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Supercritical Water Gasification of Biomass and Organic Wastes

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1. Introduction

With the exhaustion of fossil fuels and the severe pollution of the environment, it's urgent to find substitute renewable energy resources. Biomass is a kind of widespread and abundant renewable resource with lower sulfur content than fossil fuels, so the pollution to environment from biomass usage is much slighter than that from fossil fuels usage. Besides, zero emission of CO_2 can be realized in the cycle of growing and energy conversion of biomass.

Supercritical water gasification (SCWG) is an innovation biomass conversion process which takes advantage of the special properties of supercritical water (temperature above 374˚C and pressure above 22.1MPa) to transform biomass into hydrogen-rich gaseous products. Comparing with conventional gasification and pyrolysis in normal pressure, SCWG has many advantages:

- Most organic materials of biomass can be dissolved in supercritical water for the relatively high dielectric constant of supercritical water (SCW), thus SCWG of biomass is homogeneous reaction, which can decrease the mass transfer resistance between phases.
- High pressure of the gaseous product make it easy for transportation, usage, carbon capture and further purification of the product gas through steam reforming or PSA (pressure swing adsorption).
- Higher energy efficiency can be achieved in SCWG of biomass especially for high moisture content biomass as the drying process is not required in SCWG.
- The reaction temperature is much lower than that in conventional gasification and pyrolysis. For example, the temperature of conventional steam gasification is always above 1000°C, while the complete gasification of glucose can be achieved at 650°C, 35.4MPa in supercritical water gasification.
- The gaseous product can be very clean. As almost no NOx and SOx were generated in supercritical water gasification, and the CO concentration is very low, especially with the catalyst to enhance the water-gas shift reaction.

Supercritical water gasification was firstly described by Modell in reforming of glucose and wood residues (Modell 1977; Modell 1980). In recent decades, much important progress has been made in SCWG technology by the researchers around the world. Elliott et al in PNNL (Pacific Northwest National Laboratory) have done a series of research on the reactions of kinds of biomass and organic wastes in high-pressure aqueous environments since 1980s.

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They studied the effect of various catalysts on the reaction under the conditions around 350˚C, 20MPa and the methane-rich gaseous products was achieved in these conditions. Antal's group at the University of Hawaii proposed activated carbon as the catalyst in SCWG and realized complete gasification of biomass in 650°C, 34.5MPa. The researchers in FK(Forschungszentrum Carlsruhe) of Germany have done much research on SCWG since 2000, and found that the addition of alkali salt can not only increase the reaction rate and hydrogen yield but also can inhibit the generation of tar and char. In 2005, an excellent review about the status of biomass supercritical water gasification(Matsumura et al, 2005) was reported by several researchers. Since 1997, Guo's group in SKLMF of Xi'an Jiaotong University has done a series of research on supercritical water gasification of biomass and much progress on SCWG of biomass has been made, including the gasification of various feedstocks, the system development and the exploration of the influence rule of the various parameters.

In this chapter, the progress have been made on SCWG in recent decades will be reviewed. Firstly, the different biomass feedstocks used in supercritical water will be introduced, which include the model compound, real biomass and organic wastes. Secondly, the engineering problems in the supercritical water gasification process will be discussed and the solutions to these problems will also be presented. Thirdly, the influence factors on supercritical water gasification will be discussed and the relevant investigation results will be also introduced. Then a brief review of the catalyst used in supercritical water gasification will be presented. However, there are still some challenges to the supercritical water gasification technology, which will be discussed in the end.

2. The feedstock materials

2.1 Model compound

Using a model compound can help us to understand the basic chemical pathways occurred in supercritical water gasification. The main components of biomass are cellulose, hemicellulose and lignin. Cellulose and hemicellulose are carbohydrate while lignin includes aromatic rings.

Glucose is always used as a model compound for cellulose for these reasons: Firstly, as the main component of biomass, cellulose consists of linearly linked glucose units attached to each other; Secondly, glucose is the primary product of cellulose hydrolysis around the critical point of water (Sasaki et al, 1998) and the gasification of cellulose and glucose have the similar gasification products. In addition, glucose is easy to transport in the high pressure for its water-soluble matter property.

2.2 Real biomass

Besides the three main components (cellulose, hemicellulose and lignin), real biomass also contains other substances, such as alkali salt, sulphur and proteins. Supercritical water gasification of different real biomass may have different gasification results because of the different components, which will be described below.

In our previous study, the real biomass including wood sawdust, rice straw, rice shell, wheat stalk, peanut shell, corn stalk, corn cob and sorghum stalk were gasified in supercritical water and the results were shown in fig.1 (Lu et al, 2006). It can be found that

the gasification results are different for various biomass feedstocks. Wheat stalk, corn cob and sorghum stalk are easier to gasify than the other biomass. The unconverted TOC (Total organic carbon) in liquid effluent was high, which indicated that a portion of biomass was converted to liquid products instead of gas products. This difference may be associated with the different amount of the components mentioned above.

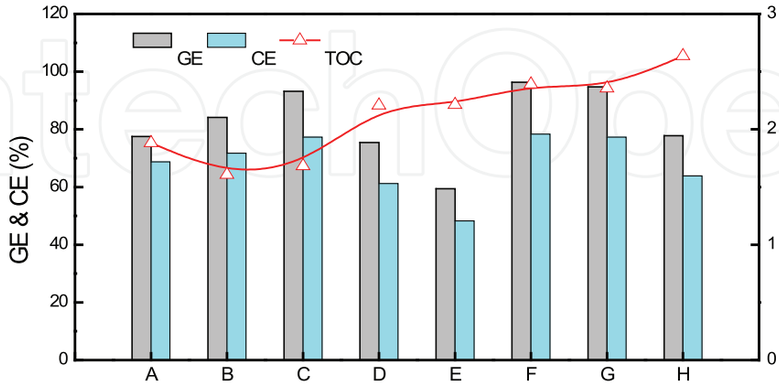


Fig. 1. Comparison of GE, CE and TOC for gasification of various biomass feedstocks in SCW (Temperature, 650˚C; Residence time, 27s; Pressure, 25MPa; Feedstock, 2 wt% biomass +2wt% CMC). A, rice straw; B, rice shell; C, wheat stalk; D, peanut shell; E, corn stalk; F, corn cob; G, sorghum stalk; H, wood sawdust.(Lu et al, 2006)

2.3 Organic wastes

Supercritical water gasification of organic wastes can realize the hydrogen production and decontamination simultaneously. Besides, the homogeneous solution of wastewater makes it easy to pump to the high pressure reactor without pretreatment. In recent years, supercritical water gasification of various kinds of organic wastes was investigated by the researchers. Xu and Antal (1998) gasified 7.69wt% digested sewage sludge in supercritical water by mixing with corn starch gel to form a viscous paste. They found that the digested sewage sludge was gasified to a gas composed of H_2, CO_2, CH_4, and a trace of CO. A carbon gasification ratio as high as 98% was achieved in their studies. The aqueous effluent from the reactor had a low TOC value, a neutral pH, and no color. But the plugging problem in the reactor in supercritical water gasification of sewage sludge occurred due to the high ash content of the material. The gasification of many kinds of organic wastes in hot-compressed water (around 350˚C, 20MPa) was investigated in PNNL (Elliott et al, 1994; Elliott et al, 2006) and methane was produced as the main product. The gasification of waste plastic in supercritical water also attracted much attention. Supercritical water gasification of waste plastics and the model compounds (such as polyethylene) were investigated by many researchers (Watanabe et al, 1998; Watanabe et al, 2001; Shibasaki et al, 2004; Su et al, 2004; Takeshita et al, 2004; Su et al, 2007).

The anaerobic organic wastewater from wheat straw includes acids (acetic acid, butyric acid) and ethanol etc. The gasification of anaerobic organic wastewater in supercritical water was investigated with a continuous operation tube flow reactor system (Ji 2006). The details of the reactor system were described in our previous report (Guo et al, 2007). The effect of temperature on SCWG of anaerobic organic wastewater was shown in fig. 2. It is showed that the main product gas are H_2, CO_2 and CH_4, with trace amount of CO and C_2. The gasification efficiency and carbon gasification efficiency were relatively high, for example,

100% gasification efficiency was achieved at the temperature of 775°C. The gasification efficiency, carbon gasification efficiency and the total gas yield increased with the temperature increased from 700˚C to 775˚C. The results show that the combination of the anaerobic hydrogen production of raw biomass with supercritical water gasification process can not only get hydrogen but also reduce the pollution.

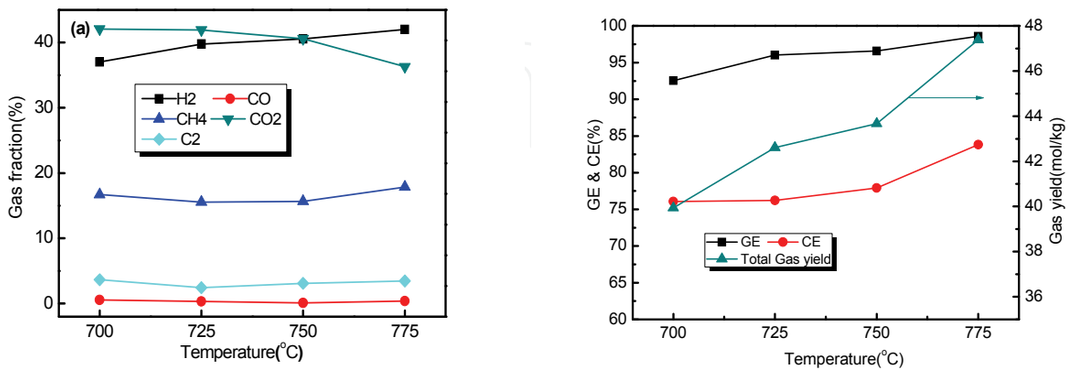


Fig. 2. The effect of temperature on SCWG of 6wt% anaerobic organic wastewater at 25MPa: (a) Gas fractions; (b)GE, CE & total gas yield.

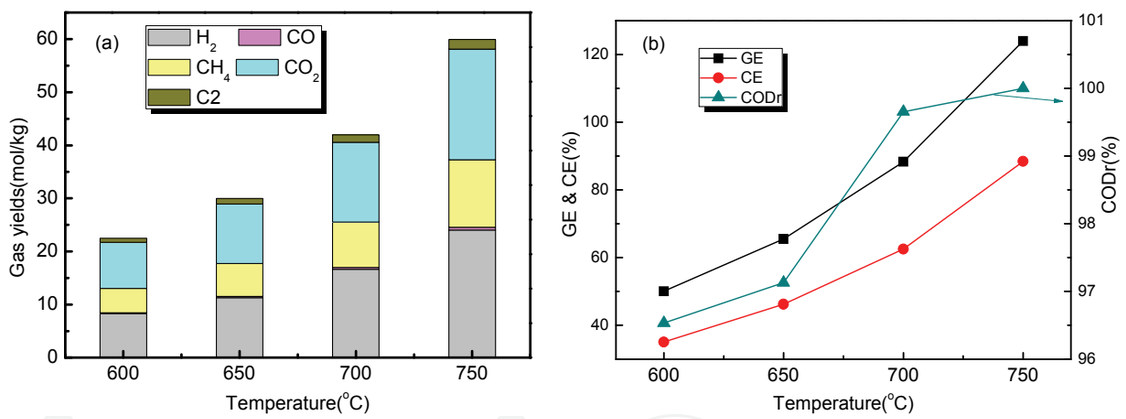


Fig. 3. The effect of temperature on SCWG of 7.8wt% black liquor at the pressure of 22.5MPa: (a)gas yields; (b)GE, CE and CODr

Black liquor is a kind of byproduct in pulping process and contains about 90% COD concentration of the pulping wastes. It mainly contains lignin derivatives which are hard to degrade and high content of alkali wastes. It is a wastewater with dark color, odor and high alkalinity. The black liquor contained 7.8wt% solid material was gasified in supercritical water with the same continuous operation tube flow reactor at the pressure of 22.5MPa. The gasification results with different temperature were shown in fig. 3. With the increasing of the temperature form 600˚C to 750˚C, the gas yield doubled and the COD removal efficiency, gasification efficiency and carbon gasification efficiency also increased significantly. The maximal gasification efficiency (123%) and carbon gasification efficiency (88%) were achieved at the temperature of 750˚C. The COD content was fully removed, which means that the complete decontamination of black liquor can be achieved at the temperature of 750˚C.

3. Engineering problems in supercritical water gasification systems

As an innovation biomass processing technology, supercritical water gasification has many new engineering problems, especially because the reaction temperature and pressure are relatively high. During decades of development on supercritical water gasification, much progress has been made in the engineering of supercritical water gasification process. Fig. 4 displays a typical continuous SCWG experimental system developed in SKLMF. Taking this system as example, some engineering problems will be discussed as below.

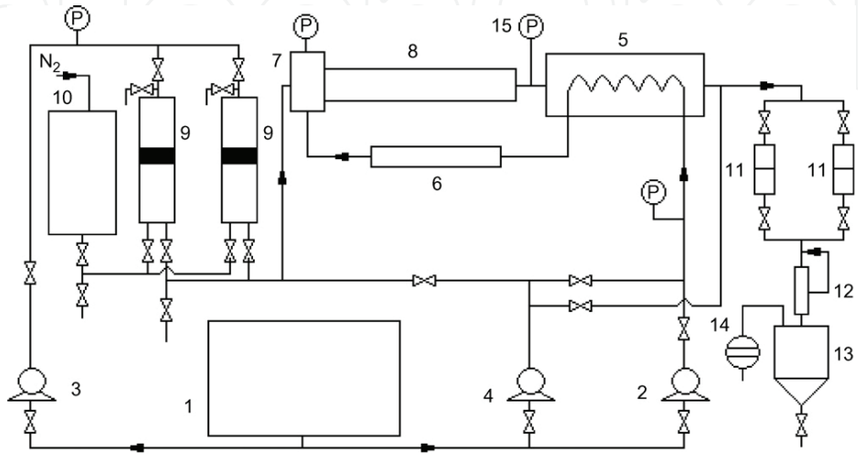


Fig. 4. Schematic diagram of bench-scale continuous SCWG apparatus: (1) Water tank; (2) Preheated water pump; (3) Feed pump; (4) Wash pump; (5) Cooler and exchanger; (6) Pre-heater; (7) mixer ; (8) Reactor; (9) Feeder; (10) Feed tank; (11) Filter; (12) Back-pressure regulator; (13) Gas-liquid separation; (14) Gas meter; (15) Pressure transducer.(Li et al, 2010)

3.1 Heating rate

The feedstock heating rate is reported to have significant influence on supercritical water gasification. Xu et al found that improving heating rate of the feedstock delays deactivation of coconut shell activated carbon catalyst, likely for the inhibition of tar formation (Xu et al, 1996). Kruse et al found that coke/char was generated with the slower feedstock heating rate (Kruse et al, 2003). They also gave the explanation for the formation of coke at low heating rates: When the biomass/water mixture spends enough time at sub-critical temperatures, furfurals or other unsaturated compounds are formed in significant yields. These compounds may polymerize as the temperature increases (Kruse 2008). Matsumura's group investigated SCWG at different feedstock heating rate and found that a heating rate of several hundreds of degrees Kelvin per minute should be desirable for the inhibition of coke formation (Matsumura et al, 2005).

In this system (fig.4), we realized the fast heating by mixing the feedstock with the water preheated by the heat exchanger (No. 5 in fig.4) and pre-heater(No. 6 in fig.4). Thus the coke formation can be inhibited as the feedstock can be heated to supercritical condition at the inlet of the reactor.

3.2 Energy recovery

High temperature reactor effluent owns a great quantity of enthalpy, so the recovery of the energy is necessary for the SCWG process. It is reported that the heat needed for

supercritical water gasification can not be supplied by the heating value of the feedstock. From the heat balance considerations, it is clear that heat exchange between the reactor effluent and the reactor feed is essential for the economics of the process (Matsumura et al, 2005).

The effects of the heat transfer efficiency of the heat exchanger between the reactor effluent and the reactor feed (No.5 in fig. 4) on total energy and exergy efficiencies were analyzed, and the results were shown in fig. 5. As expected, total energy and exergy efficiencies of the biomass gasification increased with the increase of heat transfer efficiency in the heat exchanger. The increasing tendency is even more obvious with higher heat transfer efficiency of the heat exchanger.

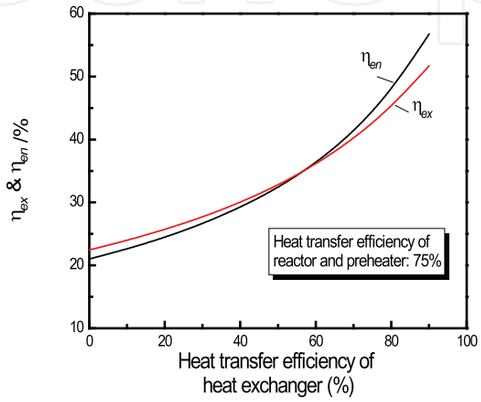


Fig. 5. The energy and exergy conversion efficiency of SCWG system with different heat transfer efficiency of heat exchanger. (Lu et al, 2007)

3.3 Plugging problem

Plugging is always a problem in biomass supercritical water gasification in tubular reactors (Antal et al, 2000). There are two reasons for plugging problem in SCWG system: The first one is the coke generated for the incomplete gasification of biomass; Secondly, as mentioned above, the solubility of inorganic salts is very low in the supercritical water and most of the salts were precipitated in the water. The plugging problem can cause the shutdown of the system which presents a severe problem for the energy conversion process (Matsumura and Minowa, 2004).

To handle with the plugging problem in SCWG of biomass, especially for the gasification of high concentration biomass, a novel SCW fluidized bed system for biomass gasification was developed in SKLMF. The details of this system were described in our previous paper (Lu et al, 2008). The innovation of the system is the application of fluidized bed reactor and the fluidizing agent is SiO_2 beads with diameters in the range of 0.1–0.15mm. In this system, high concentration model biomass (30wt% glucose) and real biomass (18wt% corn cob) feedstock were gasified successfully without plugging.

3.4 Continuous feeding

The delivery of biomass to the supercritical water gasification reactor is a technological challenge, for the precipitation will occurred in the continuous feeding for some biomass which can not dissolve in the water. The solution to this problem is to increase the viscosity of the slurry, Matsumura et al successfully applied a pre-treatment method in hot

compressed water (150°C, 30min) for feeding cabbage(Matsumura et al, 2005). They found the softening of the hard structure of biomass as observed in making soup in the kitchen. And this 'softening' effect increased with the increase of the temperature and pressure. Antal's group present a solution which suspended the biomass in a starch gel and successfully delivered the sawdust to the reactor via a 'cement pump'(Antal et al, 2000). In SKLMF, the sodium carboxymethylcellulose (CMC) was chosen as an additive to mix with the solid biomass feedstock and water, and realized the continuous pumping of the sawdust (Hao et al, 2003).

3.5 The separation of products

The main product gas compositions of biomass SCWG are H_2, CH_4, CO and CO_2. To remove carbon dioxide to raise the heating value of the product gas, separation of gas and liquid before depressurization is effective. Based on the higher solubility of carbon dioxide than hydrogen in water, utilization of high-pressure separator for hydrogen and carbon dioxide was proposed. Above 90mol% hydrogen purity gas phase was achieved with the addition of excess water to the product gas mixture under high pressure (Matsumura et al, 1997a).

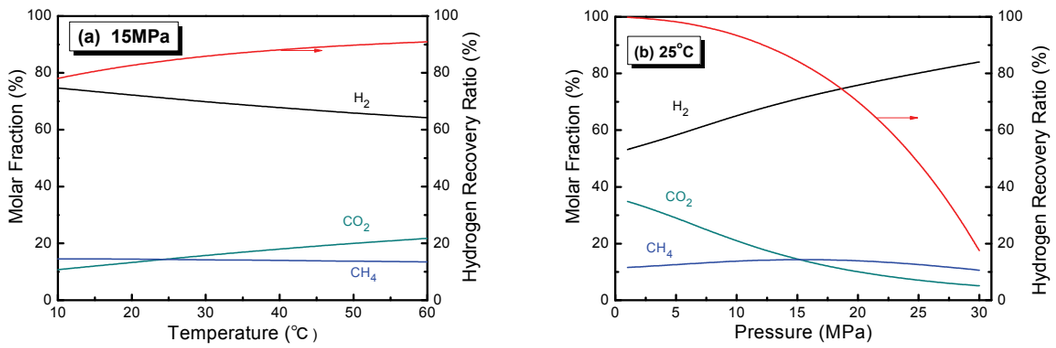


Fig. 6. The gas fractions and the hydrogen recovery ratio in the gas phase of the high pressure separator with different: (a)pressure; (b)temperature(Lu et al, 2007).

The gas-liquid equilibrium of the products in the high pressure separator was analyzed with the assumption that the chemical equilibrium is reached in the reactor at 600˚C, 25MPa. The effects of the operation temperature and pressure of the high pressure separator on the gas fractions and hydrogen recovery ratio in the gas phase were studied. The results shown in fig.6 revealed that as operation temperature increases, the molar fraction of H_2 in gas phase decreased while the CH_4, CO_2 fractions and hydrogen recovery ratio increased. Purity of H_2 in the gas phase is 86.24% at 283K and 75.7% at 333 K, respectively. As a result, proper operation temperature of the high pressure separator should be selected to consider both H_2 purity and hydrogen recovery ratio. Fig. 6(b) shows that the molar fraction of hydrogen in the gas phase increases from 65.56% to 92.41% and the molar fraction of CO_2 decreases sharply from 33.11% to 6.12% with the pressure increasing from 0.1MPa to 30MPa. Hydrogen recovery ratio decreased and the molar fraction of CH_4 increased a little with the increasing pressure. The results suggested that the increase of pressure in the separator favors the purity of H_2 in the gas phase but decreases the hydrogen recovery ratio, so appropriate operation pressure of high pressure separator must be selected. The predicted results show that H_2 of 82.45% and recovery ratio of 88.15% are obtained at 15MPa, 298 K.

H_2 and CH_4 in the liquid phase can be separated in a low pressure separator and combust with oxygen to produce heat, which can be recovered for the gasification system to reduce external heat input.

4. The influence factors on supercritical water gasification

4.1 The influence of main operating parameters

Based on minimizing Gibbs free energy principle, chemical equilibrium of sawdust SCWG was predicted by thermodynamic calculation code (Yan et al, 2006; Lu et al, 2007). 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. The influence of the main operating parameters in SCWG was predicted and shown in fig.7-10.

(a) Influence of temperature

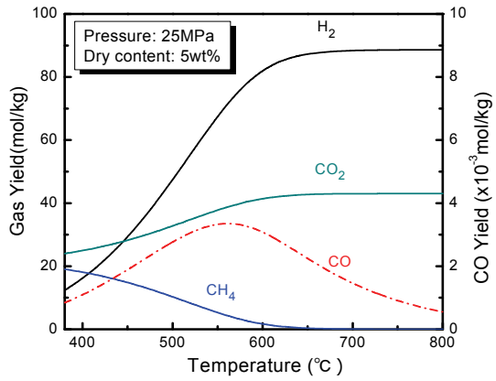


Fig. 7. Equilibrium gas yields of SCWG of 5wt% sawdust with change of temperature.

Fig. 7 shows the equilibrium gas yields of sawdust gasification as a function of reaction temperature at 25 MPa. 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 about 10^{-3} mol/kg. As temperature increases from 400 to 800˚C, the CO yield firstly increases and then drops down. The maximum CO yield is reached at about 550°C. Hydrogen yield increases at a low speed at rather higher temperature. When the reaction temperature is above 650˚C, 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).(x and y are the elemental molar ratios of H/C and O/C in biomass, respectively). The maximal equilibrium H_2 yield of 88.623 mol/kg dry biomass is obtained. From the viewpoint of thermodynamics, higher temperature is essential to hydrogen production.

As shown above, temperature has significant effect on biomass gasification in SCW and this conclusion was confirmed by the experimental results. Xu et al (1996) reported that 1M glucose was gasified completely at 600˚C, and a thin layer of dark brown oil-like tar was observed at the temperature below 580˚C. For the gasification of high concentration

feedstocks, the temperature of 650–800˚C is needed (Antal et al, 2000). Further more, the higher temperature drove the methane steam-reforming reaction to increase hydrogen yield (Sealock et al, 1993).

(b) Influence of pressure

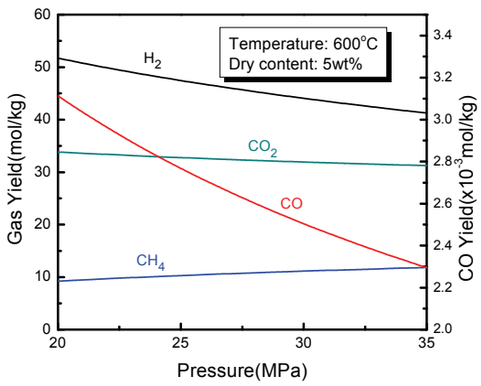


Fig. 8. Equilibrium gas yields of SCWG of wood sawdust with change of pressure.

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 SCWG of biomass, which requires the presence of H^+ or OH^-. With increasing pressure, the ion product increases, therefore the hydrolysis rate also increase. Besides, high pressure favors water–gas shift reaction, but reduce decomposition reaction rate.

Fig. 8 shows the effect of pressure on equilibrium gas yield at 600˚C with 5 wt% biomass content. It reveals that the pressure has no significant effect on equilibrium gas yield. The similar experimental results were achieved when we gasified the 2wt% wood sawdust in supercritical water at the temperature of 650˚C, in the pressure range of 18-30MPa (Lu et al, 2006). It is found that 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 (2004) also found that hydrogen yield increased as pressure increased from 23 to 48 MPa in SCWG of fruit shell and it is considered that the increase of the pressure increased the mass transfer and the solvent diffusion rates of the water. Thus the gasification efficiency of supercritical water gasification increased with the pressure.

(c) Influence of feedstock concentration

Fig. 9 displays the effect of feedstock concentration on equilibrium gas yield at 600˚C and 25 MPa. The product gas mainly consists of 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.

The similar results were achieved in the SCWG of wood sawdust in a batch reactor (Lu et al, 2006). The gasification results showed that the dry biomass content has significant effect on biomass gasification and the high concentration feedstock is more difficult to gasify. With higher feedstock concentration, the gasification efficiency and H_2 yield decreased, while the

CO yield increased. But the gasification of high concentration feedstock is necessary to achieve a thermal efficiency high enough to establish an economic process. For high efficiently gasification of high concentration feedstock in supercritical water, the high temperature, high heating rate and catalyst are required (Antal et al, 2000).

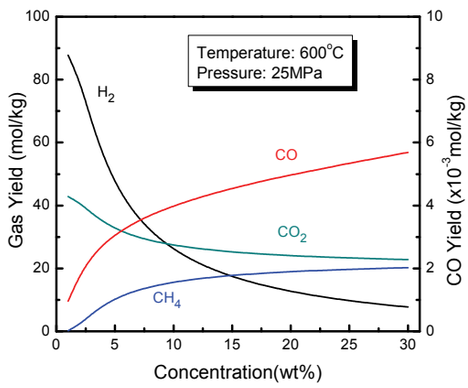


Fig. 9. Equilibrium gas yields of SCWG of wood sawdust with change of concentration.

(d) Influence of the oxidant

The oxidant is expected to decompose the complex compound of the reactant or the intermediate products in supercritical water, such as the phenols which is considered to be 'the last hurdle' to get over to complete gasification of biomass (Kruse et al, 2003).Thus the formation of tar and char can be decreased. In addition, the in-situ heat generated from the oxidation reaction can heat the feedstock rapidly, which favors the process of gasification (Watanabe et al, 2003; Matsumura et al, 2005). The effect of oxidant addition on equilibrium gas yield was predicted and the results were shown in fig.10. It revealed that with the increase of the oxidant addition, the yields of H_2, CO and CH_4 decreased and the yield of CO_2 increased. The addition of oxidant can enhance the efficiency of biomass SCWG and provide the heat for the reactions in SCW, but decreased the hydrogen yield.

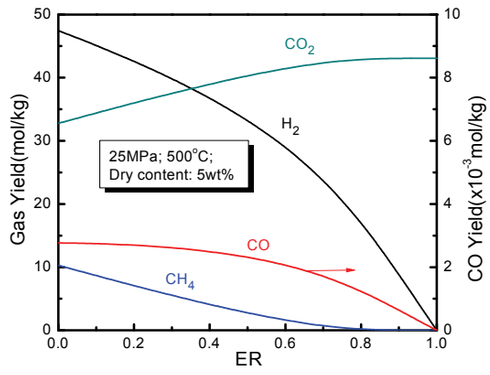


Fig. 10. Equilibrium gas yields of SCWG of wood sawdust with change of oxidant addition.

The influence of the oxidant addition on SCWG of model compounds (glucose, lignin) was investigated in a fluidized bed system (Jin et al, 2010). The results showed that the oxidant

can improve the gasification efficiency and an appropriate addition of oxidant can improve the yield of hydrogen in certain reaction condition. When ER equaled 0.4, the gasification efficiency of lignin was 3.1 times of that without oxidant. When ER equaled 0.1, the yield of hydrogen from lignin increased by 25.8% compared with that without oxidant. But when the oxidant addition increased to a certain level, the cold gas efficiency decreased for the consumption of the combustible gas in the oxidation reaction. So there is an optimum oxidant addition amount in SCWG.

(e) Influence of reaction time

From the viewpoint of thermodynamics, biomass can be gasified completely in SCW with a product formation of H_2 and CO_2, but adequate reaction time was required to complete the gasification process. Antal et al (1994) gasified 0.1 M glucose at 34.5 MPa, 600˚C with various residence times. They found that glucose can be gasified quickly and the complete gasification was achieved in only 28 s residence time. Lee et al (2002) reported the yields of all the gases remained almost constant at 700˚C, 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.

4.2 Influence of biomass properties

(a) Influence of the main component

As mentioned above, cellulose, hemicellulose and lignin are the main components of the biomass and they have different structures. So the different components may have different effect on SCWG. Yoshida et al investigated the interaction of cellulose, xylan(model compound for hemicellulose) and lignin by mixing them in different ratios in SCWG (Yoshida and Matsumura 2001). They found that the hydrogen yield by SCWG of the cellulose and hemicellulose are higher than that of lignin, there was no apparent interaction between the hydrogen production from cellulose and hemicellulose in SCWG. While with the mixing with lignin, the hydrogen production from SCWG of cellulose and hemicellulose was suppressed. In the following article (Yoshida et al, 2003), they showed that this effect depended on the species of lignin and the interaction between each component was also observed in the real biomass feedstocks (sawdust and rice straw). This result reveals the gasification of various biomass in SCW may have different results for their different components.

(b) Influence of the protein content

The proteins are contained in some biomass, such as the food industry residues or sewage sludge. Kruse et al (2005) studied the effect of proteins on hydrothermal gasification of biomass by comparison of the gasification results of two biomass feedstocks: One biomass feedstock originated from plant material (phyto mass) nearly contains no proteins and the other contains protein (zoo mass). They found that gas yield from SCWG of protein containing biomass (zoo mass) was much lower than that of phyto mass without proteins. To understand these findings, they conducted the experiments with the alanine as the model compound of protein (Kruse et al, 2007). The results showed that with the presence of alanine, the gas yield of glucose was decreased and the gas composition and the concentration of key compounds are slightly changed. They inferred that the nitrogen containing cyclic organic compounds was produced from the Maillard reaction between

glucose and amino acids or their consecutive products. And these compounds were believed to be strong free radical scavengers and inhibit free radical chain reactions that are highly relevant for gas formation. In addition, experiments with real biomass in a batch reactor were reported to verify the assumption that Maillard products reduced free radical reactions. As an example, the addition of urea to phyto mass leads to a decrease of the gas yield to a value similar to that found for zoo mass. Dileo et al. (2008) examined the gasification of glycine as the model compound of protein in supercritical water. They found that glycine was much more resistant to be gasified than phenol. Large amounts (20%-90%) of the initial carbon remained in the aqueous phase even after 1 h for both homogeneous and Ni-catalyzed reactions.

(c) Influence of inorganic elements

The K_2CO_3 content of real biomass is always slightly higher than 0.5wt% (Sinag et al, 2003). The alkali is advantageous for SCWG as a catalyst. The addition of alkali salts can enhance the water-gas shift reaction in supercritical water gasification which resulted in higher H_2 fraction and lower CO fraction in the product gas. Also the alkali salts can also lead to more liquid product and less coke/char formation. The detail of the alkali catalysis effect will be described in section 5.

Sulfur also exists in some waste biomass and it has an influence on supercritical water gasification. Elliott et al claimed that the presence of sulfur lowered the activities of ruthenium catalysts in subcritical water at 623 K(Elliott et al, 2004). Osada et al studied the effect of sulfur on SCWG of lignin at 673K with the catalysis of supported ruthenium (Osada et al, 2007a). They found that the gas yield decreased with the increase of the sulfur added. The carbon dioxide fraction in the presence of sulfur was lager than that without sulfur, and the methane fraction was lower. From X-ray photoelectron spectroscopy characterization of catalysts used for gasification, the sulfur species which poisoned the ruthenium sites were found to be ruthenium sulfide, ruthenium sulfite, and ruthenium sulfate. In the further study about the effect on SCWG of lignin with Ru/TiO_2, they come to a conclusion that sulfur poisoned the active sites for carbon-carbon bond breaking and methanation reaction; on the other hand, it did not hinder the sites for the gasification of formaldehyde and the water-gas shift reaction (Osada et al, 2007b). Therefore, the desulfurization from biomass, especially the biomass waste, is essential for the development of the supercritical water catalytic gasification.

(d) Influence of biomass particle size

Biomass was pretreated with mechanical grinding before gasification. Biomass with different particle sizes were gasified in supercritical water in a batch reactor and the results showed that higher hydrogen yield is obtained with gasification of smaller particle size (Lu et al, 2006). We inferred that with larger particle size, the diffusion resistance may be larger and decreased the gasification efficiency. More energy will be consumed to achieve the smaller particle size for the mechanical grinding, so an optimal particle size should be found with considering economy and feasibility of the process.

5. Review of SCWG catalyst

To improve the economical efficiency of SCWG, the improvement of gasification efficiency as well as lowering the operating temperature should be considered. For this purpose,

catalyst is one possible solution. Various catalysts were used for biomass thermal chemical gasification and a review of literature on catalysts for biomass gasification was published in 2001 (Sutton et al, 2001). However, the catalyst for SCWG should be different from the conventional gasification because of the particular operating conditions, such as the high pressure values, the purpose(hydrogen production instead of syngas) and the specificities of the supercritical medium (Calzavara et al, 2005). Generally, four types of catalysts were used for SCWG in the literature: alkali, activated carbon, metal and metal-oxide.

5.1 Alkali

The addition of alkali, such as NaOH, KOH, Na_2CO_3, K_2CO_3 and $Ca(OH)_2$ has significant influence on SCWG of biomass. Watanabe et al (2003) studied catalytic effects of NaOH in partial oxidative gasification of n-hexadecane and lignin in supercritical water (40MPa, 400˚C). The results showed that the H_2 yield with NaOH was almost 4 times higher than that without catalyst. Kruse et al (2000) conducted SCWG of different organic compounds in the presence of KOH. They found that the addition of KOH decreased the CO fraction and increased the fractions of hydrogen and carbon dioxide by accelerating of water-gas shift reaction. The similar results were achieved by Sinag et al(Sinag et al, 2003; Sinag et al, 2004) when they gasified glucose in SCW with 0.5wt% K_2CO_3. They also regarded that the formation of the formate salt was the reaction mechanism of the acceleration of the water-gas shift reaction by alkali salts in SCWG. The alkali is also well-known as the catalyst for the oil production from biomass, where their important role is to inhibit the char formation from the oil (Minowa et al, 1998). Thus, alkali has a positive effect to produce gaseous product such as H_2. Furthermore, the addition of the $Ca(OH)_2$ can not only catalysis the SCWG of biomass as described above, but it can also adsorb CO_2 to decrease the CO_2 fraction in the product gas(Lin et al, 2001; Lin et al, 2002; Lin et al, 2003; Lin et al, 2005). The high hydrogen purity gases were produce from this process.

5.2 Activated carbon

Xu et al (1996) 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. Complete conversion of glucose was achieved at 600˚C, 34.5MPa. Subsequently, Antal and Xu (1998) and Antal et al (2000) gasified the high concentration biomass feedstocks completely above 650˚C with carbon-based catalyst in SCW. The produced gases were mainly composed of hydrogen and carbon dioxide and the extraordinary hydrogen yield could be more than 100 g/kg of dry biomass. The carbon is thought to react with supercritical water. However, the rate of the supercritical water gasification of activated carbon was found to be very slow under typical SCWG conditions (Matsumura et al, 1997b). For the notable catalysis effect on SCWG and the stability of the carbon in SCW, activated carbon is used widely as the catalyst and the catalyst support. The catalysis effect of Ru/C and Pb/C on gasification of cellulose and sawdust in SCW was examined in our laboratory and it was found that these catalysts have remarkable effect on SCWG. 10wt% cellulose or sawdust with CMC can be gasified near completely with Ru/C and 2-4g hydrogen yield and 11-15g potential hydrogen yield per 100g feedstock were produced at the condition of 500˚C, 27MPa and 20min residence time in an autoclave reactor (Hao et al, 2005).

5.3 Metal catalyst

Metal is widely used as catalyst in biomass conventional gasification and supercritical water gasification. Elliott et al (Elliott et al, 1993; Elliott and Sealock 1996) demonstrated that Ru, Rh and Ni had significant activity for the conversion of *p*-cresol and Pt, Pd and Cu was reported to have less activity. Sato et al. (2003) gasified alkylphenols as lignin model compound in the presence of supported noble metal catalysts in SCW at 40˚C. The activity of the catalyst was in the order of Ru/a-alumina> Ru/carbon, Rh/carbon > Pt/a-alumina, Pd/carbon and Pd/a-alumina. Usui et al (2000) presented Pd/Al_2O_3 had the highest catalytic activity for cellulose gasification among the supported Ni, Pd or Pt. Nickel is cheaper than noble metals, so it is more suitable for large-scale hydrogen production by biomass gasification. Elliott et al (1993) tested several forms of nickel catalysts at 350˚C and 17–23 MPa using a batch reactor, and the CH_4-rich gas was produced. Minowa and co-workers (Minowa & Ogi, 1998; Minowa et al, 1998; Minowa and Inoue, 1999) studied the effect of a reduced nickel catalyst on cellulose decomposition in hot-compressed water. They found that the nickel catalyst can accelerate the steam reforming of aqueous products and the methanation reaction.

5.4 Metal oxide

Although metal-oxide is not usually employed as a catalyst for biomass gasification, It was reported that (Watanabe et al, 2002) the hydrogen yield and the gasification efficiency of glucose and cellulose gasification in SCW with zirconia was almost twice as much as that without catalyst. The similar results were found in the partial oxidative gasification of lignin and n-C16 in SCW (Watanabe et al, 2003). Park and Tomiyasu (Park & Tomiyasu 2003) achieved nearly complete gasification of aromatic compounds in SCW with stoichiometrically insufficient amounts of RuO_2. We examined the catalytic effect of CeO_2 particles, nano-CeO_2, and nano-$(CeZr)_xO_2$ on SCWG of cellulose in our previous study (Hao et al, 2005) and found that these metal-oxide has limited catalytic effect on SCWG.

6. Challenges and prospect

As described above, much progress has been made in biomass supercritical water gasification, but there are still some problems to be resolved:

- Optimizing the process parameters especially in view of higher feed concentration necessary to achieve a thermal efficiency high enough to establish an economic process.
- The high pressure in SCWG process brings about challenge for the catalyst, such as the durable and life time of the catalyst. So developing long-life and cheap catalyst is important to increase economical efficiency of SCWG through improving the gasification efficiency and lowering the gasification temperature. On the other side, the recycling of the catalyst, especially the water soluble catalysts have also to be handled to decrease the cost of the process.
- Detailed kinetics should be developed based on the gasification mechanism and reaction path to give guidance to the design of supercritical water gasification system. So the detailed gasification mechanism have to be explored, especially the qualitative and quantitative analysis of the intermediate and end products.
- The corrosion is an inevitable problem for biomass supercritical water gasification as the reactor was exposed in severe conditions. Besides, the compositions of the biomass and intermediate products are complex. So it is important to find a construction

material which is resistant to corrosion or find a way to protect the reactor material from contacting with the reactant and products.

The energy conversion from biomass will be more urgent as the fossil fuel is running shorter nowadays. Though there are so many problems, supercritical water gasification is still a promising biomass conversion technology for its advantages over conventional gasification process. Especially for the organic wastes, supercritical water gasification can realize both the goals of energy recovery and decontamination simultaneously.

7. Nomenclature

GE: gasification efficiency, the mass of product gas/the mass of feedstock, %;
CE: carbon gasification efficiency, carbon in product gas/carbon in feedstock, %;
CODr: COD removal efficiency, 1-COD of aqueous residue/COD of feedstock, %;
ER: oxidant equivalent ratio, amount of oxidant added/the required amount for complete oxidation by stoichiometry calculation, %;

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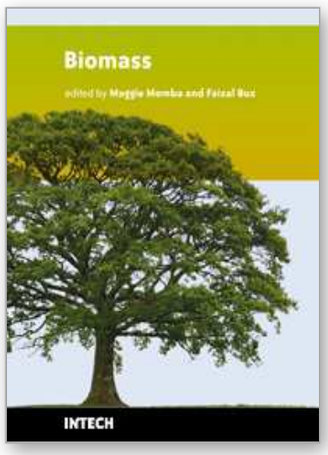
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Due to demands placed on natural resources globally and subsequent deterioration of the environment, there is a need to source and develop appropriate technology to satisfy this requirement. For decades mankind has largely depended on natural resources such as fossil fuels to meet the ever increasing energy demands. Realizing the finite nature of these resources, emphasis is now shifting to investigating alternate energy source governed by environmentally friendly principles. The abundance of biomass and associated favorable techno-economics has recently changed global perceptions of harnessing biomass as a valuable resource rather than a waste. To this end this book aims to make a contribution to exploring further this area of biomass research and development in the form of a compilation of chapters and covering areas of ecological status of different types of biomass and the roles they play in ecosystems, current status of biomass utilization and deriving energy and other value added products from biomass. In this context biomass can be defined as large plants and trees and different groups of microorganisms. This book will serve as an invaluable resource for scientists and environmental managers in planning solutions for sustainable development.

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