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Hydrogen production by biomass gasification in supercritical water: A systematic experimental and analytical study

L.J. Guo [*], Y.J. Lu, X.M. Zhang, C.M. Ji, Y. Guan, A.X. Pei

State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi Province 710049, China

Abstract

Hydrogen production from biomass gasification in supercritical water is a new technology, which was developed in last two decades. Biomass energy of low quality can be converted to hydrogen energy of high quality by supercritical water gasification. Particularly, supercritical water gasification is an elegant way of wet biomass utilization. Up to now, many important progresses have been made in supercritical water gasification technology by the studies of researchers around the world. Since 1997, supercritical water gasification, which include reaction system, rule of biomass gasification and theory, have been studied in State Key Laboratory of Multiphase Flow in Power Engineering of Xi'an Jiaotong University. In this paper, we summarize the results from systematic experimental and analytical study on biomass gasification in supercritical water in our laboratory. Also, the development status and future prospect on supercritical water gasification is evaluated.

Keywords: Hydrogen production; Biomass gasification; Supercritical water

1. Introduction

Recently, due to the environmental considerations as well as the increasing demand for energy in the world, more attention has been paid to develop new energy sources, e.g. hydrogen, which may become an important fuel to be used as an energy carrier in the future for electric vehicles and electric power plants.

As is well known, hydrogen is renewable and found in many compounds such as water, fossil fuels, and biomass. Comparing with fossil fuel, biomass for hydrogen production can lead to zero CO_2 emission in a very short life cycle period since carbon in the form of CO_2 and energy are fixed by photosynthesis during biomass growth [1].

Biomass has always been a major source of energy for mankind, and it contributes about 10–14% of the world's energy supply today [2]. Hydrogen typically makes up about 6% by weight of dry biomass. To obtain hydrogen from biomass, pyrolysis or gasification can be applied, which typically produces a gas containing 20% hydrogen by volume, which can be further steam-reformed to make higher-purity streams for various fuel cells.

However, a large portion of biomass wastes is wet biomass containing up to 95% water and this wet biomass causes high drying costs if classical gas-phase gasification process is used [3]. Hydrogen production by biomass gasification in supercritical water (SCW) is a promising technology for utilizing high moisture content biomass.

SCW possesses properties very different from those of liquid water. The dielectric constant of SCW is much lower, and the number of hydrogen bonds is much lower and their strength is much weaker. As a result, SCW behaves like many organic solvents so that organic compounds have complete miscibility with SCW. Moreover, gases are also miscible in SCW, thus a SCW reaction environment provides an opportunity to conduct chemistry in a single fluid phase that would otherwise occur in a multiphase system under conventional conditions [4]. Gasification of biomass in SCW have many advantages such as high gasification efficiency, high molar fraction of hydrogen, and no need of a drying process for wet biomass as compared to other biomass conversion methods.

The earliest report on supercritical water gasification (SCWG) of wood is that of Modell and co-workers [5,6]. In 1978, the author issued a patent and reported the gasification of glucose and maple sawdust with a catalyst composition that

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[*] Corresponding author. Tel.: +86 29 8266 3895; fax: +86 29 8266 9033.
E-mail address: lj-guo@mail.xjtu.edu.cn (L.J. Guo).

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promotes hydrogenation, reforming and cracking in water in the vicinity of its critical state.

Elliott and co-workers [7–13], from PNNL (Pacific Northwest National Laboratory), conducted a lot of studies on biomass gasification in a high pressure aqueous environment. They used nickel catalysts for organic wastes gasification in sub- and SCW in a batch reactor [8] for 1–2 h running time at 623 K and 20 MPa, and a CH_4-rich gas was obtained.

Yu et al. [14] from Hawaii University presented studies of glucose gasification at 873 K, 34.5 MPa with a 30 s residence time. Following this work, Xu et al. [15] gasified glucose and other organic compounds at 873 K, 34.5 MPa with different carbon catalysts. Antal et al. [16] used carbon-based catalysts for high concentration biomass gasification in SCW. The gas formed was mainly composed of hydrogen and carbon dioxide, and the hydrogen yield could be more than 100 g/kg dry biomass. However, they observed reactor plugging caused by the accumulation of chars and tars and occurring several hours after the feedstock injection.

Minowa and co-workers [17–19] found that biomass can be gasified in hot-compressed water (623 K, 20 MPa) with reduced nickel catalyst and sodium carbonate. Furthermore, they showed that the amounts of residual chars and tars were significantly decreased and that at 673 K with a nickel catalyst [18].

Some Japanese teams were interested by the process as well and conducted some fundamental or technological studies. Yoshida and his coworker [20,21] have studied the SCWG in a batch reactor at 673 K and 25 MPa of the three main components of biomass, i.e. cellulose, hemi-cellulose and lignin. They highlighted, in particular, the difficulty to gasify lignin and its influence on the gasification of the other compounds. Osada et al. [22] have conducted the gasification of lignin and cellulose at 673 K in SCW. They found that the catalytic conversion of biomass with ruthenium in SCW is an efficient method for biomass gasification at temperatures of $\sim$673 K.

In 2001, Lin et al. [23] proposed a new H_2 production process named the HyPr-RING process, which used calcium oxide (CaO) or/and calcium hydroxide $Ca(OH)_2$ as the adsorbent of carbon dioxide to improve the hydrogen fraction in product gas. In 2002, Watanabe et al. [24] reported that zirconia (ZrO_2) was effective for H_2 production from biomass in supercritical water.

In Forschungszentrum Karlsruhe, Schmieder et al. [25] found that wet biomass and organic wastes were completely gasified by addition of KOH or K_2CO_3 at 873 K and 25 MPa in 2000, forming a H_2-rich gas containing CO_2 as the main carbon compound. Later, Kruse and coworkers [26–30] treated both model compounds and real wastes in batch and continuous reactors in order to synthesize a hydrogen rich gas in SCW.

In 2002, Cortright et al. [31] from University of Wisconsin reported that hydrogen could be produced from sugars and alcohols at temperatures near 500 K in a single-reactor aqueous-phase reforming process using a platinum-based catalyst. After that, a tin-promoted Raney-nickel catalyst was used for hydrogen production and the performance of this non-precious metal catalyst compares favorably with that of platinum-based catalysts for production of hydrogen from ethylene glycol, glycerol, and sorbitol [32]. Following these works, several researches have studied the reforming of biomass-derived sugars by aqueous phase reforming and some significant progresses have been made [33–39].

More recently, Williams and Onwudili [40] gasified glucose, as biomass model compound, under sub-critical and supercritical water, and obtained the composition of products from glucose gasification in SCW. A reaction mechanism was proposed that described a possible reaction route for the formation of characteristic compounds found in the oils. Also, two review papers [41,42] were published for evaluating the development of SCWG technology.

Some theoretical studies of biomass gasification in SCW were also conducted. Tang and Kitagawa [43] developed a thermodynamic model to estimate equilibrium composition for SCWG of biomass. Feng et al. [44] from Delft University of Technology carried out phase equilibria, driving force and exergy analysis for two biomass conversion processes, the hydrothermal upgrading (HTU) process and SCWG process. Matsumura [45] evaluated the energy, environmental, and economic aspects of two wet biomass gasification processes, namely the SCWG and biomethanation. Considering the costs of treating wastewater and fermentation sludge, SCWG can be competitive with biomethanation. Yoshida et al. [46] compared efficiency and CO_2 emissions between various methods of biomass energy conversion from the viewpoint of life-cycle evaluation.

Since 1997, a series of studies on hydrogen production from biomass in SCW have been conducted by the group of SKLMF, Xi'an Jiaotong University, China. Early, an miniature plant of continuous operation tube flow reactor [47] was designed for the wall temperature of reactor up to 700 °C and working medium pressure up to 35 MPa, and a patent [48] was issued. After that, a bench-scale apparatus and a batch autoclave reactor were developed in SKLMF. A series of experimental investigation [49–53] on model compounds and real biomass gasification in SCW were conducted in three apparatuses. Also, some theoretical analyses of biomass gasification in SCW were preformed by Hao et al. [54], Yan et al. [55] and Lu et al. [56].

In this paper, we summarized the experimental and theoretic results from biomass SCWG in SKLMF. The progress and status on hydrogen production by biomass gasification in SCW were also reviewed.

2. Thermodynamic considerations

The biomass gasification in SCW is a complex process, but the overall chemical conversion can be represented by the simplified net reaction:

$$CH_xO_y + (2-y)H_2O \rightarrow CO_2 + (2-y+x/2)H_2 \tag{1}$$

where x and y are the elemental molar ratios of H/C and O/C in biomass, respectively. The reaction product is syngas whose quality depends on x and y. The reaction (1) is an endothermic.

It is known from the reaction (1) that water is not only the solvent but also a reactant and the hydrogen in the water is released by the gasification reaction.

Eq. (1) summarizes the overall reaction, but a group of competing intermediate reactions, which are essential for the successful gasification, need to be considered as follows:

$$\text{Steam reforming}: \quad CH_xO_y + (1-y)H_2O \rightarrow CO + (1-y+x/2)H_2 \qquad (2)$$

$$\text{Water-gas shift}: \quad CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (3)$$

$$\text{Methanation}: \quad CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad (4)$$

The objective of biomass gasification in SCW is hydrogen production, so reaction (4) must be restrained and CO reacting with water to form CO_2 and H_2 is desired in the reaction (3).

Chemical equilibrium of wood sawdust gasification in SCW was predicted by thermodynamic calculation code [55], which was based on minimizing Gibbs free energy. In order to simplify the problem, nitrogen, sulfur and other impurities contained in the raw materials are assumed to be neglected, so wood sawdust is represented by a general formula of $CH_{1.35}O_{0.617}$. The predicted results show that the product gas includes mainly H_2, CH_4, CO and CO_2. Fig. 1 shows the equilibrium gas yield as a function of reaction temperature at 25 MPa and a temperature range of 673–1073 K with 5 wt% biomass content. At the chemical equilibrium state, the yields of H_2 and CO_2 increase with the increasing temperature, but the yield of CH_4 decreases sharply. The equilibrium CO yield is very small, and it is about10^{-3} mol/kg dry biomass. As temperature increases from 673 to 1073 K, the CO yield also increases and then drops down. The maximum CO yield is reached at about 823 K. Hydrogen yield increases at a low speed at rather high temperature. When the reaction temperature is above about 923 K, biomass gasification goes to completion and the equilibrium gas product consists of H_2 and CO_2 in a molar ratio equal to $(2 - y + x/2)$, so the gasification process can be represented by Eq. (1). The maximal equilibrium H_2 yield of 88.623 mol/kg dry biomass is obtained. Consequently, from the viewpoint of thermodynamics, higher temperature is not necessary to hydrogen production.

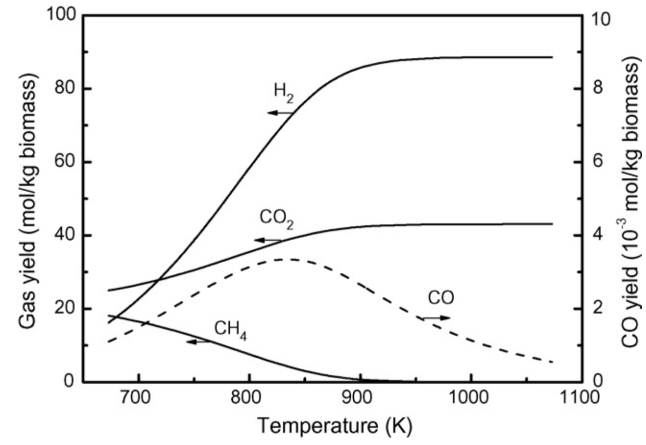

Fig. 1. Equilibrium gas yields as a function of temperature for biomass gasification at 25 MPa with 5 wt% dry biomass content.

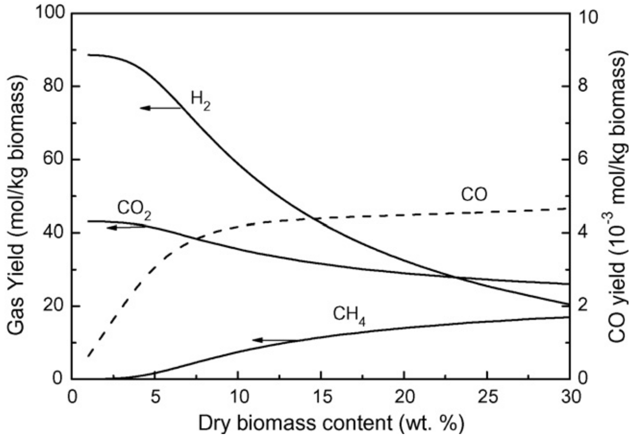

Fig. 2. Equilibrium gas yields in the reactor as a function of dry biomass content for biomass gasification at 25 MPa, 873 K.

Fig. 2 displays the effect of feedstock concentration in the reactor on equilibrium gas yield at 873 K and 25 MPa. The product gas consists of mostly H_2 and CO_2 when biomass feedstock with low concentration is gasified, but the CH_4 yield is very high when the high concentration feedstock is gasified. High reaction temperature is necessary in order to achieve high H_2 yield with high concentration feedstock gasification. Fig. 3 shows the effect of pressure on equilibrium gas yield at 873 K with 5 wt% biomass content. It can be seen from Fig. 3 that the pressure has no significant effect on equilibrium gas yield.

3. Apparatus and experimental procedures

3.1. Apparatus

There are many reactor systems for biomass gasification in SCW, such as tubular reactor [14–16,25,26], batch reactor [8,9,18–24,40], continuous stirred tank reactor [3,27–30], fluidized bed micro-reactor [57], and so on. At present, three

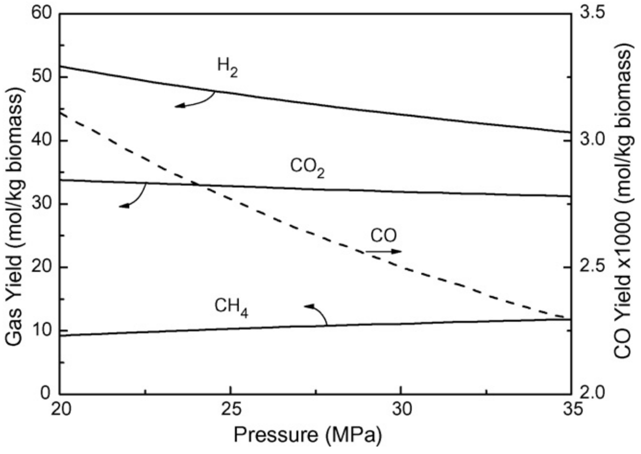

Fig. 3. Equilibrium gas yields in the reactor as a function of pressure for biomass gasification at 773 K with 5 wt% dry biomass content.

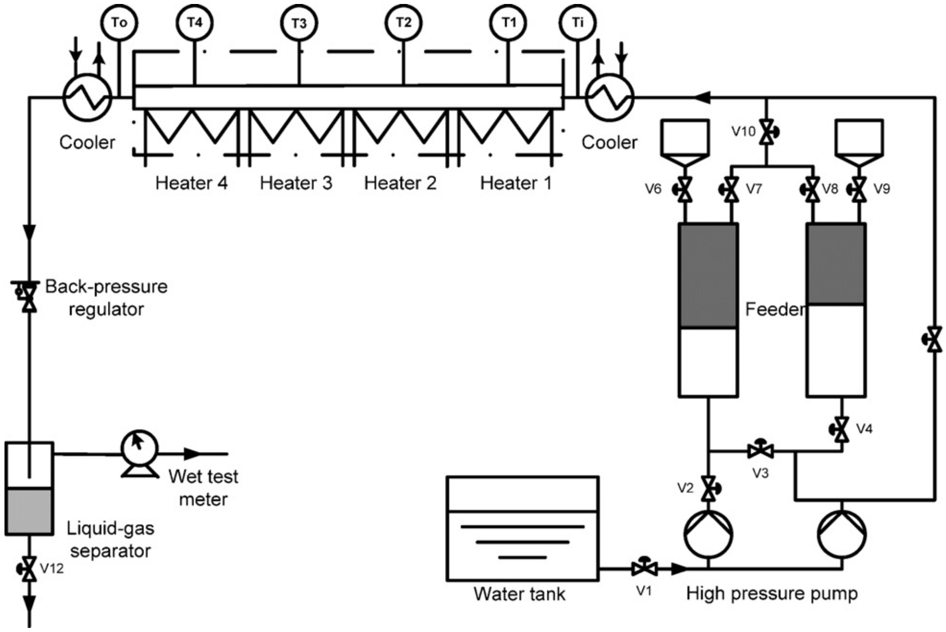

Fig. 4. Schematic diagram of the miniature plant [53].

reactor systems are running and a SCW fluidized reactor is being developed in SKLMF.

Fig. 4 displays schematic representation of the miniature plant. It is designed for the temperature up to 700 °C and pressure up to 35 MPa. The maximum throughput capacity of the system is 1 kg/h. Two kinds of reactor were used in our Laboratory. The reactor #1 was made of special alloy tube with the inner diameter of 9 or 6 mm and reactor #2 was made of Hastelloy C-276 tubing with 13.4 mm o.d. × 7.7 mm i.d. The reactors were heated by some electrical heaters that are coiled around the outer surface of the reactor tube. The unique feature of the experimental apparatus is its ability to realize the overall continuous reaction by operating the valves. There are two feed tanks in the experimental system. One tank can be kept at high pressure for reaction and the other can be fed with the material at atmospheric pressure simultaneously. Both the feeder and the reactor were pressurized at the beginning of a run. Water was pumped into the reactor tube directly and pressurized. The reactor was heated to bring up the system to the set temperature and pressure. When the temperature and pressure reached the desired values, the feeder was connected to the reactor. Then water flowing to the reactor was terminated and that to the feeder was initiated. A back-pressure regulator was used to reduce the exit pressure of product fluid from the high pressure to atmospheric pressure.

Fig. 5 displays the bench-scale apparatus in SKLMF. The reactor is made of special stainless steel with 9 mm inner diameter, and designed for temperatures up to 650 °C and pressures of 35 MPa. The maximum throughput capacity of the system is 16 kg/h. The Bench-scale apparatus is developed

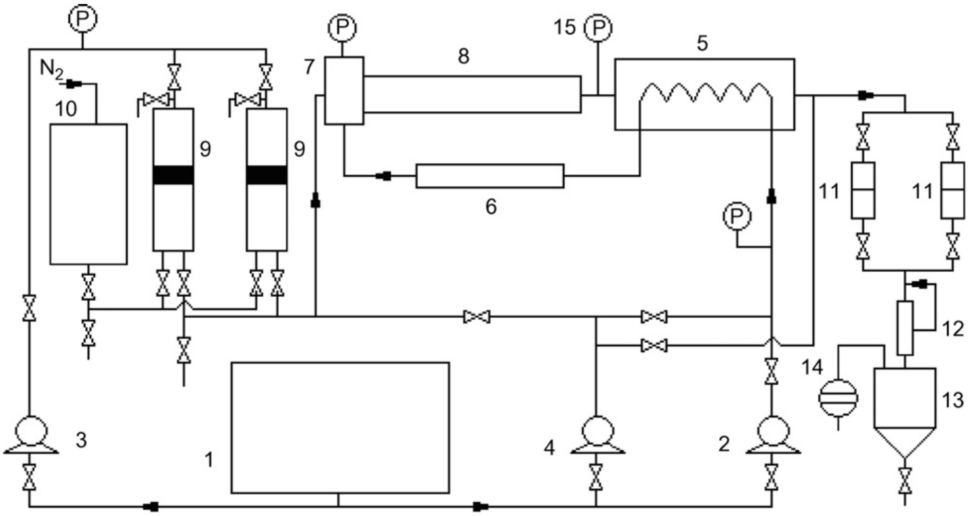

Fig. 5. Schematic diagram of bench-scale apparatus: (1) Water tank; (2) Preheated water pump; (3) Feed pump; (4) Wash pump; (5) Cooler and exchanger; (6) Preheater; (7) mixer ; (8) Reactor; (9) Feeder; (10) Feed tank; (11) Filter; (12) Back-pressure regulator; (13) Gas-liquid separation; (14) Gas meter; (15) Pressure transducer.

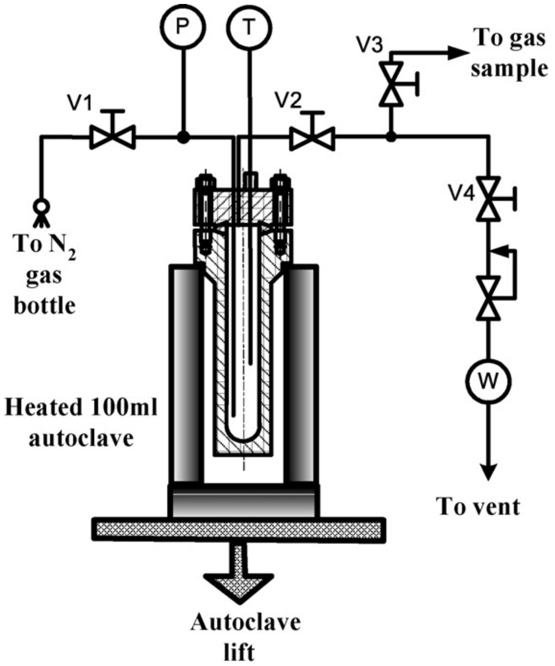

Fig. 6. The autoclave schematic diagram [51].

based on the miniature plant. As compared to the miniature plant, the throughput of bench-scale apparatus is larger. A high heating rate of biomass was attained by mixing the feedstock with preheated water. Also, the thermal can be recycled by the exchanger of the reactor exit and the energy efficiency is advanced.

Fig. 6 displays autoclave reactor. The autoclave is fabricated from 316L stainless steal with 140 ml and the lines of purging and sampling are made of 1Cr18Ni9Ti stainless steal. The system was operated at temperatures up to 650 °C and pressures up to 35 MPa. The pressure was monitored by means of pressure transducer system in the line of N_2 purging. The temperature inside the reactor was monitored by type K thermocouple. The autoclave was heated by 1.2 kW temperature controlled electric furnace and cooled by water. After cooling down to room temperature, the product gas is sampled and measured using a wet test meter. Then the autoclave is demounted, and the reaction mixture is recovered for separation. The aqueous phase is separated by washing the reaction mixture with water and by filtration. The detailed experimental procedure was described in Ref. [51].

3.2. Feedstock preparation

For water-soluble feedstock such as glucose, it is easy to transport at high pressure. However, it is difficult for continuous feeding of the real biomass feedstock at high pressure. Antal et al. [16] suspended real biomass in a starch gel, and delivered the mixture to the reactor by the feeding system which consists of a HPLC pump, a cylinder, a movable piston and two end-caps. Hong and Spritzer [58] suspended biomass is in a sodium carboxymethylcellulose (CMC) gel, and delivered the feedstock to the reactor via a slurry pump. The maximum pumpable concentration of wood dust slurries is in the range of 10–15 wt% dry basis. Matsumura's group [42] used a hydrothermal pretreatment to successfully deliver cabbage, a model material for herbaceous biomass.

In this work, various biomass model compounds (cellulose, xylan and lignin) and real biomass feedstocks including wood sawdust, rice straw, rice shell, wheat stalk, peanut shell, corn stalk, corn cob and sorghum stalk are used. The continuous feeding of multi-phase mixture of real biomass feedstock is realized by using CMC [48,49]. Real biomass is ground with plant mill to 40–80 mesh before it is mixed with CMC. Water is added to achieve the desired solids loading and the mixture is continually stirred until it is homogeneous. Generally, the concentration of CMC was about 2–3 wt%.

3.3. Sample analysis

Analyses of the product gas are accomplished with a Hewlett-Packard model 6890 gas chromatograph with thermal conductivity detectors. The carrier gas is helium and its flow rate is 10 ml min^{-1}. A Carbon-2000 capillary column is used, operating at 333 K for 2 min, followed by a 30 K min^{-1} ramp to 423 K, and hold 2 min at 423 K. The total carbon contents of the liquid phase were determined using Elemental High TOCII.

4. Gasification of different biomass materials

Gasification of biomass in SCW shows far-ranging applicability of material, and a large number of carbonaceous organic compounds can be gasified in SCW. The feedstocks for hydrogen production in SCW mostly include model compounds, real biomass and organic wastes.

Glucose and cellulose are the most common biomass model compounds. Cellulose is one species of the biomass. Glucose is the primary product of cellulose hydrolysis around the critical point of water [59]. A large number of experimental investigations on glucose [14,15,25,29,40,49] and cellulose [17–19,51] gasification in SCW were conducted. Also, Yoshida and co-workers [20,21] gasified cellulose, hemi-cellulose and lignin mixtures at 623 K and 25 MPa. Kruse et al. [26] gasified pyrocatechol, which is used as a model compound for lignin in biomass and for aromatic compounds in wastewaters, in SCW. Schmieder et al. [25] gasified successfully different model compounds (glucose for cellulose, catechol and vanillin for lignin, glycine for proteins) for hydrogen production in SCW.

Real biomass, such as wood sawdust, is usually used as gasification material. Minowa et al. [60], Antal et al. [16], Xu and Antal [61], Schmieder et al. [25] and Lin et al. [23] researched on wood sawdust gasification in SCW. Antal and co-workers [62,63] gasified different real biomass, including hyacinth, sugar cane bagasse, sewage sludge, simulated biodiesel waste product, cornstarch, potato waster, banagrass, onion, and poplar wood sawdust in SCW.

Sealock et al. [7] gasified many real biomass feedstocks including herbaceous (napier grass, sorghum, sunflower and corn stover), aquatic (hyacinth and kelp) and processed wastes (potato wastes, spent-grain, grape, pomace, cheese whey, coffee

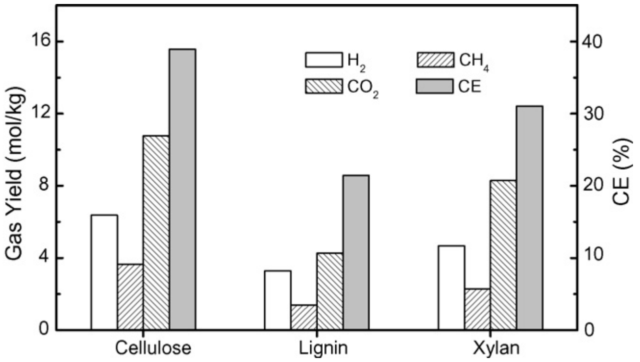

Fig. 7. Comparison of gas yields for gasification of cellulose, xylan and lignin in the batch reactor (temperature, 723 K; pressure, 27.5 MPa; biomass, 1 g; water, 11 g; K_2CO_3, 0.1 g; heating time, 30 min; reaction time, 20 min. CE (carbon efficiency) is define as the total carbon in the product gas/the total carbon in the dry feed).

grounds, fish processing waste, etc.) in high-temperature liquid water. Gasification results showed a wide range of reactivity/ convertability based on the composition of feedstocks. Feedstocks containing high cellulose content showed a high reactivity similar to cellulose. The reactivity of most terrestrial biomasses will reduce with the increase of lignin in the feedstock. Aquatic feedstocks such as kelp and hyacinths exhibited similar rates of reaction, but produced a large fraction of unreacted material. Residues from food processing operations generally react at a slower rate but nearly to completion.

Fig. 7 is the comparison of gas yields for gasification of cellulose, xylan and lignin with K_2CO_3 with the batch reactor in SKLMF. K_2CO_3 content catalyzing the gasification reaction resulted in low carbon monoxide content in the product gas. It can be seen from Fig. 7 that cellulose is easier to gasify than xylan and lignin, and lignin is the most difficult to gasify. The hydrogen yield, methane yield and carbon efficiency (CE) of cellulose gasification are 6.367 mol/kg, 3.639 mol/kg and 38.95%, respectively. The hydrogen yield, methane yield and CE of lignin gasification are only 3.289 mol/kg, 1.363 mol/kg and 21.44%, respectively. Consequently, complete gasification of lignin is the sticking point of the real biomass gasification in SCW.

Fig. 8 shows the results of different real biomass (wood sawdust, rice straw, rice shell, wheat stalk, peanut shell, corn stalk, corn cob and sorghum stalk) gasification under the same conditions in a miniature plant. It can be seen from Fig. 8(a) that the gas compositions for different biomass gasification are nearly identical. The molar fraction of hydrogen is about 40% while the molar fraction of CO is less than 1%. The K_2CO_3 content in biomass and the high excess water maybe resulted in the low CO content. The molar fraction of CH_4 is more than 10% here, but it is not in agreement with the chemical equilibrium calculation. CH_4 is possibly mainly formed by free-radical reactions [27]. Also, it can be seen from Fig. 8(b) that certain biomass components such as wheat stalk, corn cob and sorghum stalk are easier to gasify than the other. The reason for difference of various biomass gasification is that the cellulose, lignin and hemi-cellulose contents of biomass is different, and the lignin content of wheat stalk, corn cob and sorghum stalk is maybe lower than that of other biomass. The unconverted total organic carbon (TOC) in liquid effluent is high. It is said that a portion of biomass are converted to liquid product instead of gaseous products.

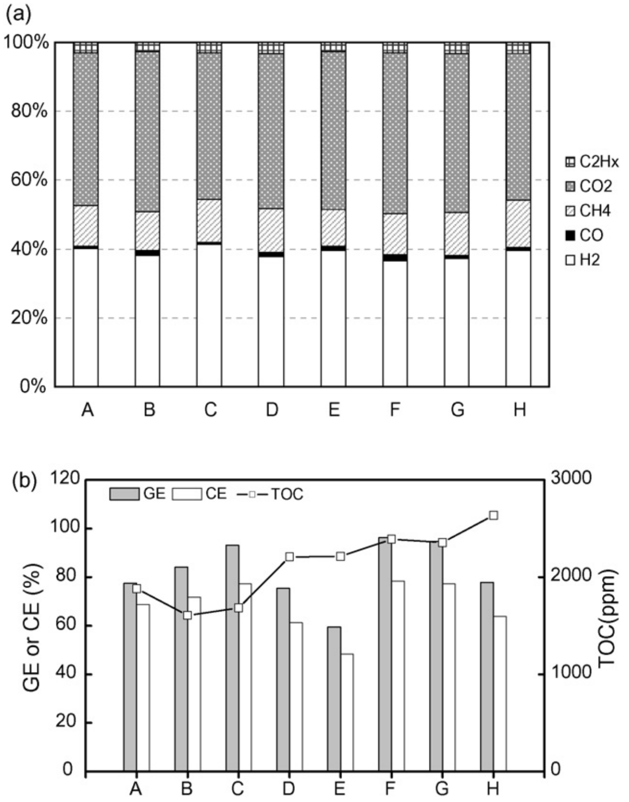

Fig. 8. Comparison of gas composition (a), GE, CE and TOC (b) for gasification of various biomass feedstocks in SCW [53] (temperature, 923 K; residence time, 27 s; pressure, 25 MPa; feedstock, 2 wt% biomass + 2 wt% CMC; (A) rice straw; (B) rice shell; (C) wheat stalk; (D) peanut shell; (E) corn stalk; (F) corn cob; (G) sorghum stalk; (H) wood sawdust. GE (gasification efficiency) is defined as the total mass of the product gas/the total mass of the dry feed.).

5. Operation conditions

5.1. Temperature

Temperature shows a significant effect on biomass gasification in SCW, particularly when no catalyst or less-effective catalysts are present. Xu et al. [15] reported that 1.0 M glucose was gasified completely at 873 K, and yellow liquid effluent and a thin layer of a dark brown oil-like tar was observed as the temperature fell below 853 K. For the gasification of feedstocks with high biomass content, the temperature of 923–1073 K is needed [16]. The higher temperature drove the methane steam-reforming reaction to increase hydrogen yield [7]. Also, high temperature will achieve high reaction rate and gasification efficiency. Karagoz et al. [64] reported that biomass had started to be converted to liquid productions, such as 2-furancarboxaldehyde, 2-methoxy phenol and so on, at 453 K by hydrothermal treatment. These liquid products cannot be gasified at higher temperature, which will cause reactor plugging. As a result, faster heating rate of

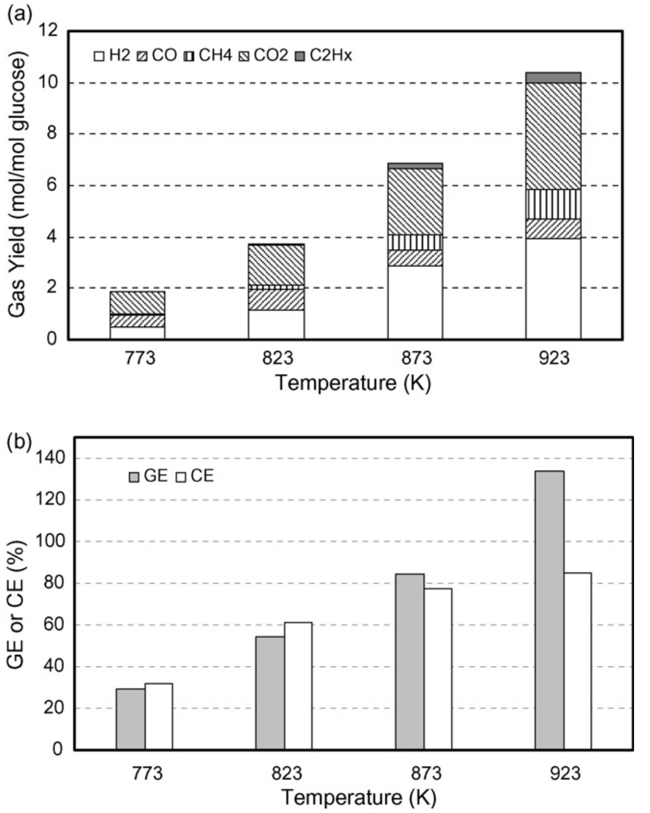

Fig. 9. Gasification of 0.1 M glucose at 25 MPa with various temperatures in the miniature plant using reactor #1: (a) gas yield; (b) GE and CE [49].

reaction stream is necessary for biomass to completely gasify in SCW. Figs. 9 and 10 display the effects of temperature on glucose and lignin gasification in SCW. With an increasing temperature, hydrogen yield, GE and CE all increase sharply. Also, it can be seen from Fig. 10 that the CE of 1.5 wt% lignin gasification at 923 K is only 40.96%, but CE of 3 wt% lignin gasification above 973 K is excess of 90%. Consequently, the temperature of about 973 K or higher is necessary for complete gasification of lignin.

5.2. Pressure

Pressure shows a complex effect on biomass gasification in SCW. The properties of water, such as density, static dielectric constant and ion product, increase with pressure. As a result, the ion reaction rate increases and free-radical reaction is restrained with an increase of pressure. Hydrolysis reaction plays a significant role in biomass gasification in SCW, but it requires the presence of H^+ or OH^-. With increasing pressure, the ion product increases, and therefore the hydrolysis rate also increases. Also, a high pressure is in favor of water–gas shift reaction, but reduce decomposition reaction rate. As shown in Fig. 11, pressure has no significant effect on sawdust gasification. The hydrogen yield, GE and CE is not monotonic functions of pressure when the pressure is near the critical pressure, but the hydrogen yield, GE and CE increase a little as pressure increases from 25 to 30 MPa. Demirbas [65] also found that hydrogen yield increase as pressure increase from 23

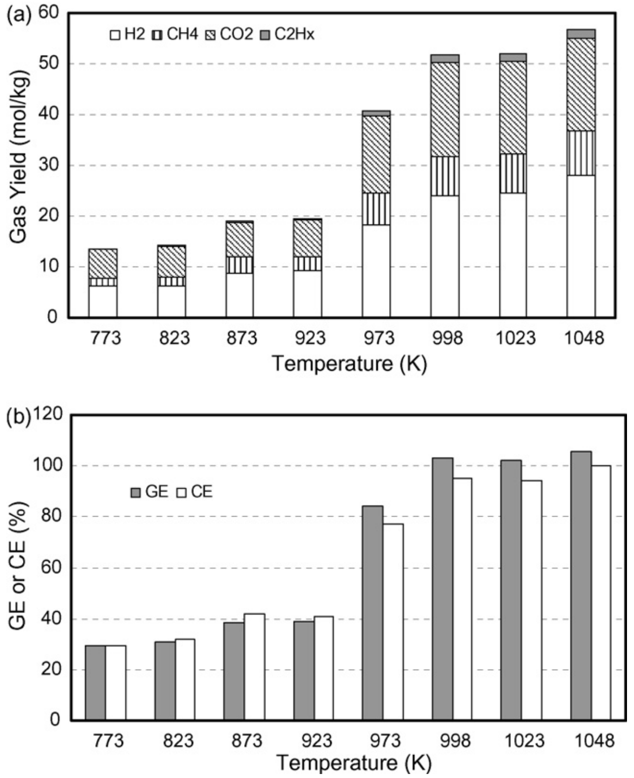

Fig. 10. Effect of temperature on lignin gasification at 25 MPa in the miniature plant: (a) gas yield; (b) GE and CE (when the temperature is 773–923 K, the feedstock with 1.5 wt% lignin content is gasified using reactor #1 and the flow rate is 6 g/min; when the temperature is 973–1048 K, the feedstock with 3 wt% lignin content is gasified using reactor #2 and the flow rate is 6 g/min).

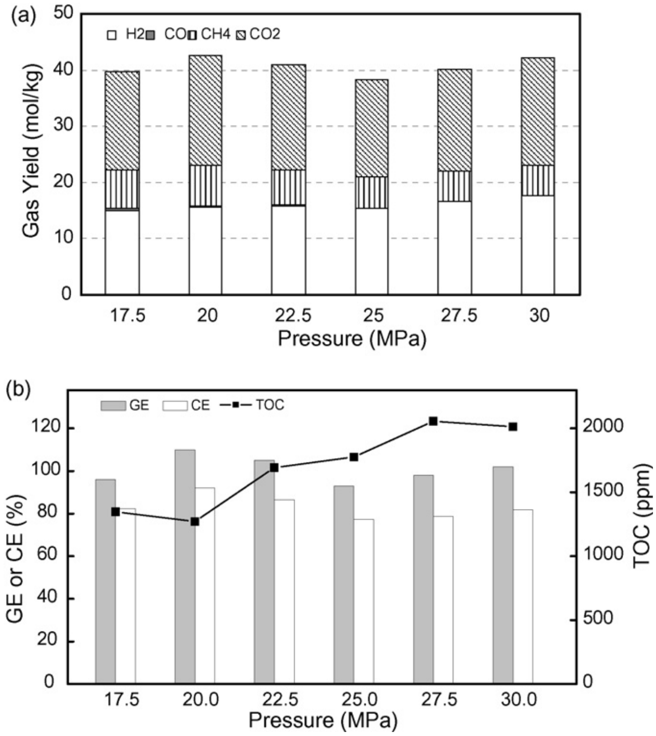

Fig. 11. Effect of pressure on sawdust gasification in SCW in the miniature plant using reactor #1: (a) gas yield; (b) GE, CE and TOC [53] (temperature, 923 K; residence time, 27 s; feedstock, 2 wt% wood sawdust + 2 wt% CMC).

to 48 MPa with fruit shell gasification in SCW using an autoclave. Also, Fig. 11 shows that the unconverted TOC value increases with increase of the pressure. It is said that high pressure favors the formation of liquid product.

5.3. Residence time

From the viewpoint of thermodynamics, biomass can be gasified completely in SCW with a formation of H_2 and CO_2. The gasification reaction was controlled by kinetics and a few seconds was required to complete the gasification process. Antal et al. [66] gasified 0.1 M glucose at 34.5 MPa, 873 K with various residence times. He found that glucose can be gasified quickly and the CE of 100% was achieved with 28 s residence time. Lee et al. [67] reported the yields of all the gases remained almost constant at 973 K, being independent of the residence time except for the shortest residence time of 10.4 s when the 0.6 M glucose was gasified at 28 MPa. Fig. 12 displays the effect of increasing residence time on gasification of wood sawdust at 923 K and 25 MPa. As shown in Fig. 12(a), it is obvious that the H_2 and CH_4 yields increase sharply as the residence time increases from 9 to 46 s. At the same time, the CO yield has a tendency to decrease with increasing residence time. Fig. 12(b) shows that the GE and CE increase with increasing residence time but the unconverted TOC in the liquid effluent decreases.

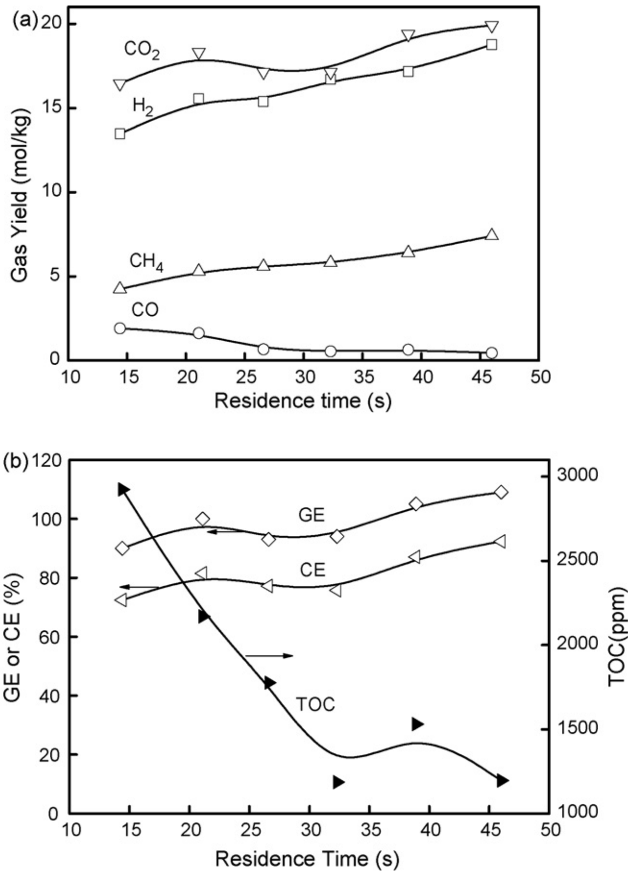

Fig. 12. Effect of residence time on wood sawdust gasification in the miniature plant: (a) gas yield; (b) GE, CE and TOC [53] (temperature, 923 K; pressure, 25 MPa; feedstock, 2 wt% wood sawdust + 2 wt% CMC).

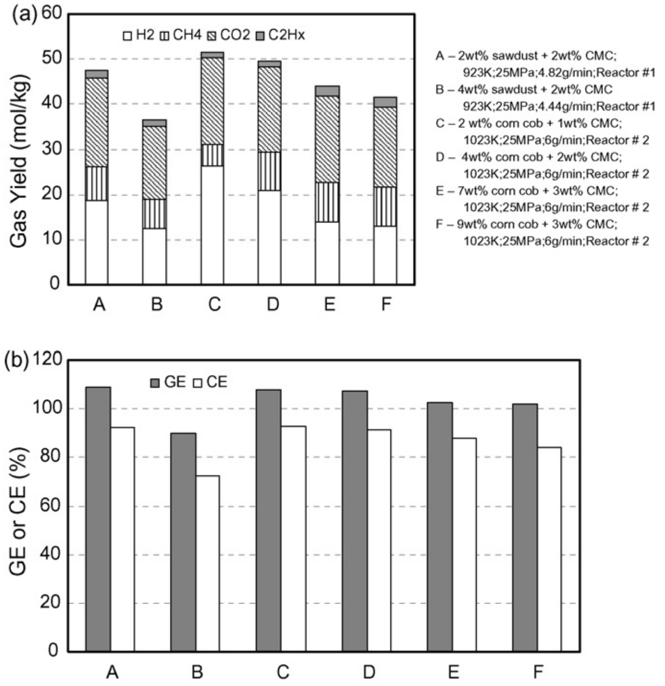

Fig. 13. Gasification of feedstock with different biomass content in SCW: (a) gas yield; (b) GE and CE.

5.4. Concentration

Gasification of feedstock with high biomass content is more difficult than that with low biomass content. Fig. 13 compares results from the gasification of feedstock with different biomass content. As shown in Fig. 13, hydrogen yield, GE and CE decrease with increasing feedstock concentration. Also, it can be seen from Fig. 13(b) that the CE was 84.04% for gasification of feedstock with 12 wt% (9 wt% corn cob + 3 wt% CMC) biomass content at 1023 K, but the CE was 72.3% for gasification of feedstock with 6 wt% (4 wt% sawdust + 2 wt% CMC) biomass content at 923 K. Thus, it can be seen that a high reaction temperature is necessary for high concentration feedstock to complete gasification in SCW, which is consistent with the thermodynamic calculation.

5.5. Addition of oxidizer

Biomass gasification in SCW is an endothermic reaction, so the process requires the addition of heat to drive the chemistry. Generally, heat is supplied to the reactor by the external heat resource, but exergy and energy efficiency are obtained because of low heat transfer efficiency. Also, heating quickly and complete gasification of biomass are difficult to achieve. Biomass can be oxidized by oxygen in SCW to form CO_2 and H_2O:

$$CH_xO_y + (1 + x/4 - y/2)O_2 \rightarrow CO_2 + x/2H_2O \quad (5)$$

The oxidization reaction is an exothermic reaction. Consequently, biomass can be gasified with addition of less than stoichiometric quantities of oxygen and the reactor gets its heat from the in situ exothermic oxidation reaction. High heat transfer efficiency and gasification efficiency are gained by the interior heat transfer in the reactor. Matsumura's group tested the effect of partial oxidation on SCWG at 673 K and 25 MPa [33]. They successfully improved the gasification efficiency by adding hydrogen peroxide, but the cold gas efficiency decreased when the hydrogen peroxide concentration was too high. Yoshida [68] have developed a new flow reactor system that smoothly gasifies glucose and glucose–lignin mixture solution with addition of oxidizer at 673 K, 25 MPa. The reactor system consists of three continuous reactors, which are a pyrolysis reactor, an oxidation reactor, and a catalytic reactor. The results indicated that this three-reactor system is promising for low-temperature (i.e., around 673 K) biomass gasification in SCW. Hong and co-workers [58,69] established a versatile pilot plant for exploring gasification in SCW at the General Atomics' facility in San Diego. Preliminary testing of the SCW partial oxidation process has found hydrogen yields of about 10 g per 100 g of feed, comparable to those found in prior laboratory-scale work carried out at the University of Hawaii [16]. Fig. 14 shows the effects of oxygen addition on equilibrium gas yield at 25 MPa with various temperatures. From Fig. 14, it can be seen that H_2 and CH_4 yields at chemical equilibrium state decrease with the increasing amounts of oxygen addition under the same temperature and pressure, and it is easy to know that CO_2 yield increases.

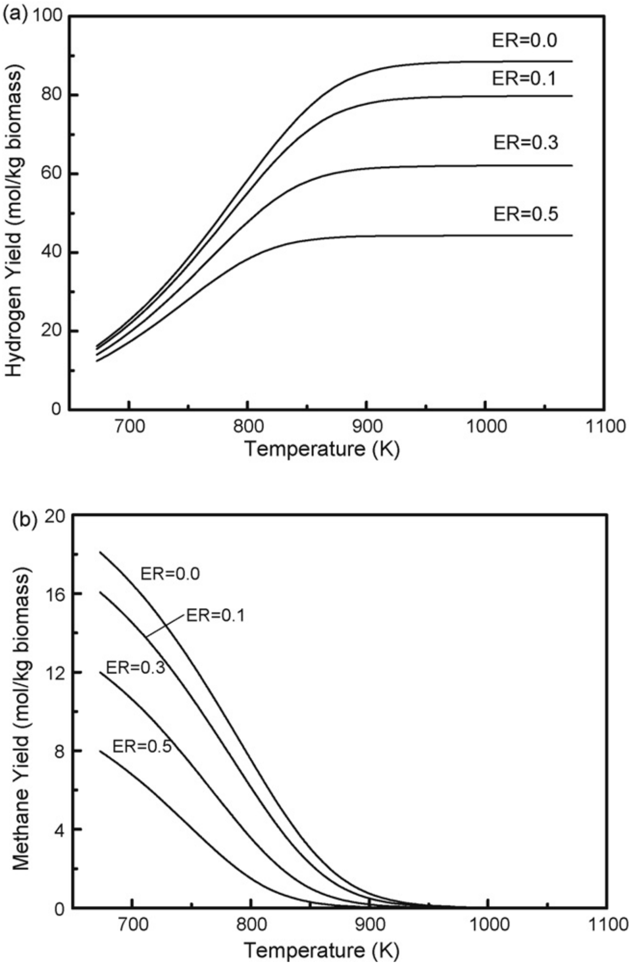

Fig. 14. The equilibrium hydrogen yield (a), methane yield (b) as a function of reaction temperature with different oxygen equivalence ratio [56] (equivalence ratio (ER) represents the amount of oxygen addition, defined by ER = (weight oxygen/weight dry biomass)/(stoichiometric/biomass ratio). The dry biomass content in the reactor is 5 wt% and the reaction pressure is 25 MPa).

6. Catalysts

There are a lot of catalysts used for biomass thermal chemical gasification and Sutton et al. [70] published a review of literature on catalysts for biomass gasification. However, the catalyst for SCWG will be different from that for the conventional gasification because of the different operating conditions, e.g. pressure values for the purpose (hydrogen production instead of syngas) and the specificities of the supercritical medium [41]. There are four types of catalysts, including activated carbon, metal, metal-oxide and alkali, used for SCWG in the literature.

Generally, alkali, such as NaOH, KOH, Na_2CO_3, K_2CO_3 and $Ca(OH)_2$, is used as a catalyst or promoter for biomass gasification in SCW. Minowa used Na_2CO_3 as a catalyst with cellulose decomposition in sub-critical water. Sinag et al. [28,29] gasified glucose in SCW with 0.5 wt% K_2CO_3. Kruse et al. [26] conducted gasification of different organic compounds in SCW in the presence of KOH. Also, Lin et al. [23], Wang and Takarada [71] and Sato [72] gasified coal and other organic compounds in SCW with addition of $Ca(OH)_2$ or $Ca(OH)_2$ mixed NaOH.

Xu et al. [15] used carbon-based catalysts, such as coal activated carbon, coconut shell activated carbon macadamia shell charcoal and spruce wood charcoal, for organic compounds gasification in SCW. The feedstocks included glycerol, glucose, cellobiose and whole biomass feedstocks. Complete conversions of these feedstocks were achieved at 873 K, 34.5 MPa. Subsequently, Antal et al. [16] gasified completely the high concentration biomass feedstocks above 923 K with carbon-based catalyst in SCW. The gas formed was mainly composed of hydrogen and carbon dioxide, and the extraordinary hydrogen yield could be more than 100 g/kg of dry biomass.

Nickel is a metal catalyst that is usually employed not only for the conventional gasification [70], but also for SCWG. Elliot et al. [8] tested several different forms of nickel catalysts at 623 K and 17–23 MPa using a batch reactor, and the product of CH_4-rich gas was obtained. Minowa and co-workers [17–19] studied the effect of a reduced nickel catalyst on cellulose decomposition in hot-compressed water. He found that the nickel catalyst catalyzed the steam reforming of aqueous products and the methanation reaction. Some noble metal catalysts were used for biomass gasification in SCW. Sato et al. [73] gasified alkylphenols as lignin model compounds in the presence of supported noble metal catalysts in SCW at 673 K. The activity of the catalyst was in the order of Ru/α-alumina > Ru/carbon, Rh/carbon > Pt/α-alumina, Pd/carbon, and Pd/α-alumina. Osada et al. [22] gasified lignin and cellulose at 673 K in SCW with a ruthenium catalyst. Comparing with the noble metal, the nickel is cheaper, so

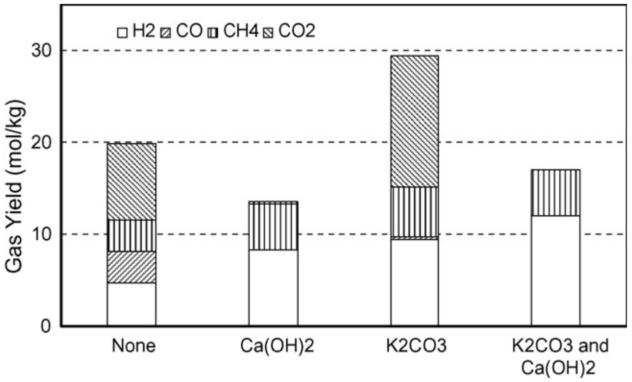

Fig. 15. Comparison of gas yield for cellulose gasification with different alkali catalysts in SCW using the batch reactor (batch reactor; water, 11 g; cellulose, 1.0 g; CMC, 0.2 g; 773 K; reaction time, 20 min; initial pressure, 4.0 MPa; K_2CO_3, 0.2 g; $Ca(OH)_2$, 1.6 g).

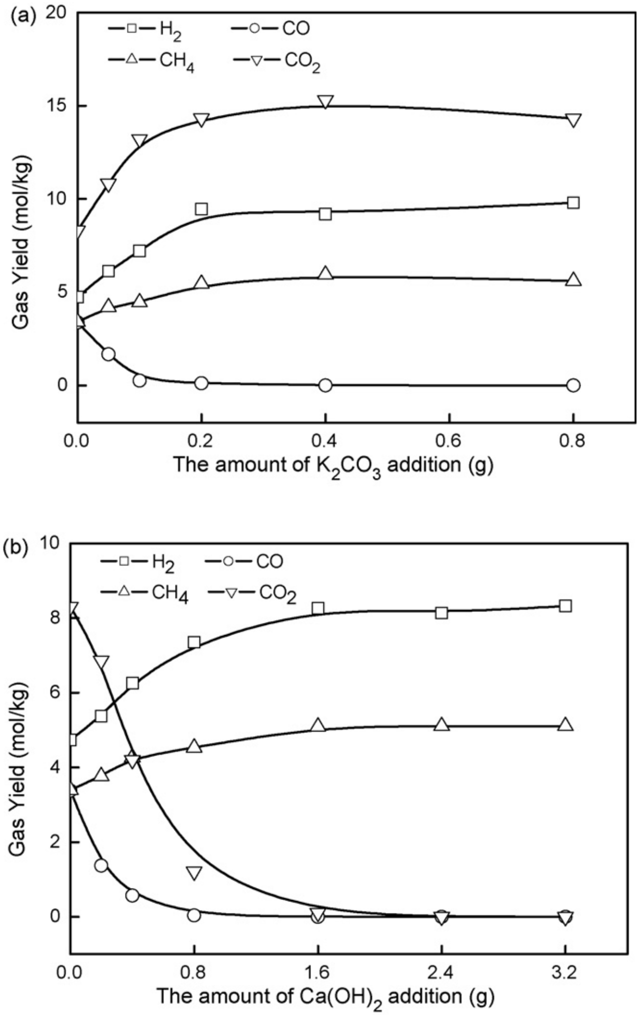

Fig. 16. Effect of the amount of catalyst on gas yield: (a) K_2CO_3; (b) $Ca(OH)_2$ (batch reactor; water, 11 g; cellulose, 1.0 g; CMC, 0.2 g; 773 K; reaction time, 20 min; initial pressure, 4.0 MPa).

the nickel is more suited for large-scale hydrogen production by biomass gasification.

Although metal-oxide is not usually employed as a catalyst for biomass gasification, Watanabe et al. [24] found that the hydrogen yield of glucose and cellulose gasification in SCW with zirconia was almost twice as much as that without catalyst. Park and Tomiyasu [74] achieved nearly complete gasification of aromatic compounds in SCW with RuO_2.

Fig. 15 displays results from the gasification of cellulose with different alkali catalysts in SCW using the batch reactor. Hydrogen yield of cellulose gasification in SCW with $Ca(OH)_2$ catalyst was almost twice as much as that without catalyst. CO_2 and CO yields were very low for cellulose gasification with addition of $Ca(OH)_2$. The $Ca(OH)_2$ was not only catalyst but also CO_2 sorbent. CO_2 was captured as $CaCO_3$ by Eq. (6) as follows:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \tag{6}$$

The overall equation of biomass gasification in SCW with addition of $Ca(OH)_2$ should be

$$CH_xO_y + (1-y)H_2O + Ca(OH)_2 \rightarrow CaCO_3 + (2-y+x/2)H_2 \tag{7}$$

It can be also seen from Fig. 15 that K_2CO_3 can catalyze the cellulose gasification with formation of more hydrogen and fewer CO. The activity of K_2CO_3 is higher than that of $Ca(OH)_2$ and K_2CO_3 cannot capture CO_2. Sinag et al. [28] summarized the catalytic mechanism of K_2CO_3 for biomass gasification in SCW as follows:

$$K_2CO_3 + H_2O \rightarrow KHCO_3 + KOH \tag{8}$$

$$KOH + CO \rightarrow HCOOK \tag{9}$$

$$HCOOK + H_2O \rightarrow KHCO_3 + H_2 \tag{10}$$

$$2KHCO_3 \rightarrow H_2O + K_2CO_3 + CO_2 \tag{11}$$

$$H_2O + CO \leftrightarrow HCOOH \leftrightarrow H_2 + CO_2 \tag{12}$$

Also, more hydrogen was obtained for cellulose gasification with the mixture of K_2CO_3 and $Ca(OH)_2$ and the CO_2 was captured. Fig. 16 shows the effect of the amount of K_2CO_3 and $Ca(OH)_2$ addition on gas yield for cellulose gasification in SCW, respectively. The amount of catalyst had an optimal value, and it can be seen from the figure that the optimal amount of K_2CO_3 was 0.2 g and the optimal amount of $Ca(OH)_2$ was 1.6 g under the experimental conditions.

Fig. 17 compares the results from the gasification of peanut shell in SCW with addition of K_2CO_3, $ZnCl_2$, R-Ni and the mixture of $ZnCl_2$ and R-Ni using the batch reactor. In 1998, Encinar et al. [75] reported that the hydrogen yield of bagasse gasification by CO_2 with $ZnCl_2$ was five to eight times higher than that obtained in the presence of other chlorides. It can be seen from Fig. 17 that $ZnCl_2$ exhibits higher activity than K_2CO_3 for hydrogen production from biomass gasification in SCW. The catalytic activity of R-Ni is higher than $ZnCl_2$ and K_2CO_3, but the hydrogen selectivity of R-Ni is lower than $ZnCl_2$ and K_2CO_3. R-Ni can catalyze the gasification reaction with formation of more CH_4. When a mixture of R-Ni and $ZnCl_2$ was added, higher hydrogen yield was obtained.

Fig. 18 shows results of cellulose gasification in SCW with different noble metal and metal-oxide. It can be seen from the

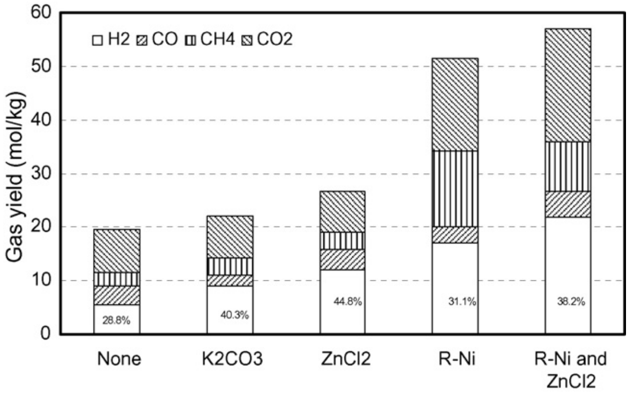

Fig. 17. Peanut shell gasification in SCW with different catalysts (batch reactor; water, 10 g; cellulose, 1.0 g; CMC, 0.3 g; 723 K; reaction time, 20 min; initial pressure, 4.0 MPa; catalyst, 1 g; the mixture of R-Ni and K_2CO_3 is composed of 1 g R-Ni and 0.2 g $ZnCl_2$).

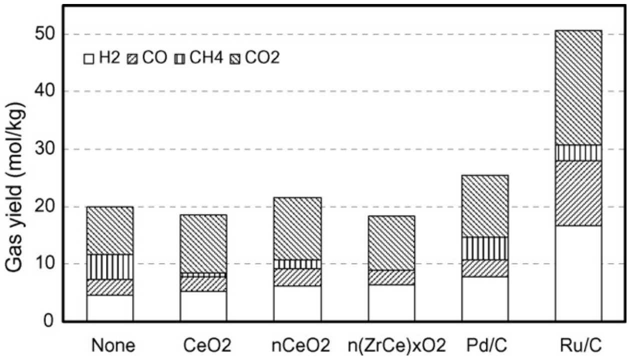

Fig. 18. Comparison of gas yield for gasification of cellulose with various catalysts in SCW [51] (batch reactor; water, 10 g; cellulose, 1.0 g; catalyst, 0.4 g; CMC, 0.2 g; 773 K; reaction time, 20 min; initial pressure, 4.0 MPa).

figure that the metal-oxide including CeO_2, nano-CeO_2 and nano-$(ZrCe)_xO_2$ behaves a little activity for cellulose gasification in SCW. The activity of metal is higher than that of metal-oxide and Ru metal has more catalytic activity than Pd metal. The largest hydrogen yield of 16.64 mol/kg cellulose was obtained with Ru/C catalyst. Metal-oxide and noble metal are not good catalysts for hydrogen production by biomass gasification in SCW because of low activity and economic consideration.

7. Summary and outlook

Biomass gasification for hydrogen production in SCW is a promising technology for high moisture biomass utilization. A large number of experimental and theoretical studies were conducted by SKLMF and other research groups, and significant progresses have been made. Compared to the traditional gasification process, SCWG is suitable for biomass with high moisture content. High energy conversion efficiency is achieved as the process avoid the drying step. A hydrogen-rich gas with low CO content can be generated in a single step process. In addition, the SCWG process also suppresses the formation of tar and char formation.

However, SCWG is currently in the research and development stage, and technological improvement including gasification and continuous delivering of high concentration biomass, reactor plugging, material corrosion, and catalysts should be made before studying the possibility of building scaled-up reactors. Also, further studies are needed to investigate the detailed reaction mechanism.

In the near future, a SCW fluidization bed reactor system will run in SKLMF. Preventing reactor plugging and gasification efficiency improvement are excepted. At the same time, the system of biomass SCWG driven by the solar energy is being established and genuine renewable energy conversion process will be achieved.

Acknowledgements

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