Temperature variation of reaction liquid of ultrafine corn stover in photosynthetic hydrogen production

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Abstract: The thermo-physical phenomena existing in the process of hydrogen production by photosynthetic bacteria with ultrafine corn stover directly affect the energy consumption of biological hydrogen production system, the activity of hydrogen production, and hydrogen production rate. In order to discover theoretical basis for optimizing process parameters of the photosynthetic bioreactor for ultrafine corn stover, experimental investigation was conducted to identify the effects of the granularity of ultrafine corn stover on the temperature variation using a self-developed photosynthetic bio-hydrogen thermal-effect experimental device. This paper describes experimental research on temperature variation of reaction liquid with ultrafine-ground corn stover in photosynthetic hydrogen production, and on the temperature field and change trend of reaction liquid of corn stover with different granularities in bio-hydrogen production. Experimental results showed that, the greater the granularity of corn stover, the slower the temperature rising speed of the reaction liquid with corn stover in the initial phase of photosynthetic hydrogen production, and the lower the relative average temperature of reaction liquid in photosynthetic hydrogen production. This result is of great significance in research on the photosynthetic hydrogen production technology from biomass, providing a theoretical basis for thermal effect in solar photosynthetic hydrogen production.

Keywords: corn stover, photosynthetic hydrogen production, ultrafine grinding, bioreactor, granularity, temperature

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1 Introduction

Significant consumption of fossil energy source has caused many serious global problems including energy shortage, resource depletion and environmental deterioration, and threatened the existence and sustainable development of human beings. Therefore it is critical to develop and utilize new, clean and efficient renewable energy sources. With its characteristics of zero-pollution, high energy density and renewable energy source, hydrogen energy is recognized as the optimal substitute for

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fossil energy[1-3]. The bio-hydrogen production technology in which hydrogen gas is produced in microbe metabolism is a new environmentally friendly hydrogen production method that is promising in future development, and is widely concerned by the communities[4-7]. The commonly used bio-hydrogen production methods include anaerobic hydrogen production, algae-based hydrogen production, and photosynthetic hydrogen production[8]. The photosynthetic microbial hydrogen production combined with solar utilization and waste recycling is one of better bio-hydrogen production methods that is promising in future development.

China has plenty of biomass, such as agricultural residues, which is estimated at approximately 5.0×10^9 tons per year[9]. Photosynthetic hydrogen production can be improved by utilizing abundant industrial and agricultural organic matters, with greater available spectrum range, energy utilization and hydrogen production rate[10,11]. Previous studies have shown that with ultrafine crushing of biomass combined with other pretreatment methods, the carbohydrate that produced by the biomass can be fermented by photosynthetic bacteria to produce biofuels[12-15]. However, these processes still suffer from numbers of restrictions, and much further study work is needed to be done[16].

Photosynthetic hydrogen production is a complex biochemical and physical process, and the photo-fermentation needs light supply and conducting under a constant temperature, because dramatic temperature variation can adversely influence biohydrogen production[17,18]. Knowing that heat is a key feature of life process, the temperature in the process of biohydrogen production needs to be monitored. Heat will produce from the biochemical reaction in the process of photosynthetic biohydrogen production and accumulate in the reaction liquid, which not only affects mechanical and thermophysical properties of the photosynthetic bioreactor, but also has close relationship with hydrogen production volume and hydrogen production rate. Therefore, the heat effect should be studied. In this study, ultrafine corn stover was utilized for photosynthetic hydrogen production, the enzyme hydrolysis was preliminarily carried out to degrade the cellulose contained in the corn stover. Temperature is an important factor for cellulase activity, and the photosynthetic hydrogen production is an exothermic reaction, so the thermal emission in the photosynthetic hydrogen production of ultrafine corn stover has direct influence on the hydrogen production rate, and shows great significance in research on temperature field of liquid ultrafine corn stover in the photosynthetic bio-hydrogen production system[19-21].

In this research, a self-developed photosynthetic bio-hydrogen thermal-effect experimental device was used: 1) to study the temperature variation of liquid ultrafine corn stover with different granularities during their photosynthetic hydrogen production with the same illumination intensity, pH value, inoculum concentration and environmental temperature; 2) to analyze and examine the influence of the granularity of ultrafine corn stover on the temperature variation law during the photosynthetic hydrogen production; and 3) to identify the temperature field distribution in the photosynthetic hydrogen production system, so as to provide scientific references for optimizing process parameters of the photosynthetic bioreactor for ultrafine corn stover.

2 Materials and methods

2.1 Experimental materials

In this experiment, high-performance photosynthetic bacteria flora were used, which were obtained from 24 samples in Zhengzhou Xinda Stock Raising Plant, Zhengzhou Sewage Treatment Plant, and Zhengzhou Lake Xiliu in different seasons. The highly-performed photosynthetic bacteria flora were screened out after flora enrichment, separation, and cultivation in different growth conditions.

The corn stover used in the experiment was obtained from a test field of Henan Agricultural University. After being ground, the corn stover samples with granularities of 0.180 mm, 0.096 mm and 0.060 mm were screened out as hydrogen production matrix, and were dried for use.

The culture media for hydrogen production include 0.40 g NH_4Cl, 0.20 g $MgCl_2$, 0.50 g K_2HPO_4, 2.00 g NaCl, 3.56 g sodium glutamate, 0.10 g yeast extract, 1 L distilled water, and 20% inoculum concentration.

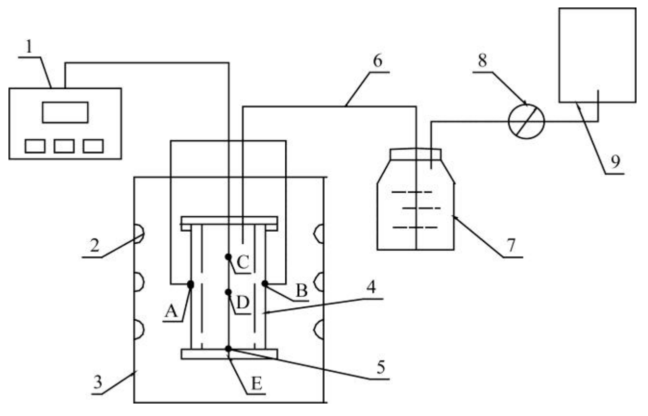
2.2 Experimental methods

2.2.1 Preliminary enzyme hydrolysis of corn stover

Two point five gram (2.5 g) of each ground biomass was put into a 250 mL clean and dry conical beaker. The beaker was filled with 10 mL buffer fluid and placed in a water basin at 50℃ for 30 min. Then the beaker was taken out, and mixed and shaken well with 125 mg cellulose power to enable its contents to dissolve completely. The beaker was sealed with seal paper, and enzyme hydrolysis was performed for corn stover in a 50℃, 150 r/min constant-temperature agitator. After the enzyme hydrolysis, neutralization titration in 70% KOH solution to neutral, and sterilization of the hydrolyzate in the sterilization pot, hydrolysis reaction stopped. We added 20% of photosynthetic bacteria into hydrolyzate, then injected them into a dual-layer vacuum bioreactor for hydrogen production.

2.2.2 Determination of thermal effect in the photosynthetic bioreactor

The determination of photosynthetic thermal effect required the following devices, as shown in Figure 1.



1. Precise digital thermometer 2. Light source 3. Incubator 4. Dual-layer vacuum reactor 5. Temperature sensor 6. Gas duct 7. Gas washing bottle 8. Gas flowmeter 9. Gas collector A, B. Sidewalls of the dual-layer vacuum reactor C. Top of the dual-layer vacuum reactor D. Middle of the dual-layer vacuum reactor E. Bottom of the dual-layer vacuum reactor

Figure 1 Photosynthetic bio-hydrogen thermal-effect experimental device

The required culture media were installed in a 500 mL dual-layer vacuum glass reactor. Temperature sensor probes were installed at the top, middle and bottom of the reactor along its axis to measure the reactor temperature at these three positions. Additionally, temperature sensor probes were installed at two sides of two reactor openings and at two sides in the middle to measure the temperature at the top and middle of the reactor. Also, at the top of reactor a gas line was connected to a gas washing bottle for purification of produced gas. Then the produced gas entered the gas collector via gas flow meter. After inoculation in the reactor, the reactor mouth was sealed with a rubber stopper and glass cement. To maintain constant environmental temperature in the photosynthetic bio-hydrogen thermal effect experiment, the reactor was placed in an automatic incubator whose temperature was set to 30℃, and some 30 W incandescent lamps were installed in the automatic incubator to control the illumination intensity to 2 000 lux.

Temperature sensor probes were installed at two symmetrical sidewalls of the dual-layer vacuum reactor and its top, middle and bottom points along its axis, which were denoted as A, B, C, D, and E. After neutralization titration of enzyme-hydrolyzed ultrafine corn stover, culture media and 20% bacteria were added into the corn stover, and then the mixture of culture media, bacteria and corn stover was filled in the dual-layer vacuum reactor. The temperature sensor probes were arranged in the material liquid in the reactor and connected to a TC-2A multiple temperature tester. The whole photosynthetic bio-hydrogen thermal effect experiment system was placed in the 30℃ automatic incubator, and at the illumination intensity of 2 000 lux, the material liquid temperature from each sensor probe at each measurement point was recorded periodically.

3 Results and discussion

3.1 Temperature variations at different positions in reaction liquid with the same granularity corn stover

By using temperature sensor probes at the sidewall (A) of the dual-layer vacuum reactor and its top (C), middle (D) and bottom (E) along its axis, temperature of liquid corn stover with the same granularity in photosynthetic hydrogen production was monitored in real time, and the temperature variations of reaction fluid are shown in Figures 2, 3, and 4.

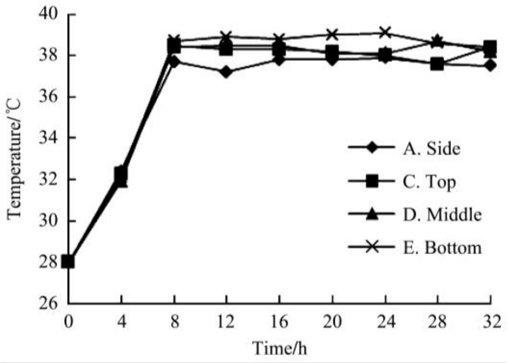


Figure 2 Temperature variation of 0.160 mm liquid ultrafine corn stover in photosynthetic hydrogen production

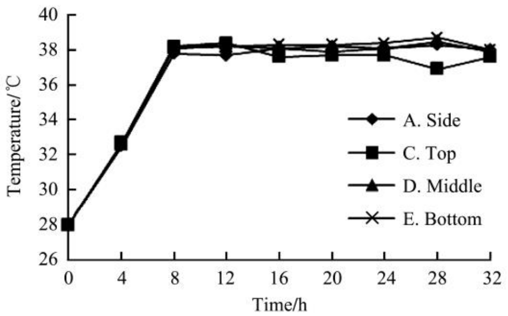


Figure 3 Temperature variation of 0.096 mm liquid ultrafine corn stover in photosynthetic hydrogen production

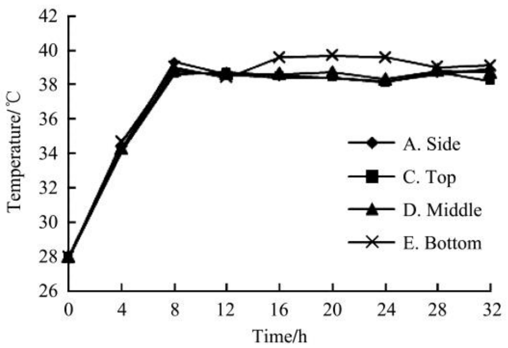


Figure 4 Temperature variation of 0.060 mm liquid ultrafine corn stover in photosynthetic hydrogen production

From the analysis of temperature curves in these figures, it was found that the photosynthetic hydrogen production experiment with corn stover of different granularities as hydrogen production matrix showed the same temperature variation range, i.e. from the initial room temperature (approximately 28℃) to the setting system temperature (approximately 38-39℃) for hydrogen production with photosynthetic bacteria. In the initial eight hours, the system temperature increased rapidly and then it kept constant. The heat exchange process between the hydrogen production system and the incubator internal is basically over. By comparing among the change value ΔT of the initial temperature and the maximum temperature in each of the reaction process measured at two sidewalls of the dual-layer vacuum reactor and its top, middle and bottom, it was found that $\Delta T_{0.160}(E)>\Delta T_{0.160}(D)>\Delta T_{0.160}(C)>\Delta T_{0.160}(A)$, $\Delta T_{0.096}(E)>\Delta T_{0.096}(D)>\Delta T_{0.096}(C)>\Delta T_{0.096}(A)$, $\Delta T_{0.060}(E)>\Delta T_{0.060}(D)>\Delta T_{0.060}(C)>\Delta T_{0.060}(A)$, the temperature at the bottom (E) was slightly higher than those at other points after the system temperature kept constant. This was because most of corn stover rested at the bottom after settling down for eight hours, and reacted drastically with photosynthetic bacteria in the highly-performed hydrogen production with enzyme-hydrolyzed corn stover as hydrogen production matrix, causing a higher temperature. From the temperature profiles of the temperatures at the sidewalls (A) during the initial heating stage, the sidewall temperature changes were the most significant within the first four hours, maybe due to the radiant heat brought by the external light source, and with the straw particle size decreased, temperature changes of point A were consistent with other respective positions, which should be due to the decrease in particle size, the hydrogen production feed solution turbidity decreases, the transfer performance of the heat and mass was enhanced, this was consistent with the rheological properties of the solid-liquid mixing multiphase flows. Overall, as the particle size decreases, the change in the temperature of the system increased, but the temperatures at the sidewalls and at the top and middle were essentially identical with each other with similar reaction heat, which was attributable to smaller concentration of materials in the liquid, while the bottom had the higher temperature because of the accumulation of heat. Thus in this phase, intensifying the agitation of material liquid for uniform concentration was an important task to improve the hydrogen production efficiency and increase the reaction heat.

3.2 Temperature variation of corn stover with different granularities in photosynthetic hydrogen production

In the liquid temperature observation at the same special position in the photosynthetic bio-hydrogen production of ultrafine corn stover, the top (C), middle (D) and bottom (E) of the hydrogen production reactor were chosen to analyze the influence of granularity on thermal effect in the photosynthetic bio-hydrogen production, as shown in Figures 5-7.

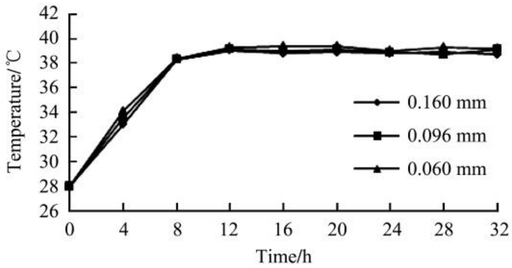


Figure 5 Temperature variation of liquid corn stover with different granularities at the point C

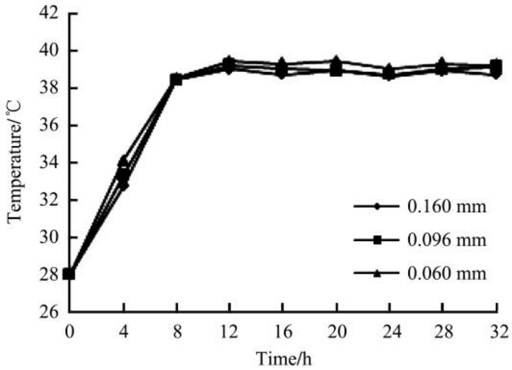


Figure 6 Temperature variation of liquid corn stover with different granularities at the point D

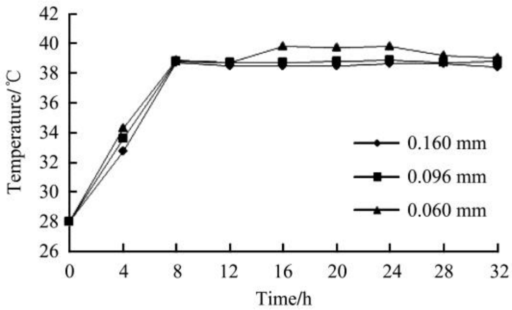


Figure 7 Temperature variation of liquid corn stover with different granularities at the point E

The results showed that, regardless of the granularity of corn stover, the system temperatures increased during photosynthetic hydrogen production and varied with photosynthetic bacteria flora. The ranges of temperature increases were essentially identical, from initial room temperature to the reaction temperature when the hydrogen production kept constant. In the analysis of the influences of corn stover with different granularities on the system temperature in photosynthetic hydrogen production, it was found that the temperature rising rate was greater with 0.060 mm corn stover than that with 0.096 mm corn stover, while the latter was also greater than 0.160 mm corn stover. This illustrated that the smaller the size of the granularity of reaction liquid, and the quicker the temperature rising rate. This was because, 1) the corn stover of smaller granularity had a higher light transmittance than that of larger granularity straws, and thus in the initial temperature rising phase, the temperature rising rate of reaction fluid increased with the decreasing granularity; 2) the finer the corn stover were ground, the easier the fibrous particles to be enzyme-hydrolyzed into carbohydrate that could be utilized by photosynthetic bacteria, and the finer particles in the reaction solution, the flora growth more quickly, the stronger of biochemical reaction, the more heat released. In the hydrogen production process used ultrafine corn stover of the particle size of 0.060 mm, 0.096 mm, 0.160 mm as matrix photosynthetic organisms, the order of the hydrogen yield was that the 0.060 mm had a larger hydrogen yield than 0.096 mm, and the latter had a larger hydrogen yield than 0.160 mm, this law was consistent with the law of the heating rate of the system. The more drastically the photosynthetic hydrogen production reaction was performed with photosynthetic bacteria, the more the released reaction heat, and the higher the system temperature. However, considering that the bacterial reaction heat had only a little influence on the whole experiment system, these variations were insignificant in these temperature curves. Ultrafine corn stover as hydrogen production matrix had its own specialty, such as the bottom had the higher temperature than any other positions, but the change rule was similar with the verified results that obtained from the experiments using glucose, acid and other small molecules as hydrogen production matrix in photosynthetic hydrogen production process, which showed a stable trend after the first increase in the temperature of each position.

3.3 Temperature variation of liquid corn stover with different granularities in photosynthetic hydrogen production

The reactor center (D) was chosen to analyze the temperature variation of liquid ultrafine corn stover with different granularities in the temperature rising phase of photosynthetic bio-hydrogen production, as shown in Figures 8 -10.

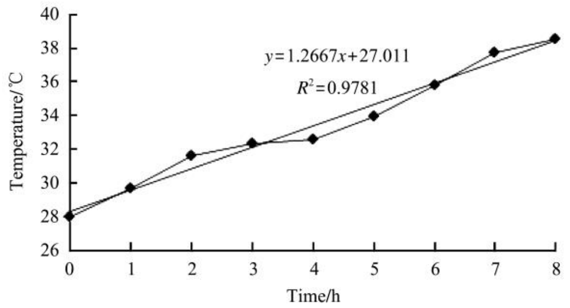


Figure 8 Initial temperature variation of 0.160 mm liquid corn stover at the center

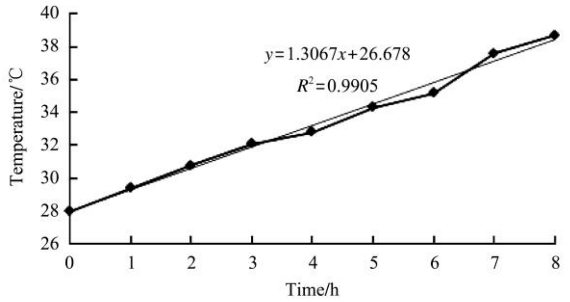


Figure 9 Initial temperature variation of 0.096 mm liquid corn stover at the center

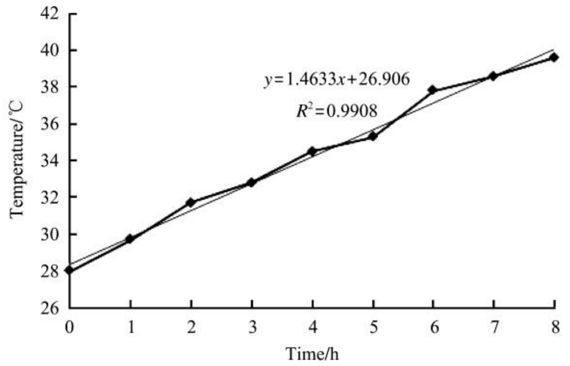


Figure 10 Initial temperature variation of 0.060 mm liquid corn stover at the center

From the analysis of temperature curves in these figures, it was found that in the initial phase of 8-hour temperature rising in the photosynthetic hydrogen production experiment with corn stover of different granularities as hydrogen production matrix, the system temperature increased from room temperature to the temperature when the hydrogen production kept constant, and the temperature variations were approximately linear. Linear regression analysis of experiment data yielded a straight line equation of initial temperature variation of liquid corn stover with different granularities at the center, i.e. y=Ax+B; by observing the factor “A” in the equation, it could be seen that the smaller the granularity of corn stover, the greater the slope of temperature curves in the initial phase of photosynthetic hydrogen production, the quicker the temperature variation was, and the faster the temperature increase was. This was because the smaller the granularity of corn stover, the light permeability in photosynthetic hydrogen production system of biomass multiphase flow was enhanced, the turbidity was decreased, the heat transfer performance was enhanced, which was consistent with the results of studies of the rheological properties of the biomass multiphase flow system, and the smaller the particle size, the more thoroughly and rapidly the corn stover were enzyme-hydrolyzed after photosynthetic bacteria were added, it was also consistent with the experimental results of the verified hydrogen production with ultrafine straws in the enzymatic process, the more drastically the hydrogen production reaction was performed in the material fluid, and the higher the temperature rising speed.

4 Conclusions

The research on temperature variation of liquid with ultrafine corn stover in photosynthetic hydrogen production has shown that, the photosynthetic hydrogen production reaction at the bottom is more drastic than those at the top, middle and two sidewalls, and also the temperature at the bottom is higher than those at other positions. The greater the granularity of corn stover, the less the slope of temperature curves in the initial phase of photosynthetic hydrogen production, and the lower the temperature rising rate. The granularity of corn stover influences the hydrogen production temperature to some extent. The experimental results have shown that when the illumination intensity is 2 000 lux, pH value is 7, the inoculum concentration is 20%, and the incubator temperature is 30℃ in photosynthetic hydrogen production; the smaller the granularity of corn stover, the quicker the temperature rising of reaction fluid system. After the thermal balance, the system keeps constant, the internal temperature of reaction fluid system with smaller granularity is slightly higher than that of reaction fluid system with larger granularity. This provides scientific references for optimal design of process parameters of the photosynthetic bioreactor for ultrafine corn stover.

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[References]

[1] Hallenbeck P C, Benemann J R. Biological hydrogen production; fundamentals and limiting processes. International Journal of Hydrogen Energy, 2002; 27(11): 1185–1193.

[2] Akkerman I, Janssen M, Rocha J, Wijffels R H. Photo-biological hydrogen production: photochemical efficiency and bioreactor design. International Journal of Hydrogen Energy, 2002; 27(11): 1195–208.

[3] Das D, Veziroğlu T N. Hydrogen production by biological processes: a survey of literature. International Journal of Hydrogen Energy, 2001; 26(1): 13–28.

[4] Li D M, Chen H Z, Li Z H. Research and development of hydrogen production by biological technology. Biotechnology Information, 2003; 4: 1－5.

[5] Kawaguchi H, Hashimoto K, Hirata K, Miyamoto K. H_2 production from algal biomass by a mixed culture of Rhodobium marine A-501 and lactobacillus amylovorus. Journal of Bioscience and Bioengineering, 2001; 91: 277–282. DOI: 10.1016/S1389-1723(01)80134-1.

[6] Yang Y, Lu D N, Cao Z A. Promising bioenergy in the 21st century. Chemical Industry and Engineering Progress, 2002; 21: 299–302.

[7] Li J Z, Ren N Q. Study and development in quo of hydrogen production biotechnology. Energy Engineering, 2001; 2: 18－20.

[8] Committee on Alternatives and Strategies for Future Hydrogen Production and Use, Board on Energy and Environmental Systems, Division on Engineering and Physical Sciences, National Research Council, National Academy of Engineering. 2004. The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs: National Academy Press.

[9] Li M, Wang H X. The analysis of comprehensive utilization measures of agricultural waste. China Population Resources and Environment, 2012; 22(5): 37–39.

[10] Zhang Q G, Wang S L, You X F. Effects of the influencing factors of photosynthetic bacteria group on hydrogen production. Transactions of the CSAE, 2006; 22(10): 182－185.

[11] Zhang L N, Cai J. Modified material from Natural Polymers and their applications. Beijing: Chemical Industry Press. 2006.

[12] Zhang Z P, Yue J Z, Wang Y, Zhang Q G. The optimization of the ball milling pretreatment process for hydrogen production from straw biomass. Biomass Chem. Eng, 2012; 46(1): 19–22.

[13] Yue J Z, Xu G Z, Li G, Zhang Q G, Shen X W. Effects of microwave radiation pretreatment on enzymatic hydrolysis of sorghum straw. Journal of Henan Agricultural University, 2010; 44(5): 549–552.

[14] Yue J Z, Zhang Q G, Li G, Jiao Y Z, Shen X W. Effects of mechanical grinding on micro-structure of sorghum straw and enzymatic hydrolysis. Acta Energiae Solaris Sinica, 2010; 19(5): 51–53.

[15] Zhang Z P, Yue J Z, Zhou X H, Jing Y Y, Jiang D P, Zhang Q G. Photo-fermentative bio-hydrogen production from agricultural residue enzymatic hydrolyzate and the enzyme reuse. Bioresources, 2014; 9(2): 2299–2310.

[16] Hallenbeck P C, Ghosh D, Skonieczny M T, Yargeau V. Microbiological and engineering aspects of biohydrogen production. Indian J. Microbiol, 2009; 49(1): 48–59.

[17] Sasikala K, Ramana C V, Raghuveer R P, Kovacs K L. Anoxygenic phototrophic bacteria: Physiology and advances in hydrogen production technology. In: Neidleman S, LaskinA I (Ed.), editors. Advances in Applied Microbiology. New York: Academic Press, 1993; pp. 211–295.

[18] Won S G, Lau A K. Effects of key operational parameters on biohydrogen production via anaerobic fermentation in a sequencing batch reactor. Bioresour. Technol, 2011; 102(13): 6876–6883.

[19] Gao Z T, Liu Y, Huang Y P, Shen P, Qu S S. Thermokinetic study on the growth metabolism of ura-auxotrophic mutant of saccharomyces cerevisiae AY. Acta Physico-Chimica Sinica, 2002; 18(7): 590–594.

[20] Shi Y Z, Zhang Q G, Wang Y, Jing Y Y. Experimental study on continuous culture of photosynthetic bacteria for hydrogen production from biomass. Transactions of the CSAE, 2008; 24(6): 218－221.

[21] Wang S L, Zhang Q G, Zhou X H. Experimental study on change in temperature of the system during the biological hydrogen production. Acta Energiae Solaris Sinica, 2007; 28(11): 1253–1255.