

# An Experimental Investigation of Hydrogen Production from Biomass

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**Abstract:** In gaseous products of biomass steam gasification, there exist a lot of CO, CH<sub>4</sub> and other hydrocarbons that can be converted to hydrogen through steam reforming reactions. There exists potential hydrogen production from the raw gas of biomass steam gasification. In the present work, the characteristics of hydrogen production from biomass steam gasification were investigated in a small-scale fluidized bed. In these experiments, the gasifying agent (air) was supplied into the reactor from the bottom of the reactor and the steam was added into the reactor above biomass feeding location. The effects of reaction temperature, steam to biomass ratio, equivalence ratio (ER) and biomass particle size on hydrogen yield and hydrogen yield potential were investigated. The experimental results showed that higher reactor temperature, proper ER, proper steam to biomass ratio and smaller biomass particle size will contribute to more hydrogen and potential hydrogen yield.

**Key words:** air-steam gasification; biomass; hydrogen production

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## 1 INTRODUCTION

There are abundant resources of biomass energy over the world. The conversion of biomass into hydrogen-rich gas provides a competitive means for producing energy and chemicals from renewable sources<sup>[1]</sup>. It was proved by Cox et al.<sup>[2]</sup> that high hydrogen yields can be achieved through control of gasification conditions and reactor design.

Much work has been done concerning biomass gasification<sup>[2-13]</sup>. Only a few of them put the emphasis on hydrogen production<sup>[2-4,10,12]</sup>. Cox et al.<sup>[2]</sup> combined biomass gasification and hydrogen separation into a single process step by using a membrane reactor, which showed good performance through concurrent separation of the hydrogen. Turn et al.<sup>[3]</sup> utilized an oxygen-nitrogen-steam mixture as the gasifying agent, under their experimental conditions, the hydrogen yield varied from 23 to 60 g/kg of dry, ash-free biomass. Many researchers investigated the effect of catalysts on gas composition<sup>[5-11]</sup>. Till now the catalysts studied are mainly calcined dolomite and Ni-based steam reforming catalysts.

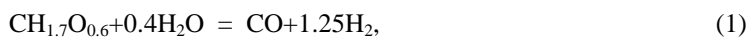
Less emphasis has been given to experimental conditions investigation of hydrogen production via biomass gasification. Ultimate analysis of pine sawdust was a typical mass composition of 50.54% carbon, 41.11% oxygen and 7.08% hydrogen with the balance comprised of traces of

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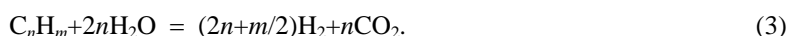
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nitrogen, sulfur and mineral species. Considering the major elements, the fuel may be represented on a molar basis as  $\text{CH}_{1.7}\text{O}_{0.6}$ . Using steam as oxidizer, the following balanced chemical equations can be written:



The present paper reports results of initial biomass gasification tests over a range of reactor temperatures, steam to biomass ratio (S/B), equivalence ratio (ER) and biomass particle size. S/B is defined as the steam mass flow rate divided by the fuel mass flowrate (wet basis). ER is defined as the actual oxygen to fuel ratio divided by the stoichiometric oxygen to fuel ratio required for complete combustion. Particular emphasis is given to measured hydrogen yields and hydrogen yield potential. Hydrogen yield potential (HYP) is defined as the measured hydrogen plus hydrogen which could theoretically be formed by completely reforming hydrocarbon species according to the following reaction:



## 2 EXPERIMENTAL

### 2.1 Feed Material

Pine sawdust obtained from a timber mill in Guangzhou City, Guangdong Province, China was used as the feedstock for experiments. The pine sawdust was sieved into four size samples for use, with the size range of 0.6~0.9 mm, 0.45~0.6 mm, 0.3~0.45 mm, and 0.2~0.3 mm respectively.

### 2.2 Apparatus

The tests were performed at atmospheric pressure, in an indirectly heated fluidized-bed gasification system, as shown schematically in Fig.1.

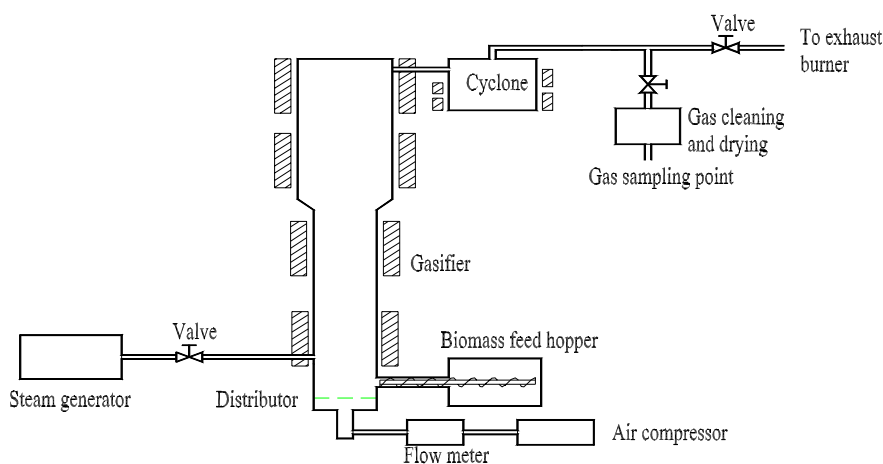


Fig.1 Schematic diagram of biomass air-steam gasification in a fluidized bed

The reactor is made of a stainless steel pipe and is externally heated by two electric furnaces. The total height of the reactor is 1400 mm, with a bed of 800 mm length and diameter of 40 mm and

a freeboard diameter of 60 mm. The biomass is fed into the reactor through a screw feeder driven by a variable speed metering motor. Air is used as the fluidizing agent. Before it enters the reactor, it is preheated to 65°C in the preheater for better performance. The steam of 154°C is produced in a steam generator. The gaseous product flow exits the reactor, then passes through a cyclone, which is heated to 200°C to prevent tar contained in the gas from condensing.

The pine sawdust feedrate of four particle sizes was determined over a range of screw speeds prior to testing. At the beginning of the experiment, the fluidized bed was charged with 30 g silica sand (particle size 0.2~0.3 mm) as bed material, which helped in stable fluidization and better heat transfer. Typically, it took 15 min for the test stabilized. 3 samples were taken in a period of 3 min in each experimental run.

### 2.3 Sampling, Gas Analysis and Mass Balance Calculation

After the char carried in the produced gas was separated in the cyclone, the gas flow was passed through a dry ice trap and a cotton fiber filter for drying and cleaning. The volume of gaseous product was measured by a gas meter. The dry and clean gas was sampled using gas bags and analyzed on a gas chromatograph (Model GC-2010, Gas Chromatograph, SHIMADZU, Japan), which was fitted with a GS-Carbonplot column (30 m×0.530 mm×3.00 μm), with helium as a carrier gas, to detect H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>.

To insure the reliability of test data, the mass balance calculation was performed for each test. The typical calculation results are listed in Table 1 and the mass balance error of this run is 2.1%. The error mainly comes from incomplete collection of tar and the neglect of heavier hydrocarbons than C<sub>2</sub> species.

**Table 1 Experimental conditions, results and mass balance calculation**

Experimental conditions				Mass balance calculation								
				Input mass (g/h)			Output mass (g/h)					
Biomass feed rate (g/h)	Air (m <sup>3</sup> /h)	Steam (g/h)	T (°C)	Biomass	Air	Steam	Total	Gas	Char	Tar	Condensate	Total
512	0.7	600	750	512.0	812.1	600.0	1924.1	1323.2	34.8	16.3	510.2	1884.5
				Recovery 97.9% (, ω)								
Gaseous product composition (% , ϕ) and gas yield (m <sup>3</sup> /h)												
H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub>	Gas yield			
15.84	0.36	41.85	4.34	19.38	13.88	1.88	0.09	0.13	1.3			

## 3 RESULTS AND DISCUSSION

### 3.1 Typical Experimental Results

Typical operation parameters and results are listed in Table 2. From Table 2, it can be seen that the main components of fuel gas are H<sub>2</sub>, CO and CO<sub>2</sub>. The average content of H<sub>2</sub> exceeds over 20%. Table 2 shows that HYP varies slightly under different experimental conditions. This indicates that HYP is mainly controlled by the characteristic of biomass itself. Under the conditions reported in Table 2, hydrogen yield ranges between 49.47 and 70.79 g/kg (H<sub>2</sub>/biomass), on wet basis. This shows the good performance of this fluidized-bed reactor.

### 3.2 Effect of Temperature

It is known that temperature plays an important role in the biomass gasification. Reactor

temperature was increased from 700°C to 900°C in 50°C increments holding all other conditions constant (ER=0.22, S/B=2.7, biomass particle size 0.3~0.45 mm). From results presented in Fig.2, it can be seen that gas yield increases with temperature. According to Le Chatelier's principle, higher temperatures favor the endothermic reactions. Therefore, Reactions (4)~(7) are promoted with higher temperatures, and more H<sub>2</sub> and other permanent gases can be produced. Correspondingly H<sub>2</sub> yield and H<sub>2</sub> yield potential increase with temperature as Fig.2 shows. The former increases from 22 to 70 g/kg biomass (wet basis) and the latter increases from 137 to 207 g/kg biomass (wet basis).



**Table 2** Experimental results of biomass air-steam gasification for hydrogen production

Run number	1	2	3	4	5
Feed rate (kg/h)	0.445	0.445	0.512	0.445	0.445
Biomass particle size (mm)	0.3~0.45	0.3~0.45	0.3~0.45	0.3~0.45	0.3~0.45
Air (m <sup>3</sup> /h)	0.5	0.5	0.65	0.5	0.5
Steam flow rate (kg/h)	0.9	0.9	0.8	1.2	1.2
Temperature (°C)	800	820	800	850	900
Equivalence ratio	0.22	0.22	0.25	0.22	0.22
Dry gas composition (% , $\phi$ )					
H <sub>2</sub>	20.69	22.74	19.95	24.80	26.86
O <sub>2</sub>	0.18	0.18	0.16	0.35	0.33
CH <sub>4</sub>	5.51	5.16	4.72	4.95	4.62
CO	26.37	25.41	25.44	23.48	22.89
CO <sub>2</sub>	11.69	11.93	11.58	12.88	13.26
C <sub>2</sub> H <sub>4</sub>	2.40	1.98	2.02	1.56	1.37
C <sub>2</sub> H <sub>6</sub>	0.10	0.04	0.09	0.03	0
C <sub>2</sub> H <sub>2</sub>	0.22	0.22	0.15	0.21	0.19
N <sub>2</sub>	28.30	28.07	32.45	27.36	26.53
Gas yield (Nm <sup>3</sup> /kg, wet basis)	2.34	2.37	2.18	2.45	2.53
Hydrogen yield (g/kg, wet basis)	52.08	57.68	49.47	64.53	70.79
Hydrogen yield potential (g/kg, wet basis)	214.67	208.04	192.92	204.75	207.75

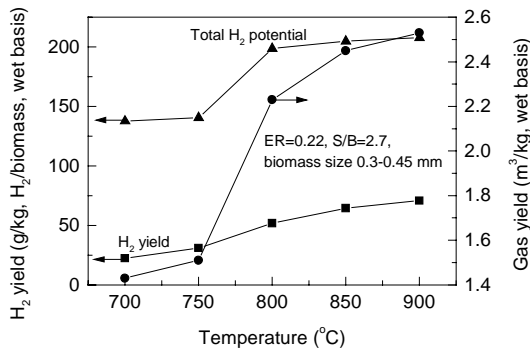


Fig.2 Effect of temperature on hydrogen yield

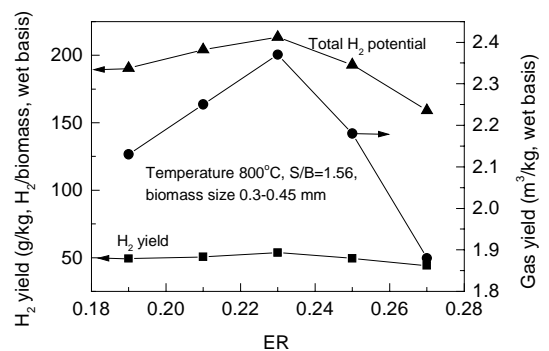


Fig.3 Hydrogen yield as a function of ER

From Fig.2, it can also be noticed that the increase of H<sub>2</sub> yield potential becomes lower when temperature is higher than 800°C. This suggests that it is not economical to apply too high a temperature in the hydrogen production process. As shown in Table 1, there exists a large amount of CO in the fuel gases, which results in a much larger amount of H<sub>2</sub> yield potential than H<sub>2</sub> yield as indicated in Fig.2.

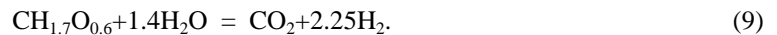
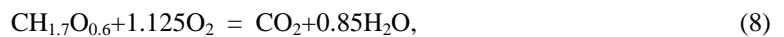
### 3.3 Effect of Equivalence Ratio

At the present study, ER was varied from 0.19 to 0.27 through changing the air flowrate and holding the other conditions constant (temperature 800°C, S/B=1.56, biomass particle size 0.3~0.45 mm). The results of varying ER are reported in Fig.3, indicating that gas yield first increases and then decreases with ER, and H<sub>2</sub> yield and H<sub>2</sub> yield potential exhibit the same trend.

ER not only represents the oxygen quantity introduced into the reactor but also is related with gasification temperature under the condition of autothermal operation. On the one side, higher ER will cause product gas to degrade because of higher extent of oxidization. On the other side, higher ER means higher gasification temperature and higher temperature can accelerate gasification rate and improve product quality to a certain extent. Therefore, gas composition is affected by the two contradictory effects of ER.

As shown in Fig.3, the process can be divided into two stages. In the first stage, ER varies from 0.19 to 0.23, the positive effect of ER plays a more important role. Then the gas yield increased from 2.13 to 2.37 m<sup>3</sup>/kg biomass, and H<sub>2</sub> yield, H<sub>2</sub> yield potential increase slightly.

In the second stage, ER varies from 0.23 to 0.27, oxidization Reaction (8) becomes more important than steam gasification Reaction (9) because of increased oxygen quantity. It is obvious that Reaction (9) produces 2.25 mol more permanent gas (represented by H<sub>2</sub>) than Reaction (8). Therefore, in the second stage, gas yield, H<sub>2</sub> yield and H<sub>2</sub> yield potential start to fall.



For H<sub>2</sub> yield, there exists an optimal value of ER, 0.23. At this value, the hydrogen yield reached 54 g/kg (H<sub>2</sub>/biomass).

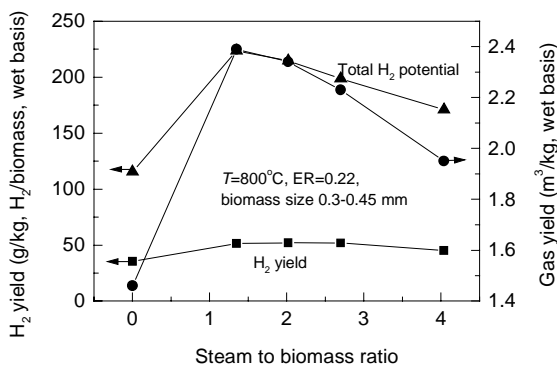


Fig.4 Hydrogen yield as a function of S/B

### 3.4 Effect of Steam to Biomass Ratio (S/B)

In this test, S/B was changed from 0 to 4.04 by varying steam flowrate while keeping all the other conditions constant (temperature 800°C, ER=0.22, biomass particle size 0.3~0.45 mm). The tests results are presented in Fig.4.

The addition of steam makes H<sub>2</sub> yield increased greatly, from 35.49 g/kg (H<sub>2</sub>/biomass) (S/B=0) to 52.08 g/kg (H<sub>2</sub>/biomass) (S/B=2.02), an increase by 47%. Over the S/B range from 1.35 to 4.04, gas yield exhibits a decreasing

trend, which can be explained by that additional steam of low temperature lowers reaction temperature and then causes gas yield, H<sub>2</sub> yield and H<sub>2</sub> yield potential to decrease.

From the analysis of the tests data with varying S/B, it is evident that introduction of steam in biomass steam gasification does benefit the increase of gas and hydrogen yield. However, excessive steam will lower reaction temperature and cause a decrease in gas and hydrogen yield.

### 3.5 Effect of Biomass Particle Size

In the biomass steam gasification process, the pyrolysis reaction of biomass particle cannot happen until it is heated to a certain temperature. The size of biomass particles affects the heating rate, thus further showing an effect on the composition of produced gas and gas yield.

The test results of biomass particle size are presented in Table 3. It is generally accepted that a high heating rate produces more light gases and less char and condensate<sup>[13]</sup>. As biomass particle size decreases, the gas yield increased from 1.53 to 2.57 m<sup>3</sup>/kg. Smallest particles lead to 1.04 m<sup>3</sup> more gas per kg of biomass than the coarsest particles. Table 3 shows that for 1 kg of biomass the smallest particles produced 56 g H<sub>2</sub>, and the biggest particles produced 35 g H<sub>2</sub>. The smallest particles yielded 21 g more hydrogen than the biggest ones for 1 kg of biomass. This can be explained as that for small particle sizes the pyrolysis process is mainly controlled by reaction kinetics. As the particle size increases, the produced gas resultant inside the particle is more difficult to pass through particle walls and the process is mainly controlled by gas diffusion.

**Table 3 Effect of biomass particle size on gas composition and hydrogen production**

Biomass particle size (mm)	0.6-0.9	0.45-0.6	0.3-0.45	0.2-0.3
Feed rate (kg/h)	0.512	0.512	0.512	0.512
Air (m <sup>3</sup> /h)	0.6	0.6	0.6	0.6
Steam flow rate (kg/h)	0.8	0.8	0.8	0.8
Temperature (°C)	800	800	800	800
Equivalence ratio	0.23	0.23	0.23	0.23
Dry gas composition (%. φ)				
H <sub>2</sub>	18.53	19.83	20.95	20.59
O <sub>2</sub>	0.20	0.11	0.16	0.16
CH <sub>4</sub>	3.88	4.66	5.07	5.26
CO	21.83	23.55	26.69	27.43
CO <sub>2</sub>	12.41	12.22	11.23	11.32
C <sub>2</sub> H <sub>4</sub>	1.55	2.05	2.26	2.46
C <sub>2</sub> H <sub>6</sub>	0.06	0.11	0.12	0.17
C <sub>2</sub> H <sub>2</sub>	0.14	0.17	0.15	0.18
N <sub>2</sub>	38.90	33.42	28.92	27.31
Gas yield (Nm <sup>3</sup> /kg, wet basis)	1.53	1.93	2.37	2.57
Hydrogen yield (g/kg, wet basis)	35.37	44.06	53.78	56.00
Hydrogen yield potential (g/kg, wet basis)	126.59	168.63	213.43	233.67

## 4 CONCLUSIONS

From the analysis of the four critical parameters (temperature, steam to biomass ratio, ER and particle size), it is found that H<sub>2</sub> yield potential is most sensitive to ER. A small increase of ER will cause H<sub>2</sub> yield potential to drop sharply when ER exceeds a certain value. Temperature plays a very important role in the process. Higher temperature will be more favorable for hydrogen yield. When

temperature is high enough, H<sub>2</sub> yield potential changes slightly. Both S/B and ER have complex effects on gasification temperature. Too high S/B and too low ER will lower reaction temperature and is not economic for hydrogen yield. There exist optimal values for S/B and ER. In the present work, the optimal values for S/B and ER were 2.02 and 0.23, respectively. Biomass particle size also has influence on hydrogen yield, and smaller particles will produce more gas.

The highest hydrogen yield (71 g/kg, H<sub>2</sub>/biomass) was achieved under the conditions of temperature 900°C, ER=0.22, S/B=2.7. It is shown that under proper operating parameters biomass air-steam gasification in a fluidized bed is an effective way for hydrogen rich gas production.

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