Hydrogen-Rich Gas Production from Biomass Catalytic Gasification

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With the use of dolomite in the fluidized-bed gasifier and the use of nickel-based catalysts in the fixed bed reactor downstream from the gasifier, the characteristics of hydrogen yield from biomass are investigated in the present study. Some calcined dolomite is placed initially in the gasifier with an amount of 120 g/(kg h^{-1}) biomass. To replace the eroded and elutriated dolomite, calcined dolomite (0.3−0.45 mm) is continuously fed and its feeding rate is determined by preliminary test. The influence of the operating conditions in the catalytic reactor on the production of gases, especially H_2, is studied over the temperature range of 650−850 °C, for weight hourly space velocity (WHSV) in the range of 2.68−10.72 h^{-1}. In the gaseous product, the average content of H_2 exceeds 50 vol %; C_2 content is lowered to below 1 vol %, and nearly half of CH_4 is converted after the catalytic reactor. Over the ranges of experimental conditions examined, the highest gas yield reaches 3.31 Nm^3/kg biomass, wet basis; the maximum hydrogen yield reaches 130.28 g H_2/kg biomass, wet basis. This system shows a good performance over a lifetime test of 350 min.

Introduction

Concerns about the depletion of fossil fuel reserves and the pollution caused by continuously increasing energy demands make hydrogen an attractive alternative energy source. Hydrogen is currently derived from nonrenewable natural gas and petroleum, but could in principle be generated from renewable resources such as biomass. At present, biomass is recognized worldwide as a rich source of renewable energy. Thus, the conversion of biomass into hydrogen-rich gas provides a potentially competitive means for producing energy and chemicals from renewable sources.[1]

Extensive literature has been published on biomass gasification with air, which produces a gas with low hydrogen content, 8−14 vol % only.[2] Generally, there are two methods to elevate hydrogen content. One is the steam addition, and the other is the use of catalysts. Many researchers have proved the usefulness and effectiveness of calcined dolomite and nickel-based steam reforming catalysts on decreasing tar yield, improving gas quality in the process of biomass gasification.[2−11] In most of the current studies, 2 reactors are installed downstream from the gasifier. The first one contains calcined dolomite, usually called the guard bed, and the second one contains nickel catalysts, named the catalytic bed. The function of the guard bed is to decrease tar content in the inlet of the catalytic bed and then prevent nickel catalysts from being deactivated. It is obvious that such a facility is quite complex and needs a large heat supply for good performance. Corella et al.[10,11] had performed a study of biomass air gasification with the direct use of dolomite in the gasifier and demonstrated that calcined dolomite has nearly the same influence on biomass gasification either in the gasifier or in the downstream fixed bed reactor. Therefore calcined dolomite can be used directly in the gasifier, and a downstream or second bed of dolomite would be unnecessary.

Until now, not so much literature has been found involving hydrogen production from biomass catalytic gasification.[12−17] There are still many subjects that need

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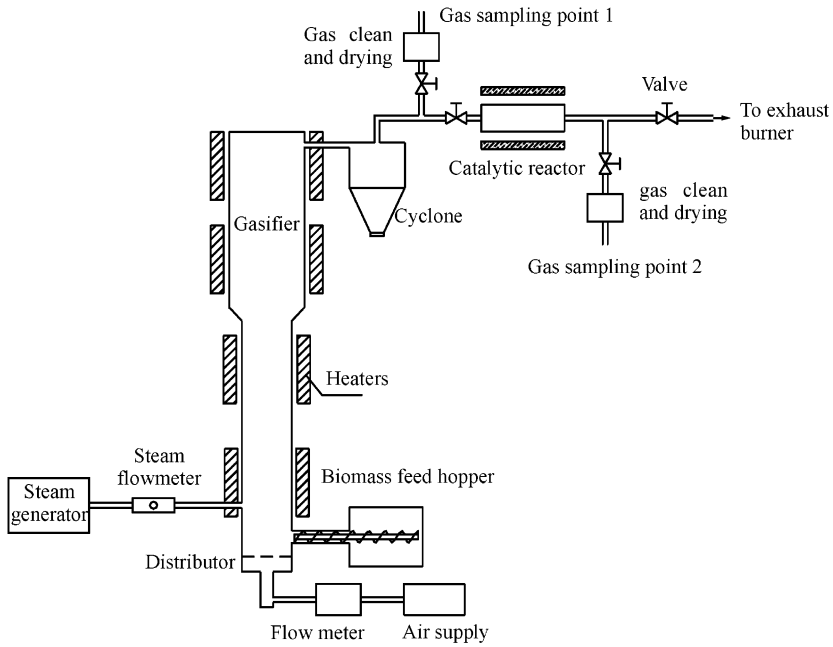

Figure 1. Schematic diagram of biomass catalytic gasification.

to be investigated further, such as proper facility design and suitable operating conditions for maximum hydrogen yield. In this study, a fluidized bed gasifier system has been developed to investigate hydrogen-rich gas production from biomass gasification with the direct use of calcined dolomite in the gasifier and a fixed bed of nickel catalysts installed downstream from the gasifier. The purpose of this study is to characterize the influence of operating parameters in the gasifier and catalytic reactor on the production of hydrogen, as well as to test the performance of this system, so as to obtain useful data for the design of industrial units.

Experimental Section

Feed Materials and Catalysts. Pine sawdust obtained from a timber mill in Guangzhou City, China, was used as the feedstock for experimental runs. The particle size of this pine sawdust is between 0.3 and 0.45 mm. Its proximate and ultimate analysis is reported in Table 1.

Calcined dolomite and nickel-based catalysts were used in experiments. The dolomite was first crushed and sieved to obtain a fraction with a particle sized 0.3−0.45 mm, and then calcined in air at 900 °C for 4 h. Nickel-based catalysts of Z409R were used in the catalytic reactor, which were produced in Qilu PetroChemical Company, Shandong Province, China. Z409R is annular, with a size of $\varphi 16 \times \varphi 6 \times 6.0-6.8$ mm and a composition of NiO ≥ 22 wt %, K_2O 6.5 ± 0.3 wt %.

Table 1. Proximate and Ultimate Analysis of Pine Sawdust

moisture content (wt % wet basis)	8
higher heating value (kJ/kg)	20197
proximate analysis (wt % dry basis)	
volatile matter	81.0
fixed carbon	18.5
ash	0.5
ultimate analysis (wt % dry basis)	
C	51.26
H	5.54
O	42.29
N	0.18
S	0.23

Apparatus. The tests were performed in an atmospheric pressure, indirectly heated, fluidized-bed gasification system, which is shown schematically in Figure 1. Its major components are the following: a fluidized-bed gasifier, a biomass feeder, a steam generator, an air compressor, a cyclone, and a catalytic fixed bed reactor.

The fluidized bed reactor is made of 1Cr18Ni9Ti stainless steel pipe and is externally heated by two electric furnaces. The total height of the reactor is 1400 mm, with a bed diameter of 40 mm and a freeboard diameter of 60 mm. Below the reactor, one air distributor is installed for better air distribution. The biomass is fed into the reactor through one screw feeder driven by a variable-speed metering motor. The air is used as the fluidizing agent and comes from the air compressor. Before the air enters into the reactor, it is preheated to 65 °C for better performance. The steam of 154 °C is produced in a steam generator. The produced gas flow exits the reactor, then passes through a cyclone, into the catalytic reactor. The cyclone is heated to 200 °C to prevent the tar contained in the gas from condensing in it. The catalytic reactor is made of the same substance as the fluidized bed and is externally heated by an electric furnace. Its length is 400 mm, with an inner diameter of 38.5 mm.

Prior to each test, an amount of 120 g/(kg h^{-1}) biomass calcined dolomite mixed with 30 g of silica sand (0.2−0.3 mm) was put in the gasifier. Since calcined dolomite is soft, it erodes during the test, and it is eluted out of the bed with the flue exit gas. Therefore, some calcined dolomite was mixed with the pine sawdust carefully by hand and continuously fed into the gasifier to attain a steady state. The feeding rate of calcined dolomite was determined by preliminary test. At the

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Table 2. Operating Conditions and Gas Composition in the Inlet and Exit of the Catalytic Reactor

	run no.				
	1	2	3	4	5
biomass feed rate (kg/h)	0.47	0.536	0.536	0.556	0.602
air (Nm^3/h)	0.65	0.70	0.65	0.65	0.60
steam (kg/h)	0.4	0.4	0.4	0.5	0.5
calcined dolomite feeding rate (g/h)	14	16	16	17	18
calcined dolomite in the gasifier (g)	56	65	65	67	72
gasifier bed temperature (°C)	800	800	800	800	800
equivalence ratio	0.30	0.28	0.26	0.25	0.22
steam-to-biomass ratio	0.85	0.75	0.75	0.90	0.83
catalytic bed temperature (°C)	850	800	700	800	820
WHSV (h^{-1}) (catalytic reactor)	2.14	4.29	2.68	2.53	2.53
catalytic bed inlet gas composition (dry, inert-free, vol %)					
H_2	38.38	40.67	38.13	38.48	35.87
CH_4	7.02	6.64	7.48	7.76	9.25
CO	24.89	22.71	26.06	26.31	29.88
CO_2	27.62	28.25	26.20	25.30	21.87
C_2	2.09	1.75	2.14	2.16	3.13
gas yield (Nm^3/kg biomass, wet basis)	1.56	1.41	1.54	1.84	2.30
hydrogen yield (g H_2/kg biomass, wet basis)	47.2	45.56	46.80	54.84	64.56
catalytic bed exit gas composition (dry, inert-free, vol %)					
H_2	52.47	50.16	49.09	52.18	50.96
CH_4	2.9	3.03	4.77	3.3	4.15
CO	14.82	16.91	14.78	16.06	19.75
CO_2	29.65	29.44	30.73	27.89	24.32
C_2	0.16	0.47	0.64	0.57	0.83
gas yield (Nm^3/kg biomass, wet basis)	2.41	1.84	2.00	2.64	3.31
hydrogen yield (g H_2/kg biomass, wet basis)	98.98	71.92	76.75	95.38	130.28

end of each test, calcined dolomite left in the gasifier is separated and measured. Thus the weight percent of calcined dolomite in the gasifier bed during operation can be known, and it is about 65−71 wt % over the ranges of experimental conditions examined.

Then the electric furnaces were turned on to preheat the fluidized bed reactor and the catalytic reactor; meanwhile the air preheater was turned on. In the interval of reactor preheating, the steam was prepared for the test. After the bed temperature reached the desired level and kept steady, the air compressor was turned on to force the air through the preheater, air distributor, and into the reactor. When the bed temperature again turned steady, the screw feeder was turned on at the desired rotation speed and the test began. Typically, it took 20 min for the test to reach a stable state. Periodically samples were taken before and after the catalytic reactor.

To ensure the reliability of test data, each experiment was repeated 2 times, and the results were in good agreement. The data reported in this paper are average values of two times.

Sampling and Gas Analysis. The cool, dry, clean gas was sampled using gas bags and analyzed on a gas chromatograph (model GC-2010, Shimadzu, Japan), which is fitted with a GS-carbon plot column (30m × 0.530 mm × 3.00 μm), FID and TCD detectors. Standard gas mixtures are used for quantitative calibration.

Results and Discussion

Typical Operating Conditions and Gas Composition. In Table 2, some typical operating conditions and test results are reported. Equivalence ratio (ER) is defined as the actual oxygen-to-fuel ratio divided by the stoichiometric oxygen-to-fuel ratio needed for complete combustion. Weight hourly space velocity (WHSV) is defined as mass flow rate of biomass fed to the gasifier, divided by the mass of catalyst in the catalytic reactor. WHSV indicates the gas residence time in the catalytic reactor.

Table 2 shows that the content of hydrogen is improved over 10 vol %; CO content is decreased about 10 vol %; CO_2 content has a slight increase; nearly half of CH_4 is converted; C_2 content is lowered to below 1 vol %. From these changes of gas composition, it can be concluded that 2 important reactions, the water shift reaction (eq 1) and CO_2 dry reforming reaction (eq 2), occur in the catalytic reactor simultaneously. CO_2 is produced by reaction 1 but consumed by reaction 2. The overall effect of these 2 reactions is a slight increase in CO_2 content.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \quad (2)$$

Corella and co-workers have performed many studies on biomass catalytic gasification.[5−7,9] Some of them are for gasification with air[5,6] and some of them are for gasification with mixtures of H_2O and O_2,[7,9] the gasifying agent being similar to the one used in this work. Therefore it is valuable to perform a comparison between this study and the work of Caballero et al.[7] which was performed under similar operating conditions. After careful analysis, it can be found that as to the variation of gas composition for H_2, CH_4, and C_2 after the catalytic reactor, the trends are the same. As to the variation of gas composition for CO and CO_2, the trends are the opposite. In the study of Caballero et al.,[7] CO content is increased while CO_2 content is decreased after the catalytic reactor. This difference possibly comes from different catalysts and a different quantity of steam addition in the gasifier. It is found that the H_2O-content used in this work is clearly higher than the one used in the work of Caballero et al.[7] Since the gasification is not at equilibrium, the water-gas shift (reaction 1) takes place more in this work than in that of Caballero et al.[7] This is the main reason the CO content decreases more and the CO_2 content increases more in this work than in the previous work of Caballero et al.[7] with $H_2O + O_2$ mixtures.

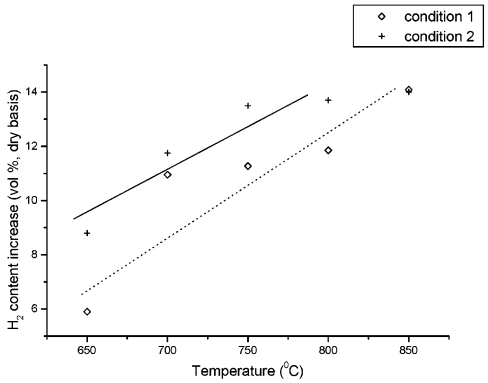

Figure 2. Increase of H_2 content vs temperature in the catalytic reactor.

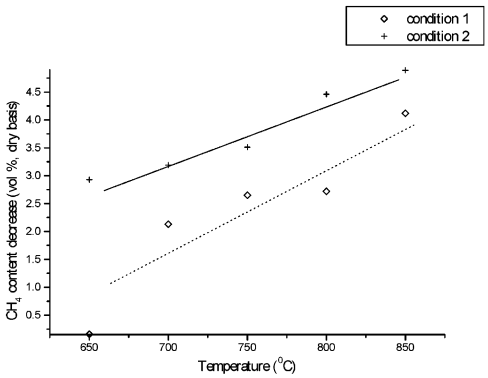

Figure 3. Decrease of CH_4 content vs temperature in the catalytic reactor.

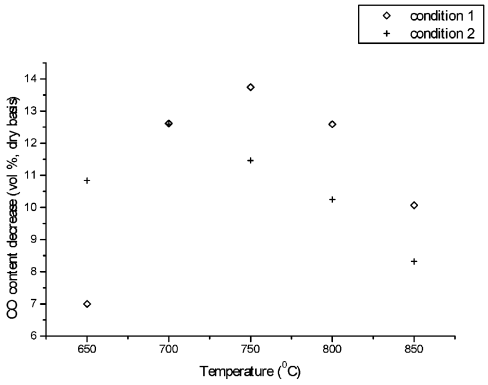

Figure 4. Decrease of CO content vs temperature in the catalytic reactor.

As shown in Table 2, at the exit of catalytic reactor, hydrogen yield is nearly doubled, and the highest one reaches 130.28 g H_2/kg biomass wet basis.

Effect of Temperature in the Catalytic Reactor on Gas Composition. The effect of temperature in the catalytic reactor on gas composition is investigated through 2 different operating conditions in the gasifier. Conditions 1 and 2 refer to runs No. 1 and 4 in Table 2, respectively.

Figures 2−6 show the increase or decrease extent of different gases. The content of H_2 and CO_2 is increased after the catalytic reactor while the other gases, CH_4, CO,and C_2, are decreased.

The content of H_2 is improved greatly, from 5.9 vol % to 14.1 vol % and from 8.8 vol % to 14.0 vol % for conditions 1 and 2, respectively. Besides, the increase of H_2 content shows an upward trend with the temperature. The decrease of CH_4 content is slight, only from 0.16 vol % to 4.12 vol % and from 2.9 vol % to 4.9 vol % for conditions 1 and 2, respectively. This is an expected result because of the small content of CH_4 in the gas. Also, the decrease of CH_4 and C_2 content shows an increasing trend with the temperature. This can be attributed to the promotion of endothermic steam reforming reactions of CH_4 and C_2 at a higher temperature. It is observed from Figures 2 and 3 that the change of H_2 and CH_4 content in condition 2 is higher than that in condition 1. This is attributed to different ER of two conditions, being 0.30 and 0.25 for conditions 1 and 2, respectively. It is obvious that there is more CO and hydrocarbons to be converted to hydrogen in condition 2 than in condition 1.

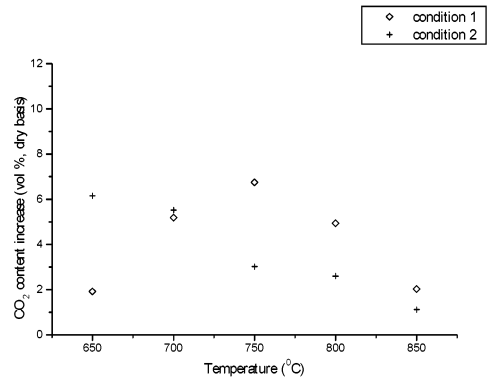

Figure 5. Increase of CO_2 content vs temperature in the catalytic reactor.

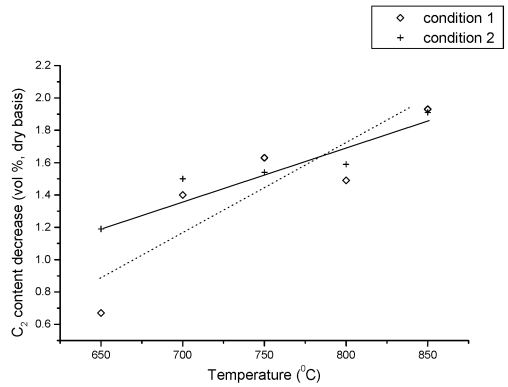

Figure 6. Decrease of C_2 content vs temperature in the catalytic reactor.

The content of CO has a similar change with H_2; that is, from 7.0 vol % to 13.74 vol % and from 8.32 vol % to 12.59 vol % for conditions 1 and 2, respectively. The increase of CO_2 content is slight, from 1.92 vol % to 6.75 vol % and from 1.12 vol % to 6.15 vol % for conditions 1 and 2, respectively.

Effect of Weight Hourly Space Velocity on Gas Composition. In these tests, the condition in the gasifier (run No.3 in Table 2) was kept constant and WHSV was varied at 2 different temperatures in the catalytic reactor. The value of WHSV ranges between 2.68 and 10.72 h^{-1}. Figures 7−11 illustrate the test results. As shown in these figures, the content variety of all the gas compositions decline with WHSV. This is an expected result because the gas residence time decreases with WHSV. As a conclusion, the content change of all gas components is listed in Table 3.

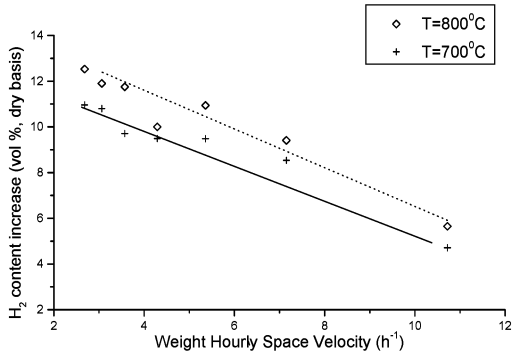

Figure 7. Increase of H_2 content vs WHSV.

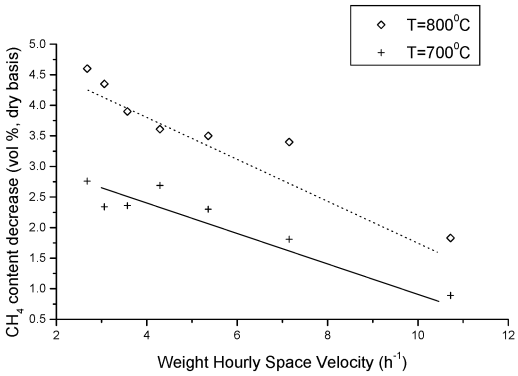

Figure 8. Decrease of CH_4 content vs WHSV.

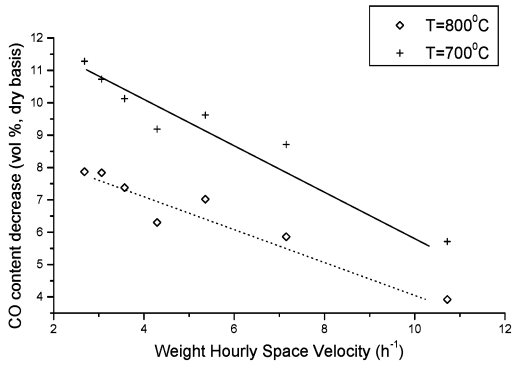

Figure 9. Decrease of CO content vs WHSV.

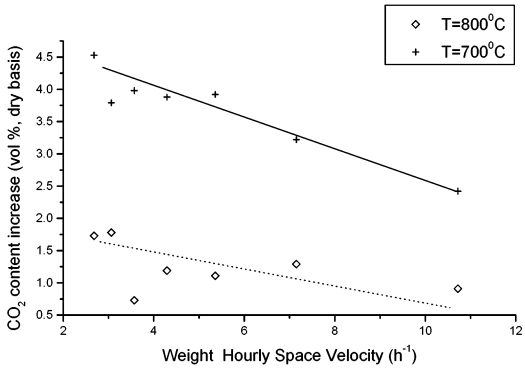

Figure 10. Increase of CO_2 content vs WHSV.

Lifetime Test For Nickel-Based Catalysts. Once the high activity of calcined dolomites and nickel-based catalysts on high hydrogen yield is proven, these materials must also be shown to have a long lifetime. Because of the continuous supply of calcined dolomite, there exists no problem on deactivation of calcined dolomites. Deactivation of nickel-based catalysts could be due, in this process, to three main causes: particulates, or dust, sulfur, and carbon deposition (mainly from tar). The sulfur content is very low in biomass and in the thus-produced gas. Therefore, the main purpose of this test is to indicate the state of dust and coke deactivation. This experiment was performed at 2 different temperatures in the catalytic reactor, while the condition (run No.1 in Table 2) in the gasifier was kept constant. It lasted as long as 350 min. The test results are shown in Figure 12, which indicates nearly no deactivation at temperature 850 °C and little deactivation at temperature 650 °C. It shows that a higher temperature is more favorable for the catalysts to keep active. This can be explained by the fact that, at a higher temperature, the carbon deposited on the surface of nickel-based catalysts is easier to be removed through reacting with steam. Therefore the appearance of steam

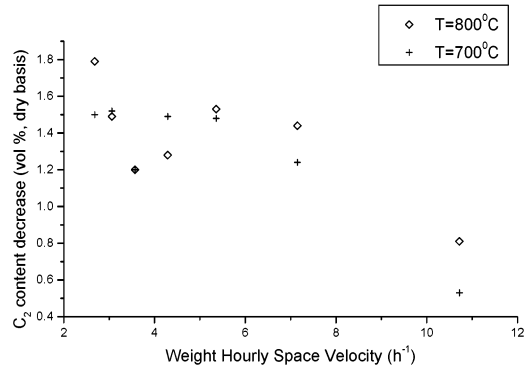

Figure 11. Decrease of C_2 content vs WHSV.

Table 3. The Content Change of All Gas Components after the Catalytic Reactor with WHSV Ranging between 2.68 and 10.72 h^{-1}

	catalytic reactor temperature (°C)	
(vol %, dry basis)	700	800
increase of H_2 content	4.71−10.96	5.65−12.53
decrease of CH_4 content	0.89−2.71	1.83−4.6
decrease of CO content	5.71−11.28	3.92−7.87
increase of CO_2 content	2.42−4.53	0.73−1.78
decrease of C_2 content	0.53−1.52	0.81−1.79

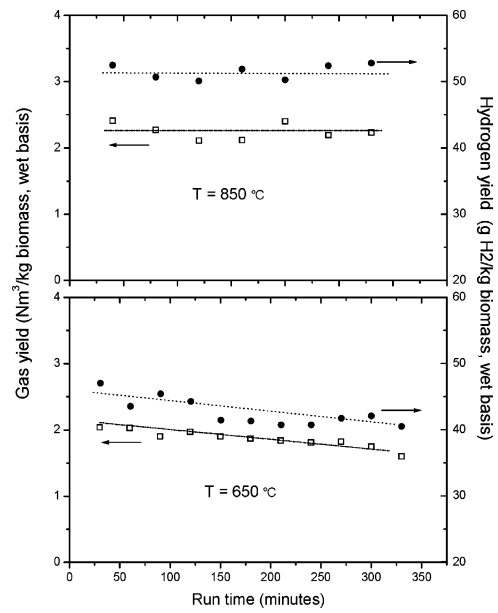

Figure 12. Lifetime test of nickel-based catalysts.

helps to prevent the nickel-based catalysts from fast deactivation caused by carbon deposition. Aznar et al.[6] demonstrated that when the tar content in the inlet of reactor of nickel-based catalysts was over 2 g/Nm^3, the catalysts would be deactivated. This proves that the tar content at the exit of this fluidized bed gasifier has been reduced to a very low level.

Conclusions

With the addition of calcined dolomite in a ratio of 120 g/(kg h^{-1}) biomass and the use of nickel-based catalysts, the system shows good performance in hydrogen-rich gas production. The content of H_2 and CO_2 is increased after the catalytic reactor while the other gases, CH_4, CO, C_2, are decreased. In the gaseous product, the average content of H_2 exceeds 50 vol %; C_2 content is lowered to below 1.0 vol %, and nearly half of CH_4 is converted after the catalytic reactor. Over the ranges of experimental conditions examined, the highest gas yield reaches 3.31 Nm^3/kg biomass, wet basis; the maximum hydrogen yield gets to 130.28 g H_2/kg biomass, wet basis.

The present study demonstrates that calcined dolomite is greatly beneficial for reducing tar yield and there appears no problem on plugging exit pipes. Nickel-based catalysts are active for decreasing CO content and increasing hydrogen content. The lifetime test of 350 min for it exhibits no deactivation at the temperature 850 °C. A higher temperature will extend its lifetime.

Finally, in order to perform the catalytic reforming in industrial units, the system has to be energy-saving enough. With regard to this, maybe fluid-cracking catalysts (FCC) of high activeness can be developed and put in the gasifier bed directly. Therefore, the catalytic reactor could be economized and the external heat supply for it can be saved.

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