Experimental Study of Phenol as Biomass Tar Model Compound Gasification for Hydrogen

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Abstract: Phenol,as one of the main constituents of biomass tar, was used to gasify for hydrogen in this paper. It was studied that the influences of the reaction temperature, steam / biomass (S / B), load and the preparationof the catalyst on the hydrogen yield, gasification efficiency and hydrogen concentration. In the experiment, the catalyst loading material is porous ceramic foam. The results indicate that the S/B molar ratio of 2,the temperature of 1073 K and the load of 8% provide favorable operating conditions for steam reforming of phenol so as to get the highest hydrogen yield,gasification efficiency and hydrogen concentration. And it was easier to produce hydrogen when catalyst was calcinated for 1hour at 973K and the porosity is 20ppi.

Introduction

During the gasification process of biomass, tar is an inevitable by-product in the pyrolysis stage. The production of tar will not only cause energy waste, reduce efficiency of gasification, and pollute the environment and equipments, but also pose a certain hazard to human health[1].Tar catalytic reforming is the most important step in the process of biomass pyrolysis and gasification[2]. Research on tar removal usually considers the use of model compounds, such as toluene[3],naphthalene[4] and phenol[5].

In viewof thecurrent researchon the impact of catalyst preparation conditions on the gasification process of phenol are relatively small. In this experiment, phenol and Ni are separately used as the tar model compound and the catalyst for the catalytic reforming of phenol vapor in the experimental platform. The catalyst loading material is porous ceramic foam. The orthogonal experimental method is adopted to reveal the influence of different reaction conditions and varied preparation conditions of the catalyst on the phenol gasification to produce hydrogen.

Experimental materials and set-up

In the experiment，phenol is used as the model compound of tar and the nickel-based catalyst is used to catalyze steam reforming of phenol in reactor[6].The catalyst loading material isporous ceramic foam made of silicon carbide.
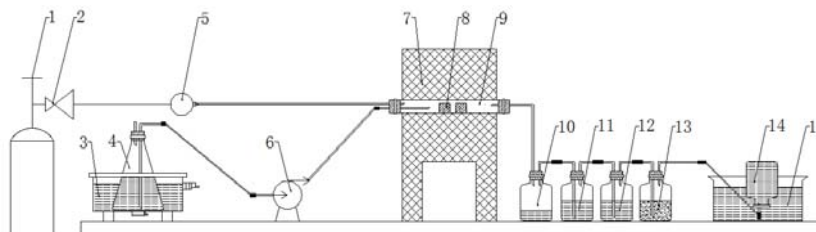
1 nitrogen bottles; 2 pressure reducing valve; 3 water-bath heater; 4 conical flask; 5 rotameter; 6 syringe pump; 7 electric furnace; 8 nickel-based catalyst; 9 quartztube; 10 safety bottle; 11 ethanol liquid; 12 water bottle; 13 desiccant; 14 cylinder; 15 flume
Figure 1 Experimental set-up for phenol steam reforming

The schematic of the experimental apparatus was shown in Fig. 1.The major equipment is the electric furnace and the evaporator consisted of the water-bath heater and the conical flask. Aqueous solution of phenol well mixed in the conical flask was heated by the water bath heater and then was introduced by the syringe pump into the quartz tube in the formation of gas to react.
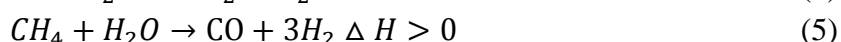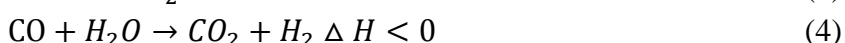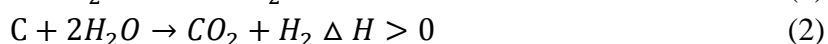
Experimental results and discussion

Influence of Reaction Temperature, S/B and Load on the Experimental Results

S/B and load on productivity of hydrogen, gasification efficiency and hydrogen concentration in the first part of this experiment. Restricted by many factors in the investigation, the orthogonal experiment is performed to investigate the influences of reaction conditions on the results, and the catalyst should be produced under same the preparation condition. The experimental scheme and experimental results are shown in table 1.

Table 1Experimental results of different reaction conditions

Experiment number	Temperature(K)	S/B	Load	Raw material - hydrogen production rate(L/g)			Gasification efficiency(%)			$H_2\%$		
				Results a	Results b	Results c	Results a	Results b	Results c	Results a	Results b	Results c
1	973	1.5	2%	0.099	0.101	0.098	43.9	43.1	43.5	39.1	39.4	39.3
2	1023	1.5	6%	0.151	0.148	0.150	58.0	58.2	57.7	42.5	42.7	42.1
3	1073	1.5	8%	0.175	0.177	0.174	70.7	70.3	70.4	46.3	45.6	46.1
4	973	2	6%	0.103	0.102	0.104	49.5	49.3	49.6	43.7	43.4	43.2
5	1023	2	8%	0.156	0.153	0.154	61.6	61.1	61.3	47.5	47.1	46.8
6	1073	2	2%	0.181	0.177	0.179	72.7	72.5	72.8	47.9	47.7	47.6
7	973	2.5	8%	0.101	0.102	0.104	49.8	49.4	49.6	41.2	41.5	40.7
8	1023	2.5	2%	0.150	0.151	0.147	61.0	61.1	60.5	45.2	45.3	45.5
9	1073	2.5	6%	0.176	0.174	0.173	71.1	71.4	70.8	46.6	46.8	46.9

The reactions of biomass during the gasification process mainly are as follows:

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H > 0 \tag{1}$$
$$C + 2H_2O \rightarrow CO_2 + H_2 \quad \Delta H > 0 \tag{2}$$
$$C + CO_2 \rightarrow 2CO \quad \Delta H > 0 \tag{3}$$
$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H < 0 \tag{4}$$
$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H > 0 \tag{5}$$

It can be seen from the experimental results:

(1) When S/B is 2 and the load is 8%，the reaction temperature is 973K, 1023K and 1073K respectively, hydrogen production rate increases from 0.108L/g to 0.183L/g, the gasification efficiency increases from 49.9% to 72.9%，the hydrogen content increases from 43.8% to 48.1%. Reaction (1)，reaction (2) and reaction (3) are endothermic reactions, the higher temperature is easier to occur for forward reaction of the endothermic reaction, thereby enhancing the hydrogen yield, gasification efficiency and hydrogen concentration.

(2) When the reaction temperature is1073K and the load is 8%，S/B increases from 1.5 to 2 and then increases to 2.5，hydrogen production rate increases from 0.176L/g to 0.183L/g and then decreases to 0.178L/g，the gasification efficiency increases from 70.6% to 72.9% and then decreases to 71.5%，the hydrogen content increases from 46.2% to 48.1% and then decreases to 47.1%.S/B can be increased in a certain range, thus the concentration of water vapor is improved, which is conducive to reactions in forward direction and improves the hydrogen yield. When S/B is increased from 2 to 2.5, an excess of the water vapor would lower the reaction temperature, decrease the reaction rate, and lower the hydrogen yield and gasification efficiency. Therefore, the most appropriate value for S/B is 2.

(3) When the reaction temperature is1073K and S/B is 2，loadincreases from 2% to 6% and then increases to 8%，hydrogen production rate increases from 0.179L/g to 0.183L/g, the gasification efficiency increases from 72.7% to 72.9%，the hydrogen content increases from 47.8% to

48.1%.The experimental results show that the productivity of hydrogen,gasification efficiency and hydrogen concentration ascend with the increaseof Ni load of the catalyst.The catalyst can accelerate the reaction rate and reduce the activation energy of the reaction.

Effect of Catalysts under Different Preparation Conditions on the Experimental Results

It is primarily to study the effects of the preparation conditions of the catalyst on hydrogen yield, gasification efficiency and hydrogen concentration in the second part of this experiment. The preparation conditions of the catalyst mainly include three aspects on calcination time, calcination temperature and porosity. The experimental conditions of the reactionare selected to be reaction temperature of 1073K, S/B of 2, and the load of 8%, and conduct the orthogonal experiment. The experimental scheme and experimental results are shown in table 2.

Table 2Experimental results of different catalyst preparation conditions

Experiment number	Calcination time(H)	Calcination temperature(K)	Porosity (ppi)	Raw material - hydrogen production rate (L/g)			Gasification efficiency (%)			$H_2\%$		
				Results a	Results b	Results c	Results a	Results b	Results c	Results a	Results b	Results c
1	1	873	10	0.161	0.159	0.162	69.7	69.5	69.8	47.5	47.2	47.4
2	1	973	20	0.177	0.176	0.173	74.1	74.2	74.4	48.7	48.5	48.9
3	1	1073	40	0.157	0.156	0.154	67.5	67.8	67.4	46.2	46.5	46.1
4	2	873	20	0.156	0.157	0.154	67.1	67.3	67.3	45.7	45.5	45.8
5	2	973	40	0.164	0.167	0.163	71.2	71.4	71.5	46.9	46.6	46.7
6	2	1073	10	0.152	0.151	0.156	66.3	66.7	66.6	44.6	44.8	44.7
7	3	873	40	0.155	0.152	0.158	67.8	67.5	67.7	45.3	45.2	45.5
8	3	973	10	0.162	0.161	0.160	69.7	69.4	69.6	46.5	46.6	46.8
9	3	1073	20	0.149	0.146	0.148	66.5	66.3	66.7	44.8	44.6	44.7

From the experimental results:

(1) When the calcination temperature is 973K and porosity is 20ppi，catalyst calcination time increases from 1H to 2H and then increases to 3H，hydrogen production rate decreases from 0.176L/g to 0.163L/g, the gasification efficiency decreases from 74.3% to 70.1%，the hydrogen content decreases from 48.7% to 46.8%.The experimental results show, that the productivity of hydrogen, gasification efficiency and hydrogen concentration decrease gradually when the calcination time of the catalyst is raised from 1H to 3H.This is mainly because the calcination time is too long, and the pore structure on the catalyst surface occurs sintering, which makes the specific surface area of the catalyst decreased, and reduces the activity of the catalyst.

(2) The catalyst calcination time is 1H and porosity is 20ppi，the calcination temperature increases from 873K to 973K and then increases to 1073K，hydrogen production rate increases from 0.164L/g to 0.176L/g and then decreases to 0.160L/g, the gasification efficiency increases from 70.3% to 74.3% and then decreases to 67.9%，the hydrogen content increases from 47.5% to 48.7% and then decreases to 46.7%.This is mainly because the calcination temperature must be strictly controlled in the process of calcination of the catalyst so as to gain crystalline phase of the catalyst, grain size, pore structure and specific surface area in a favorable state. Therefore, in order to improve the hydrogen yield, gasification efficiency and hydrogen concentration, the calcination temperature of the catalyst should be within a certain range.

(3) The catalyst calcination time is 1H and the calcination temperature is 973K，porosity increases from 10ppi to 20ppi and then increases to 40ppi，hydrogen production rate increases from 0.171L/g to 0.176L/g and then decreases to 0.172L/g, the gasification efficiency increases from

73.7% to 74.3% and then decreases to 73.9%，the hydrogen content increases from 48.2% to 48.7% and then decreases to 48.2%. If the porosity of silicon carbide is too narrow, the contact area of the catalyst and the reactants and the contact time will be decreased, impacting on the reaction rate. If the density of silicon carbide is too large, it will contribute to the uneven distribution of the catalyst. Therefore, porosity should be within a reasonable range.

Conclusions

(1)The reaction temperature has the greatest influence on the hydrogen yield, and the higher reaction temperature is more favorable to improve the hydrogen yield. The most appropriatereaction temperature in this experiment is1073K.The influence of S/B on hydrogen yield is less than that of temperature. S/B should be within a certain range. The most appropriate S/B in this experiment is 2. The influence of load on the hydrogen yield is minimal and it is more favorable for hydrogen production when the load is 8%in this experiment.

(2)The calcination temperature has the greatest influence on the hydrogen yield. Furthermore, the suitable calcination temperature is more favorable to improve the hydrogen yield, and the calcination temperature is 973K in this experiment. The influence of calcination time on the hydrogen yield is less than that of calcination temperature. The calcination time shall be not too long. When calcination time is 1H in this experiment, the hydrogen can obtain the highest yield. The influence of porosity of the catalyst on the hydrogen yield is minimal and the most suitable porosity is 20ppi in this experiment.

Acknowledgements

References

[1] Carolina Font Palma: Appl. Energy Vol. 111 (2013), p. 129

[2]YafeiShen, KunioYoshikawa: Renew. Sust.Energ. Rev.Vol.21 (2013), p. 371

[3] BaofengZhao, XiaodongZhang and LeiChen: Biomass Bioenergy Vol. 34 (2010), p. 140

[4] FurusawaT, TsutsumiA: Appl. Catal. A Vol. 278 (2005), p. 195

[5] Polychronopoulou K, Bakandritsos A and Tzitzios V: J. Catal. Vol. 241 (2006), p. 132

[6]JianfenLi, RongYan and BoXiao: Environ. Sci. Technol. Vol. 42 (2008), p. 6224

[7] ChangmingXu, Shiwei Wang and Katarina: Ceram. Int. Vol. 36 (2010), p. 923

[8] Xavier Nitsch, Jean-Michel Commandre and Jeremy Valette: Energ. Fuel. Vol. 28 (2014), p. 6936

[9] LigangWei, ShaopingXu and JingangLiu: Energ.Fuel. Vol. 20 (2006), p. 2266

[10] Z. Abu El-Rub，E.A. Bramer and G.brem: Fuel Vol. 87 (2008), p. 2243

[11] Osamu Hirohata, Tomonori Wakabayashi and Kazuhiko Tasaka: Energ. Fuel. Vol.22 (2008), p. 4235

[12] Y. G. Pan, X. Roca and E. Velo: Fuel Vol. 78(1999), p. 1703

[13] Polychronopoulou K, Fierro JLG and EfstathiouAM: J. Catal. Vol. 228 (2004), p. 417