methanol can be synthesized in CO or CO₂ hydrogenation as

$$CO + 2H_2 \rightarrow CH_3OH,$$
 (7)

 $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O. \tag{8}$

DME is synthesized by further dehydration of methanol:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O. \tag{9}$$

The molar ratios of H_2/CO and CO_2/CO should be optimized for the syntheses. To enhance the methanol and DME yields, it is also important to select a suitable catalyst such as $Cu/ZnO/Al_2O_3+Y-Al_2O_3$ [27] and $Cu/ZnO/Al_2O_3/Cr_2O_3+$ H-ZSM-5 [28].

4.5. Syngas fermentation for production of biobased products

Syngas can also be biologically converted into biobased products including organic acids, alcohols and polyesters [29-33]. Brown [29] gave an overview of syngas fermentation for production of bio-based products. Several bacteria have been investigated for their use of syngas as a source of carbon and energy for growth and biological production of a wide range of products. These bacteria include Butyribacterium methylotrophicum for butanol and ethanol [30], Clostridial bacteria for ethanol [31,32], photosynthetic bacteria for poly-3-hydroxybutyrate [33] and Rhodospirillus rubrum for H₂ and polyesters [34]. Biological conversion of syngas has several potential advantages over chemical catalysis of syngas. Most anaerobes for syngas fermentation are sulfur tolerant and not sensitive to the CO/H₂ ratio. Therefore, a biological conversion process does not require an expensive sulfur-gas cleaning process and strict control of the CO/H₂ ratio. Unlike a chemically catalytic process, a biological process is not operated under high temperature and pressure. Furthermore, product specificity of biocatalysts is higher than that of chemical catalysts [19]. However, relatively low rates of growth and production by anaerobes, difficulties in maintaining anaerobic conditions and mass transfer between gas phase and liquid phase, and product inhibition have been identified as the main barriers to commercializing syngas fermentation technology [35].

5. Conclusions

Gasification provides a competitive way to convert diverse, highly distributed and low-value lignocellulosic biomass to syngas for combined heat and power generation, synthesis of liquid fuels and production of hydrogen (H₂). Co-firing of syngas in existing pulverized coal and natural gas combustors has been successfully commercialized. However, more research is needed to improve syngas quality for its commercial uses in a high energy-efficient heat and power generator such as gas turbines or fuel cells, and the production of liquid fuels and H₂. Fluidized bed gasification with steam and indirect or external heat supply could provide a promising way to improve the syngas yield and quality. Catalysts are widely used not only for syngas cleaning but also for production of liquid fuels and H_2 from syngas. More research is needed to develop novel catalysts and supporting materials to improve the selectivity, activity, productivity and economy of a catalytic process for syngas cleaning and downstream utilizations.

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