

2012 AASRI Conference on Modelling, Identification and Control

Hydrogen Production from Biomass Pyrolysis in Molten Alkali

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Abstract

Pyrolysis of biomass to hydrogen rich gas in molten alkali media has been conducted in a stainless steel tank reactor. Molten alkali was used as thermal pyrolysis media. Six kinds of biomass were selected as feedstock. The experiments were carried out under atmospheric pressure and 350-550 °C. The pyrolysis gas was analyzed by gas chromatograph. The effects of the type of biomass, addition of additives and reaction conditions, including temperature and N₂ flow rate, on hydrogen content in pyrolysis gas and yield of hydrogen were investigated. This paper reports the feasibility for producing hydrogen rich gas through the pyrolysis of biomass in molten salt media.

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Keywords: biomass; pyrolysis; hydrogen; molten salts

1. Main text

The inter-related problems of energy and environment are one of biggest challenges facing the world recently, especially for energy sustainability and carbon emissions from the utilization of fossil fuels. Many engineers and scientists agree that the solution to these problems would be to replace the existing fossil system by the hydrogen energy system [1, 2]. There are several established and developing technologies to produce hydrogen from various sources. Hydrogen production can be environmentally friendly only if the resource used to extract hydrogen would be rather biomass than fossil fuel, such as coal, petroleum and natural gas.

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There are two main routes for biomass-based hydrogen production, namely thermo-chemical and bio-chemical. Thermo-chemical routes can produce hydrogen from continuous feed biomass rapidly. Thermo-chemical routes are gasification [3], pyrolysis of bio-oils [4], steam reforming of biomass derived higher alkanes and alcohols [5], and aqueous phase reforming of oxygenated hydrocarbons [6].

Molten alkali is ionic crystals under solid state and will melt into ionic liquid at high temperature. Molten alkali has properties of good electrical conductivity, broad service range of temperature, good thermal stability, low vapour pressure, large heat capacity, large thermal conductivity, good dissolution ability and low viscosity, as well as good chemical stability. Physical properties of molten NaOH and KOH are shown in table 1.

Table 1 Physical Properties of molten NaOH and KOH

Molten alkali	Thermal conductivity (cal/cm·sec·deg)	Specific heat capacity (cal/deg·mole)	Viscosity (Cp)	Boiling point (°C)
NaOH	0.0022(400 °C)	19.8(400~900 °C)	2.817(400 °C)	1390
KOH	0.0021(400 °C)	19.9(320~990 °C)	1.292(500 °C)	1320

In our previous work [7], molten salts ($\text{ZnCl}_2\text{-KCl}$) were used as media to produce bio-oil from biomass. In this work, pyrolysis of biomass in molten alkali media to produce hydrogen rich gas was carried out. Six kinds of biomass were selected as biomass samples. Molten NaOH was employed as media. The effects of the biomass samples type, reaction conditions, and additives on yield of gas product and content of hydrogen in gas product were investigated.

2. Experimental setup

2.1. Biomass samples

In this work, agricultural and forestry wasters, including fir sawdust, birch sawdust, redwood sawdust, rice stalk, cole stalk and rice husk were used as biomass feed. The birch sawdust was from Northeast China and other biomass samples were from East China. The element (C, H, O, N and S) content in biomass materials was analyzed by a Vario elemental analyzer. The biomass sample was sieved and the fraction saved for the pyrolysis experiments was 60-100 mesh. The biomass sample was dried at 105 °C prior to the experiments.

2.2. Reagents

Sodium hydroxide, potassium hydroxide, nickel chloride, nickel hydroxide, palladium chloride, sodium chloride, nickel, alumina, and other reagents are from SINOPHARM Chemical Reagent Co. Ltd with purity of more than 99.0%.

2.3. Test facilities

The biomass pyrolysis was performed in an atmospheric pressure in molten alkali. The schematic lab-scale configuration is illustrated in Fig. 1. The pyrolysis reactor consisted of a reactor, a biomass screw feeder, a set of heater and a set of cooler. The stainless steel reactor had an inner diameter of 95 mm and a height of 150 mm, equipped with feed inlet, gas outlet, and thermocouple tube. The heating furnace with a programmed temperature controller was self-designed. The temperature was monitored and controlled by K-type thermocouples inside the thermocouple tube. A variable-speed DC motor was employed to adjust the rotational speed of the screw feeder. The gas flow was divided so that one third went through the bottom of

the reactor and the remaining two thirds through the feeder. At the end of feed tube, a cooling jacket was equipped to prevent coking as the biomass sample meets the molten alkali soon. The liquid products (bio-oil + water) were collected by condensing in cold traps maintained at about 0 °C. The cooler system was made of quartz, in favor of observing condensation condition. The noncondensable gases were collected by gas collector after metered by flow meter.

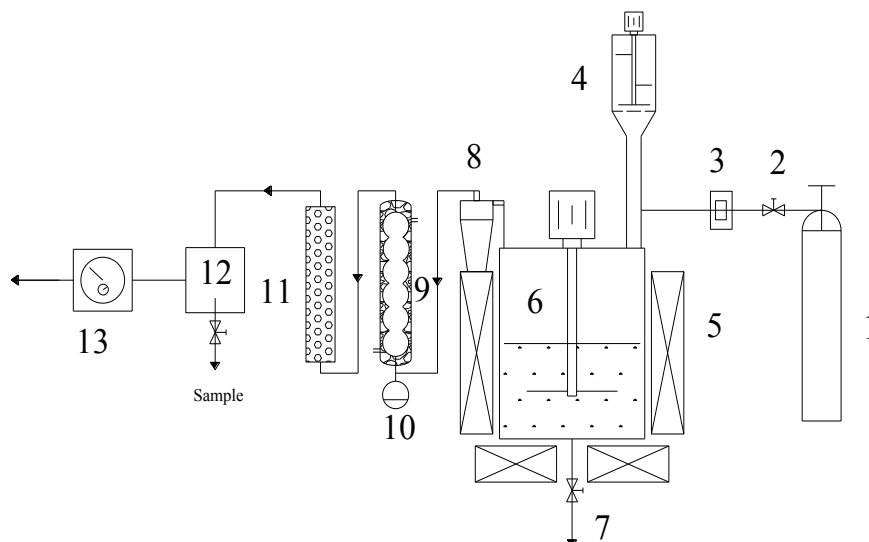


Fig. 1 Schematic diagram of experimental apparatus. (1-He cylinder, 2-pressure reducing valve, 3-flowmeter, 4-self-designed feeder, 5-oven, 6-reactor, 7-discharge valve, 8-cyclone separator, 9-glass condenser, 10-oil container, 11-water absorber, 12-gas container, 13-flowmeter.)

2.4. Procedure

Preliminary, about 700 g molten alkali was put into reactor. When the heating was started, nitrogen gas continuously flowed into the reactor to guarantee an 'oxygen-free' environment. As soon as the reactor temperature reached the reaction temperature, the circulating cooling water system began to work and the pre-treated biomass sample was injected into the reactor through feeding system. The biomass underwent a flash pyrolysis and was converted into hydrogen rich gas, liquid product (bio-oil and water), and bio-coke (only taking up a small amount of total products).

The tests were performed under atmospheric pressure at five different temperatures: 350 °C, 400 °C, 450 °C, 500 °C and 550 °C. The N₂ flow rate was kept from 60 to 200 L/h. The gas product was collected into a gas collector and examined by a SHIMADZU GC 17-A gas chromatograph equipped with a TDX-01 packed column. H₂ content in gas product was calculated through area correction normalization method. The yield of H₂ was calculated as:

$$Y_{H_2} = \frac{F_{\text{gas-product}} \times H_2\% \times M_{H_2}}{m_{\text{biomass-sample}}} \times 100\%$$

Y_{H_2} —H₂ yield; $F_{\text{gas-product}}$ —volume flow rate of gas product; $H_2\%$ —H₂ content in hydrogen rich gas; M_{H_2} —molecular weight of H₂; $m_{\text{biomass-sample}}$ —mass feed rate of biomass sample.

3. Results and Discussion

3.1. Element contents of Biomass samples

Test results for element contents test are presented in Table 2. C, H and O were found as the three most abundant elements in the biomass samples, regardless of biomass type. The carbon and hydrogen contents of selected biomass samples are in the range of 35.3–47.0%, w/w and 7.0–8.51%, w/w. Birch sawdust was proved to be the highest hydrogen content among selected biomass samples.

Table 2 Element contents in the biomass material

Biomass	N	C	S	H	O
Fir sawdust	0.444	47.007	0.524	8.500	43.525
Birch sawdus	0.190	45.690	0.528	8.513	45.079
Redwood sawdust	0.241	47.440	0.571	7.789	43.962
Rice stalk	1.174	40.790	0.486	7.664	49.886
Rice hus	0.476	39.843	0.367	7.079	52.235
Cole stalk	1.267	35.273	0.535	7.364	55.561

3.2. Effects of biomass sample type

After detection by GC, it is proved that gas product of biomass pyrolysis in molten NaOH consists of only two compounds, hydrogen and methane. Fig. 2 shows the effect of biomass samples type on yield and content of H₂ in gas product obtained through biomass pyrolysis in molten NaOH under condition of 450 °C, 1 atm, 100 L/h N₂ flow rate. The biomass type has little influence on H₂ content in pyrolysis gas. H₂ yields were significantly influenced by biomass samples type. Among selected biomass samples, redwood sawdust gave the highest H₂ yield of 65.39 g/Kg biomass, whereas the lowest H₂ yield of about 40.0 g/Kg biomass for cole stalk and rice husk.

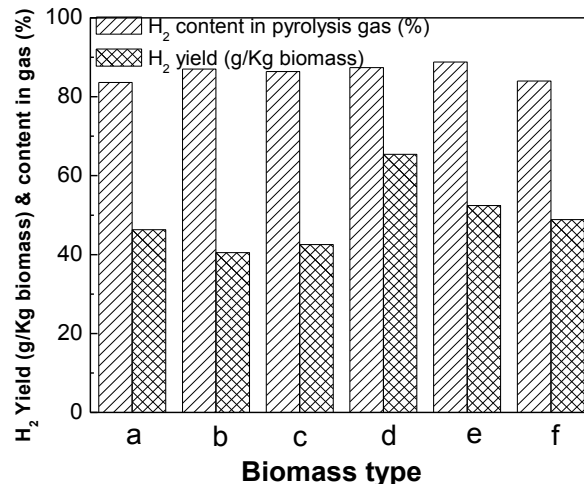


Fig. 2 H₂ content in gas and H₂ yield vs. biomass samples type. (a-rice stalk, b-cole stalk, c-rice husk, d-redwood sawdust, e-fir sawdust, f-birch sawdust; 450 °C, 1atm, 100 L/h N₂, molten NaOH.)

3.3. Effects of temperature

The pyrolysis temperature is crucial for hydrogen production from biomass pyrolysis in molten NaOH. The effects of pyrolysis temperature on H_2 yield and H_2 content in pyrolysis gas from rice stalk pyrolysis in molten alkali were examined under atmospheric pressure, 100 L/h N_2 flow rate. The experimental results were shown in Fig. 3. It can be seen that H_2 content in pyrolysis gas are slightly influenced by temperature. Higher temperatures significantly resulted in higher H_2 yields. With temperature increasing from 350 to 550 °C, H_2 yield increased from 30.7 to 66.5 g/Kg-biomass. As has been reported in the literature [8], this result is related to the fact that the H_2 yields are linked by the equilibrium of both the pyrolysis reaction and the water–gas shift reaction under test conditions.

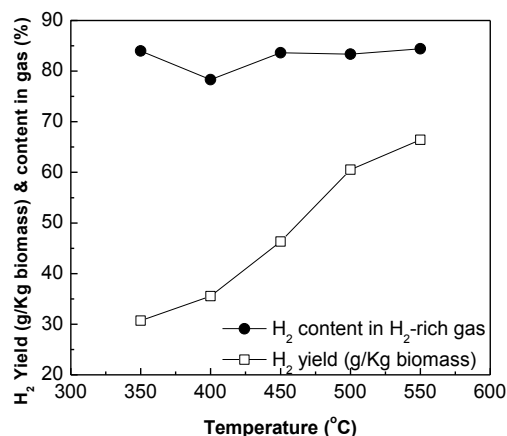


Fig.3 H_2 content in gas and H_2 yield vs. pyrolysis temperature. (1 atm, 100 L/h N_2 , rice stalk, molten NaOH.)

3.4. Effects of N_2 flow rate

Inert gas served to provide oxygen free environment, to accelerate mixing of molten salts and biomass particles, and to bring pyrolysis gas out of reactor to prevent secondary cracking reactions of the primary pyrolysis gases. As shown in Fig. 4, the effects of inert gas under atmospheric pressure and 425 °C were investigated. The flow rate of inert gas was varied from 60 L/h to 200 L/h. The results show that inert gas flow rate has little influences on H_2 yields and H_2 contents in pyrolysis gas.

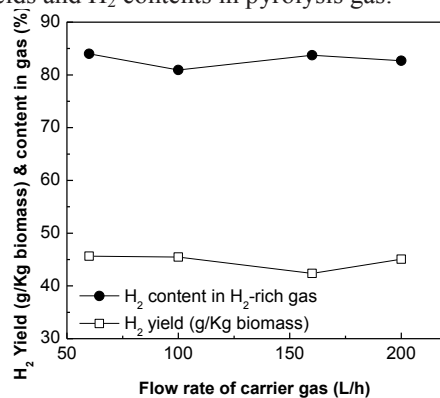


Fig.4 H_2 content in gas and H_2 yield vs. N_2 flow rate. (425 °C, 1atm, rice stalk, molten NaOH.)

3.5. Effects of additives addition

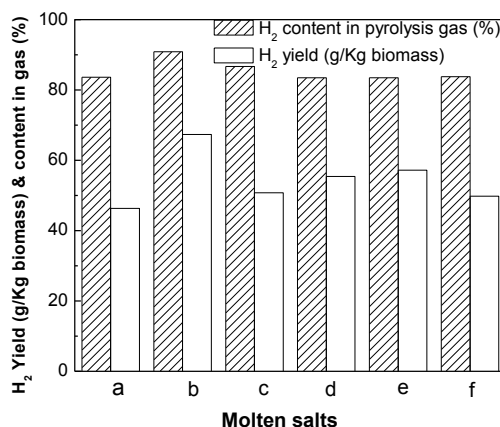


Fig.5 H₂ content in gas and H₂ yield vs. additives type. (450 °C, 1atm, 100 L/h N₂, rice stalk)

The effects of adding additives into molten NaOH are shown in Fig. 5(a-NaOH, b-NaOH-5%NiCl₂, c-NaOH-1%Ni, d-NaOH-Ni/Al₂O₃, e-NaOH-5% NaCl, f-NaOH-1% PdCl₂). These results indicated that the addition of the additives increased H₂ yield for pyrolysis of biomass. Among the additives, NiCl₂ increased H₂ yield significantly. Compared to 46.33 g/Kg yield of H₂ from pyrolysis rice stalk in molten NaOH, the H₂ yield increased to 67.34 g/Kg in molten NaOH-NiCl. However, the promotion became weak with adding Ni, NiOH and Ni/Al₂O₃.

4. Conclusions

The following conclusions can be drawn from the experimental results of biomass pyrolysis in molten NaOH to produce hydrogen rich gas. Biomass sample type, reaction temperature, and additive addition have significant influence on the H₂ yield. Higher temperature contributes to higher H₂ yield. The introduction of additives, especially NiCl, leads to increasing of H₂ yield.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (20906084) and graduate student Qi Shen for his help.

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