Hydrogen production by biomass gasification in supercritical water with a fluidized bed reactor

Y.J. Lu, H. Jin, L.J. Guo*, X.M. Zhang, C.Q. Cao, X. Guo
State Key Laboratory of Multiphase Flow in Power Engineering (SKLMF), Xi’an Jiaotong University, 28 Xianning West Road, Xi’an 710049, Shaanxi, China

A B S T R A C T
Hydrogen production by biomass gasification in supercritical water (SCW) is a promising technology for utilizing high moisture content biomass, but reactor plugging is a critical problem for biomass gasification in the tubular reactor. A novel SCW fluidized bed system for biomass gasification was developed successfully in State Key Laboratory of Multiphase Flow in Power Engineering (SKLMF) to prevent the plugging and it was designed for the temperature up to 923 K and the pressure up to 30 MPa. Model compound (glucose) and real biomass (corn cob) were gasified under SCW conditions to generate hydrogen-rich fuel gas and a performance testing of the new SCW fluidized bed system was conducted. The product gas composed of H2, CH4, CO2, CO and small amount of C2H4 and C2H6 was obtained. The effects of solution concentration, temperature, pressure and oxidant concentration on gasification were studied. 30 wt% glucose and 18 wt% corn cob feedstocks were continually and stably gasified and reactor plugging was not observed. The results showed that using fluidized bed reactor for biomass gasification in SCW has many advantages and good prospects.

1. Introduction
Biomass has always been a major source of energy for mankind, and it contributes about 10–14% of the world’s energy supply today [1]. However, a considerable portion of biomass wastes is wet biomass containing up to 95% water and for conventional gasification or liquefaction processes, this biomass has to be subjected to preliminary drying. To avoid this energy intensive drying step, the biomass may be converted in hot, pressurized water or supercritical water [2].

In 1978, Modell [3,4] reported firstly that glucose and maple sawdust could be gasified with a catalyst composition that promotes hydrogenation, reforming and cracking in water in the vicinity of its critical state. Since then, researchers from USA, Japan, EU and other countries conducted a lot of studies on biomass gasification in sub- or supercritical water [2,5–22]. The great progress has been made on supercritical water gasification in the past 30 years. However, reactor plugging is still a critical problem for the SCW gasification of biomass. Most of the research conducted in this area has employed tubular reactors, but tubular reactors are susceptible to system shutdowns due to reactor plugging resulting from the formation of char at the heating section and the buildup of ash inside the reactor. Such shutdown presents a severe problem for the energy conversion process [23]. To solve this problem, much work has to be done. The intermittent removal of the deposits that caused plugging in the tubular reactors was proposed by Antal et al. [9]. In our prior work [13], some suggestions for overcoming the reactor plugging of the tubular reactor were obtained by a parametric study. In 2003,
Matsumura and Minowa [23] proposed a novel biomass gasification process using an SCW fluidized bed and explored fundamental engineering feasibility of the SCW fluidized bed reactor instead of the tubular reactor.

Fluidized bed reactor has been widely used in conventional biomass gasification [24,25], but there is no SCW fluidized bed for hydrogen production by biomass gasification currently due to special characteristics of SCW, high pressure and temperature parameters demand. The studies on supercritical fluidized bed are mainly about supercritical CO$_2$ fluidized bed. Tarmy et al. [26] investigated the hydrodynamic characteristics of three-phase fluidized beds under a pressure of 17 MPa and a temperature of 723 K. Liu et al. [27] reported that solid particles belonging to Geldart Groups A, B and D were fluidized in liquids of changing viscosity and in CO$_2$ under ambient to supercritical conditions. The criterion of fluidized regime was also proposed. Jiang et al. [28] studied on the bed contraction and expansion in a high pressure and high temperature gas–liquid–solid fluidized bed which was designed for the pressure up to 21 MPa and the temperature up to 453 K. The bubble dynamic behavior in the bed was visualized and the effect of temperature and pressure on the bed expansion and contraction was obtained. Marzocchella and Salatino [29] studied on the fluidized characteristics of two granular materials belonging to Geldart groups A–B and B of powders in CO$_2$ at 308 K and at 0.1–8 MPa. Körber and Teipel [30] and Schreiber et al. [31] conducted the coating experiments with a supercritical CO$_2$ fluidized bed. Vogt et al. [32] carried out a comprehensive experimental study to investigate the fluidized behavior with supercritical CO$_2$ at pressure up to 30 MPa for various solids which behave as Geldart A and B powders, respectively. From pressure drop measurements, minimum fluidizing velocities and bed voidages were determined. Vogt’s research provided an important theoretical and experimental evidence for the design of supercritical fluidized bed. Potic et al. [33] introduced the concept of micro-fluidized beds. A cylindrical quartz reactor with an internal diameter of only 1 mm is used for process conditions up to 773 K and 24.4 MPa. Properties of the micro-fluid bed such as the minimum fluidized velocity, the minimum bubbling velocity, bed expansion, and identification of the fluidized regime were investigated by visual inspection. Because of the similarity of supercritical fluid, studies on the characteristics of supercritical CO$_2$ fluidized bed were very good references to SCW fluidized bed.

The useful ideals of Matsumura and Minowa [23] were absorbed in this paper and an SCW fluidized bed system for hydrogen production by biomass gasification was developed successfully in SKLMF. A performance testing of the new SCW fluidized bed system and hydrogen production characteristics by biomass gasification in SCW were conducted. Model compound (glucose) and real biomass (corn cob) were gasified with the fluidized bed system. Feedstock with high biomass content was continually and stably gasified.

2. Apparatus and experimental procedures

The schematic diagram of SCW fluidized bed system is shown in Fig. 1. The system includes reactor, heat exchanger, high-pressure pumps, feeders, separators, cooler and so on. The reactor is constructed of 316 stainless steel with a bed diameter of 30 mm and a freeboard diameter of 40 mm, and the total length is 915 mm. It is designed for the temperature up to 923 K and the pressure up to 30 MPa. The reactor is heated to the set-point temperature by three 2 kW electrical heaters that are coiled around the outer surface of the reactor tube. The temperature profile of the reactor wall is measured by some fixed, type K thermocouples held on the outer wall of the reactor in good thermal contact. Five type K thermocouples measure the temperature at the reactor centerline. Fig. 2 displays the temperature changes at centerline with the various set-point wall temperatures. It can be seen that the

![Fig. 1 – Schematic diagram of SCW fluidized bed system. 1: feedstock tank; 2,3: feeder; 4: fluidized bed reactor; 5: heat exchanger; 6: pre-heater; 7: cooler; 8–10: pressure regulator; 11: high pressure separator; 12: low pressure separator; 13,14: wet test meter; 15–18: high pressure metering pump; 19–22: mass flow meter; 23: water tank.](image-url)
thermocouples. are the temperatures at reactor centerline measured by the distance from measurement point to the distributor. Preliminary heated in the heat exchanger, then entered in the pre-heater. Preheated water was heated to 843°C by a high current heater. Water was separated from the feedstock by a high-pressure metering pump with a maximal flow rate of 125 kg/h when the amount of CO2 was large. Then, pressure was reduced from high pressure to ambient pressure. In the low-pressure separator, CO2 was finally released. The gas flow rate is measured using the wet test meter.

Model compound (glucose) was mixed directly with deionized water to the corresponding concentration. Real biomass (corn cob) was first ground with a plant mill to less than 60 mesh, and then mixed with sodium carboxymethyl-cellulose (CMC). The mixture was combined with a desired amount of water, and then the feedstock was continually stirred. Generally, the perfect concentration of CMC was about 2–3 wt%. Glucose from Tianjin Jingbei Fine Chemicals Ltd. and corn cob from Xi’an, Shaanxi were used as reactants. Table 1 shows the results of element and proximate analyses of corn cob. CMC was from Shanghai Shanpu Chemicals Ltd. and the carbon content in CMC was 33.44%. The moisture content of biomass was measured using a moisture analyzer (MASO, Sartorius) before the biomass was used. H2O2 solution from Tianjin Jingbei Fine Chemicals Ltd. was used as oxidant and the concentration was 30 wt%.

Analysis of the gas product was accomplished by the use of a Hewlett-Packard model 6890 gas chromatograph with thermal conductivity detectors. The carrier was helium, and carrier gas flow rate was 10 ml/min. A Carbon-2000 capillary column bought from CAS Lanzhou Institute of Chemical Physics was used, operating at 333 K for 2 min, followed by a 30 K/min ramp to 423 K, hold 2 min. A standard gas mixture with six kinds of contents used for calibration was bought from and compounded by Beijing AP Beifen Gases Industry Limited Company. The carbon in liquid effluent was analyzed by an Elmentar liquid model High TOC II total organic carbon analyzer.

Because the new reactor wall has a high catalytic activity for gasification which will lead to be not reproducible of experimental results [9], it is necessary to age the reactor at reaction conditions. About 30 experiments were carried out before the formal experiments in order to master experiment operation and age the reactor. The results were found to be reproducible after some experiments.

We regard the GE (gasification efficiency) = (the total mass of the product gas)/(the total mass of the dry feed), CE (carbon gasification efficiency) = (the total carbon in the product gas)/(the total carbon in the dry feed) and hydrogen yield potential (HYP, defined as the sum of measured hydrogen and the hydrogen which could theoretically be formed by completely shifting carbon monoxide and completely reforming hydrocarbon species [25]) to be indicative of the hydrogen production efficiency.

We have analyzed the uncertainty of experimental data, and the results show that the uncertainty of gas yield is less than 0.5%, that of pressure is less than 0.87%, that of...
3. Experimental results and discussions

3.1. Continuous gasification of real biomass

Fig. 3 shows changes in gas composition and gas cumulative yield from continually gasification of 10 wt% feedstock at 25 MPa, 873 K (all in Section 3, temperature refers to the set-point temperature of reactor wall). It is can be seen from Fig. 3 that product gas concentration changes rapidly in the initial stage of reaction and about 1 h later, the gasification reaction is in stable stage. At this point, the product gas is composed of H₂, CO, CO₂, C₂H₄ with a small amount of C₂H₆. The molar fraction of H₂ is about 37%, CO is about 2–3%, CH₄ is about 8%, CO₂ is 48% and that of C₂H₄ and C₂H₆ is less than 2%, which is similar to biomass gasification in a tubular reactor [13]. Also, gas cumulative yield increases linearly in the stable stage with the running time. After about more than 5 h running, the pressure drop between the inlet and outlet has not changed obviously and this is different from biomass gasification in a tubular reactor [9,13]. It is said that reactor plugging does not take place.

3.2. Effect of concentration

Fig. 4 shows the effect of solution concentration on glucose gasification at 25 MPa, 873 K. It is can be seen that hydrogen yield decreases sharply from 7.67 mol/kg to 2.51 mol/kg and CO and CH₄ yields increase as the glucose concentration increases from 5 wt% to 30 wt%. GE, CE and HYP also decrease with increasing solution concentration. As shown in Fig. 4(b), the molar fraction of hydrogen decreases from 36.03% to 16.78%, the molar fraction of CO decreases from 26.03% to 44.85% and the molar fractions of CH₄, C₂H₄, C₂H₆ have a tendency to increase with the increasing concentration. The result of high CO concentration does not agree with that of thermodynamic calculation. The results from chemical equilibrium analysis of glucose and real biomass gasification in SCW show that the molar of CO is less than 1% [14,15]. Hao et al. [12] obtained the similar results from gasification of 0.1–0.8 M glucose at 923 K, 25 MPa with a tubular reactor. The experimental results showed that 30 wt% glucose can be gasified in SCW with a fluidized bed reactor.

Fig. 5 displays the effect of solution concentration on corn cob gasification at 25 MPa, 923 K. It is can be seen that hydrogen yield decreases sharply from 11.99 mol/kg to 3.78 mol/kg and CO yield increases as the feedstock concentration increases from 5 wt% to 18 wt%. CH₄ yield increases at low concentration and decreases at high concentration with the increasing solution concentration. It can be seen from Fig. 5(b) that the molar fraction of hydrogen decreases from 45.3% to 23.02%, the molar fraction of CO decreases from 3.14% to 9.2% and the molar fractions of CO₂ increases from 43.79% to 55.91%. Compared with glucose gasification, the molar of hydrogen is much lower and the molar fraction of CO is much higher. The reason should be that the K₂CO₃ content of real biomass was slightly higher than 0.5 wt% and the K₂CO₃ content catalyzing the water gas shift reaction leaded to a preference of the formation of H₂ and CO₂ instead of CO. Sinag et al. [17] summarized the catalytic mechanism of K₂CO₃ for biomass gasification in SCW as follows.

\[
\begin{align*}
K_2CO_3 + H_2O &\rightarrow KHCO_3 + KOH \\
KOH + CO &\rightarrow HCOOK \\
HCOOK + H_2O &\rightarrow KHCO_3 + H_2 \\
2KHCO_3 &\rightarrow H_2O + K_2CO_3 + CO_2 \\
H_2O + CO &\rightarrow HCOOH \rightarrow H_2 + CO_2
\end{align*}
\]

Biomass feedstocks with high concentration were gasified successfully in experimental conditions (the fluid temperature was about 743–823 K) and reactor plugging did not occur, but experimental results of Antal et al. [9] showed that tubular reactor plugged after 1–2 h of use with feedstocks that contained about 15 wt% organic material even though at higher temperature (about 973 K), which maybe indicated that the fluidized bed was helpful to prevent plugging than tubular.
reactor. The advantages of fluidized bed are that it enhances the mass/heat transfer rates in the reactor, can be made catalytically active, can be used to collect the minerals (ash) and coke by deposition on the bed particle surface, and can be used for withdrawal of solid particles from the reactor [34]. Also, because of bed material with relatively large thermal capacity, biomass feedstock can be heated quickly when it mixed with the bed material, which was necessary for completely biomass gasification.

Fig. 4 – Effect of solution concentration on glucose gasification. Temperature, 873 K; pressure, 25 MPa; flow rate of feedstock, 25.24 g/min; flow rate of pre-heated water, 126.8 g/min.

Fig. 5 – Comparison of gas yield (a), molar fraction (b), GE, CE and HYP (c) for corn cob gasification with various feedstock concentrations. Temperature, 923 K; pressure, 25 MPa; flow rate of feedstock, 25.2 g/min; flow rate of pre-heated water, 127.3 g/min.

3.3. Effect of temperature

Fig. 6 shows the effect of temperature on corn cob gasification at 25 MPa. It can be seen from the figure that with the increasing temperature, H₂ and CH₄ yields, GE, CE and HYP increase sharply, and CO yield decreases. The molar fraction of H₂ increases from 21.78% to 38.42%, but that of CO...
decreases from 24.15% to 4.1%. It is said that temperature has a significant effect on hydrogen production by biomass gasification in SCW. Reaction rate is high at high temperature, and high temperature is also in favor of free-radical reaction, e.g. pyrolysis reaction, but inhibits ion reaction. In general, gas is formed by free-radical reaction so high temperature results in increasing gas yields. Also, physical properties, such as density, viscosity and so on, of SCW will change with various temperatures, which results in different fluidized statuses in the reactor. For example, fluid superficial velocity and viscosity are different with various temperatures when mass flow rate is constant, so bed expansion and the motion of particle also behave differently. In our experimental system, a bubbling fluidized bed is expected to form in the reactor [23], and the movement of solids is not vigorous. As a result, the effects of temperature on gasification reaction itself are much

![Graph A](image1)

![Graph B](image2)

![Graph C](image3)

**Fig. 6 – Effect of temperature on corn cob gasification.** Temperature, 873 K; feedstock, 5 wt% corn cob + 2 wt% CMC; flow rate of feedstock, 25.05 g/min; flow rate of pre-heated water, 126.7 g/min.

![Graph D](image4)

![Graph E](image5)

![Graph F](image6)

**Fig. 7 – Effect of pressure on glucose gasification.** Temperature, 873 K; feedstock, 10 wt%; flow rate of feedstock, 24.94 g/min; flow rate of pre-heated water, 125.2 g/min.
stronger than that of fluidized status change resulting from different temperatures.

3.4. Effect of pressure

Fig. 7 shows effect of pressure on gasification of 10 wt% glucose at 873 K. As shown in Fig. 6, pressure has no significant effect on gasification compared with other operation parameters, higher pressure is in favor of H₂ production and reduced CO yield. GE, CE, HYP and CH₄ yields almost remained unchanged with increasing pressure. As pressure increases from 23 MPa to 27 MPa, molar fraction of H₂ increases from 32.71% to 36.67% and molar fraction of CO decreases from 31.52% to 26.31%. Under supercritical conditions, high pressure is in favor of hydrolysis and water gas shift reaction, but inhibits pyrolysis reaction [35]. Pressure changes resulted in various positive and negative effects on glucose gasification, so showed no obvious effects on gasification. However, the advantages of SCW, such as high solubility, high diffusion

Fig. 8 – Effect of oxidant addition on glucose gasification. Temperature, 873 K; pressure, 25 MPa; feedstock, 10 wt%; flow rate of feedstock, 24.7 g/min; flow rate of pre-heated water, 125.7 g/min.

Fig. 9 – Effect of oxidant concentration on corn cob gasification. Temperature, 923 K; pressure, 25 MPa; feedstock, 5 wt% corn cob + 2 wt% CMC; flow rate of feedstock, 25.1 g/min; flow rate of pre-heated water, 125.9 g/min.
coefficient and so on, disappeared with pressure decreasing below critical point, which was not favor in biomass gasification. Series experimental researches showed that pressures about 25 MPa were adequate to realize high gasification efficiencies [8,13].

3.5. Effect of oxidant addition

Biomass gasification in SCW is an endothermic reaction, so the process requires the addition of heat to drive the chemical reaction. Generally, heat is supplied to the reactor by the external heat resource, but low energy and energy efficiencies are obtained because of low heat transfer efficiency. Heating quickly and complete gasification of biomass are also difficult to achieve. The oxidation 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 [36]. Also, some compounds, such as lignin which is a main component of plant biomass and hydrocarbon, are known to be difficult to gasify even in supercritical water. Watanabe et al. [37] studied on partial oxidative gasification of lignin and n-hexadecane by use of a batch type reactor in SCW with addition of ZrO2 and NaOH. He found that gasification efficiency and hydrogen yield increased, and tar and char yields decreased for partial oxidative gasification of lignin. In our previous work [38], a thermodynamic analysis of partial oxidative gasification of biomass in SCW was also carried out. In this paper, partial oxidative gasification for hydrogen production of glucose and real biomass was conducted.

Fig. 8 displays results from glucose gasification in SCW with addition of oxidant at 873 K, 25 MPa. It is shown in the figure that with addition of oxidation, GE, CE and CO yields and molar fraction of CO increase rapidly, but the molar fraction of H2 decreases. H2 yield increases firstly and then decreases with the increasing concentration of oxidant. When the oxidant concentration is 4.53%, H2 yield reaches maximal. It is said that hydrogen production can be promoted with addition of oxidant. Similar results were reported by Williams and Onwudili [20]. Experimental results also show that tar yield decreases with increasing oxidant concentration. The research results from Sinag et al. [2] show that the key intermediate products of glucose include phenolic compounds, CH3COOH, HCOOH, CH3CHO, and HCHO. The phenolic compounds can react with HCHO to form phenolic resin [37], HCHO + phenolic compounds → resins

\[ H_2O_2 \text{ as the oxidant can form OH by free-radical reaction in SCW [35],} \]
\[ H_2O_2 + M \rightarrow OH + OH + M \] (7)

HCHO can be decomposed into CO with OH free-radical [37] so reaction (6) is inhibited, and polymer, such as tar/char, reduces with addition of oxidant.

Fig. 9 shows effect of oxidant addition on corn cob gasification in SCW at 923 K, 25 MPa. It is similar to glucose gasification that GE, CE, the molar fraction of CO2 increase but molar fraction of H2 decreases sharply with increasing oxidant concentration. When oxidant concentration is 8.74 wt%, the yield of H2 is only 17.84%. H2 yield has a tendency to decrease as the oxidant concentration increases from 0 wt% to 8.74 wt%, which is different from glucose gasification. The

![Fig. 10 – Comparison of glucose gasification between this work and others.](image)

![Fig. 11 – Comparison of real biomass gasification between this work and others.](image)
maximal hydrogen yield does not appear, because oxidant addition leads to molar fraction of H₂ decreasing sharply although GE and CE increase.

3.6. Comparison with previous work

Fig. 10 shows comparison of results from our glucose gasification experiments with the previous work. Hydrogen yield decreases and CO yield increases with the increasing solution concentration, which is similar to the experiment results from Yu et al. [7]. Fig. 11 shows comparison of results from our real biomass gasification experiments with previous work. It can be seen that results from gasification of 5 wt% corn cob with fluidized bed are similar to results from gasification with the tubular reactor [39]. Compared with results from real biomass gasification by Antal et al. [9], hydrogen yield of this work is much lower. It is because of the presence of activated carbon catalyst and the catalyst bed temperature of 923 K which is far higher than the actual experimental fluid temperature of 773–823 K in this work. Temperature is one of the most important factors, so this system needs further improvement to achieve higher fluid temperature in the reactor. Also, Antal et al. realized original material gasification with maximal concentration of 15.6 wt%, and 18 wt% original material can be continually gasified with the fluidized bed reactor.

4. Conclusions

A novel SCW fluidized bed system for biomass gasification was built successfully in SKLMF and a performance testing on the system was conducted in this paper. Model compound and real biomass were gasified under SCW conditions to generate hydrogen-rich fuel gas. The product gas was composed of mainly H₂, CO₂, CH₄, CO and a few other gases. At 873 K and 25 MPa, the gas concentrations from gasification of 10 wt% real biomass feedstocks consisted 37% H₂, 2–3% CO, 8% CH₄, 48% CO₂, and less than 2% C₂H₄ and C₂H₆. With the increasing solution concentration, hydrogen yield, GE, and HYP decreased. 30 wt% glucose and 18 wt% corn cob feedstock were continually and stably gasified and reactor plugging was not observed. Temperature is the key factor of biomass gasification. Pressure changes resulted in various positive and negative effects on glucose gasification, so showed no significant effects on gasification. GE increases and tar yield decreases with increasing oxidant concentration. The results indicated that using fluidized bed reactor for biomass gasification in SCW has many advantages and good prospects. Comparison of this work with others showed that further improvement on the SCW fluidized bed system was needed to achieve higher fluid temperature in the reactor.

Acknowledgements

This work is currently supported by the National Key Project for Basic Research of China (973 program) through contract No. 2003CB214500, the National High Technology Research and Development Program of China (863 Program) through contract No. 2007AA052147, and the National Natural Science Foundation of China through contract No. 50521604.

REFERENCES
