Effective syngas cleanup and reforming using Ni/γ-Al_2O_3 catalyst

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Abstract: This work reports the performance of a selective Ni-based catalyst in tar removal and syngas reforming. Benzene was used as the model tar to optimize catalytic reaction conditions. Parameters investigated were reaction temperature (700℃ to 900℃), gas residence time (0.1 s to 1.1 s), and catalyst loadings (3% to 21% of the weight of γ-Al_2O_3 support). On the basis of the benzene test, a reaction temperature of 800℃, catalyst loading of 15wt%, and residence time of 0.3 s were chosen as optimum reaction conditions. Testing of these conditions showed that the Ni/γ-Al_2O_3 catalyst removed more than 99% of tars in syngas in the downdraft gasifier and 98% in the updraft gasifier. Concentrations of combustible compounds of syngas also increased significantly. H_2 concentration increased from 19.96% to 51.78% in the downdraft gasifier and from 23.97% to 37.39% in the updraft gasifier; CO concentration increased from 16.26% to 21.10% in the downdraft gasifier and from 22.95% to 25.64% in the updraft gasifier. The results indicate that the Ni/γ-Al_2O_3 catalyst and associated catalytic conditions could not only effectively eliminate tars but also improve the quality of syngas in biomass gasification.

Key words: gasification, Ni/γ-Al_2O_3 catalyst, syngas reforming, tar removal
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1 Introduction

Because of depletion of fossil fuel sources and global warming, utilization of biomass gasification for energy production has attracted tremendous attention in recent years[1]. Gasification is a century-old, theoretically complicated thermochemical process in which biomass materials experience incomplete combustion in a medium such as air, oxygen, or steam to produce combustible gases called syngas. Syngas is a mixture of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O), nitrogen (N_2), and small amounts of methane (CH_4) and higher hydrocarbons. It can be burned directly in furnaces, boilers, stoves, internal combustion engines, or micro-turbines for heat and power generation. It can also be further converted to a wide variety of useful, high-margin petrochemicals or transportation fuels, such as synthetic diesel (via the Fischer-Tropsch method), ethanol (via fermentation), and dimethyl ether and methanol (via catalytic reactions).

However, syngas from biomass gasification also contains unwanted impurities, such as tars, that are a major obstacle to commercial applications of syngas in engines, turbines, and fuel cells[2]. Tar is a generic term comprising all organic compounds present in syngas excluding gaseous hydrocarbons. It can condense to more complex structures in pipes, filters, and heat exchangers of downstream equipment and processes that may cause mechanical breakdown of the entire system. Tar may also deactivate catalysts in the refining process. Generally, tar content varies from about 0.5 to 100 g/m^3 in biomass gasification syngas depending on the type and design of the gasifier, feedstock used, and operating conditions[3]. Most applications of syngas require tar content below 50 mg/m^3. Thus, tar removal is one of the most important and urgent problems in biomass gasification.

Several types of tar removal technologies are available, among which catalytic cracking is considered

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the most promising in large-scale applications because of its fast reaction rate and reliability. Moreover, by breaking long-chain or ring-structured hydrocarbons into simpler molecules, catalytic cracking cannot only remove unwanted condensable tars but also increase the quantity of useable gases such as CO and H_2 in syngas. Catalytic tar cracking has been investigated for more than two decades[4,5]. Various materials, including natural minerals (e.g., olivine and dolomite), alkali metals, NiO, and activated alumina, have been investigated as the catalyst[6,7]. Of these, Ni-based catalysts have shown great promise for biomass gasification tar removal. They have high tar cracking reactivity with an additional advantage of syngas reforming to enhance combustible gases in syngas. However, Ni-based catalysts are relatively expensive and their performances are somehow gasifier and biomass specific, thus it is necessary to choose optimum parameters for maximum tar removal and CO/H_2 enhancement for certain gasifiers and biomass. The objective of this work was to determine appropriate cracking parameters, including catalytic reaction temperature, gas residence time, and Ni loading, for effective tar removal and syngas reforming in two types of lab-scale biomass gasifiers, one downdraft, and the other one updraft, fueled by pine sawdust.

2 Materials and methods

2.1 Catalyst preparation

Commercial γ-Al_2O_3 balls (Delta Adsorbents Company, Roselle, IL) with a diameter of 1/8 inch and surface area of 355 m^2/g were used as the catalyst support. $Ni(NO_3)_2\cdot 6H_2O$ (Fisher Scientific, Pittsburgh, PA) was used as the Ni precursor. To prepare 3% and 6% Ni loading catalysts using the single-step process, precisely weighed $Ni(NO_3)_2\cdot 6H_2O$ was placed into a 100 mL beaker and dissolved into deionized water under vigorous stirring at room temperature. The homogeneous solution was then transferred to a 500 mL beaker containing precisely weighed alumina spheres and stirred gently for 2 h to ensure complete impregnation of $Ni(NO_3)_2\cdot 6H_2O$ into alumina. After that, the Ni/γ-Al_2O_3 spheres were dried in an oven at 75℃ for 12 h. Finally, the dried spheres were calcined in a tubular furnace at 400℃ for 4 h in the air. To prepare catalysts with higher than 6% Ni loadings, a two-step impregnation process was adopted. The procedure was exactly the same as the single-step process except that only half as much $Ni(NO_3)_2\cdot 6H_2O$ was used in the first step without calcination. Dried γ-Al_2O_3 spheres were then impregnated with the other half of the $Ni(NO_3)_2\cdot 6H_2O$ solution, dried, and calcined in a tube furnace at 400℃ for 4 h in the air.

2.2 System setup

The experimental system was composed of four subsystems:

1) model tar generation unit, which provided constant flow of benzene as a model tar at a specific flow rate to the cracking unit;

2) biomass gasifier system;

3) tar/benzene cracking unit;

4) tar/benzene collection unit.

A schematic diagram of the system is shown in Figure 1, and details of each system are presented in the following sections.

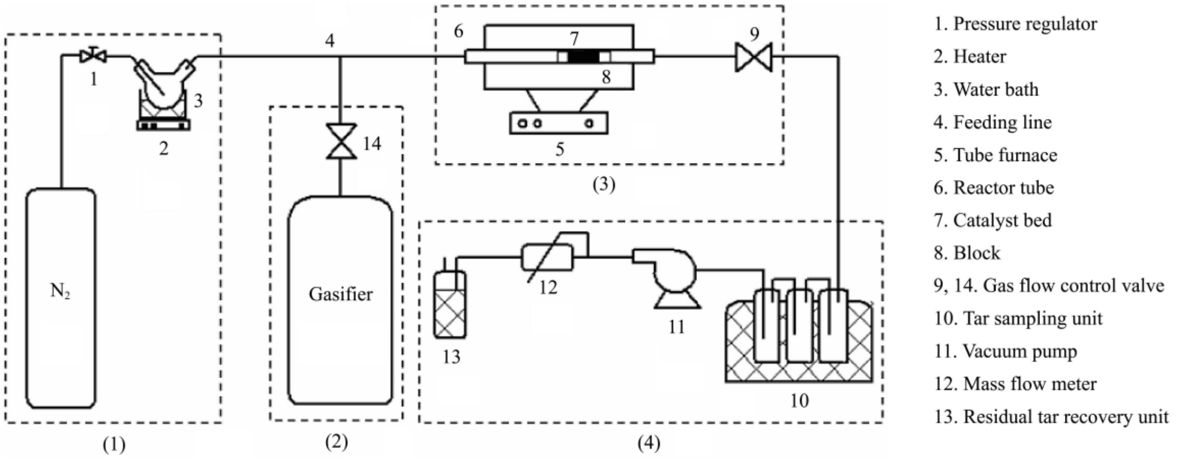


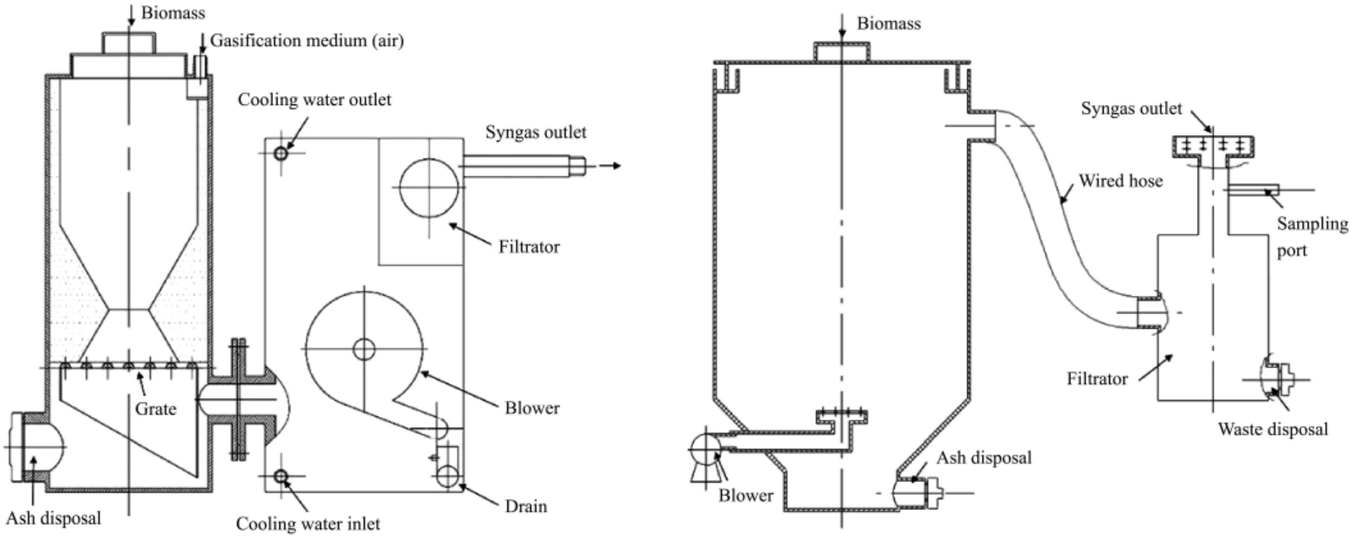
Figure 1 Schematic diagram of the experimental system

2.3 Model tar generation

Benzene was chosen as the model tar because of its chemical stability and easy condensability[8]. The principle of the model tar generation system was based on the relationship between benzene vapor pressure and temperature/pressure[9,10]. In each experiment, 0.66 g benzene was placed in a 100 mL Knotes flask with three angle necks. High-purity nitrogen flowed from a high-pressure cylinder regulated by a pressure regulator (at an outlet pressure of 1 atm, flow rate of 3 L/min) into the flask. The flask was placed in a water bath at (24 ± 1)℃. All feeding lines were wrapped with heat insulation material to prevent benzene from condensing before entering the cracking unit.

2.4 Biomass gasification

The biomass in this work was locally obtained pine sawdust with a moisture content of about 15% and a particle size of one to five mm. The ultimate analysis showed that the pine sawdust had about 48.27% C, 6.45% H, 45.19% O, and 0.09% N on the mass basis. The downdraft gasifier (Figure 2a) consists of a reaction chamber, grate, gas cooler, filtration unit, and blower assembly. The gasifier has an overall syngas production rate of 2.8 to 5.6 cfm. Syngas flows into the gas cooler, in which steam and a fraction of tars are condensed and collected. The filtrator is filled with charcoal to remove particulate matters and a fraction of tars. The updraft gasifier (Figure 2b) consists of a reaction chamber, gas cooler/burner, and a blower assembly. The gasifier has an overall syngas production rate of 5 to 50 cfm depending on the voltage supply to the 15-W blower (Deilibang, Zhejiang, China). Raw syngas flows into the gas cooler, in which steam and a fraction of tars condense and are collected before syngas is burned. In gasification tar cracking experiments, syngas from the sampling port was directed to the cracking tube. In both gasifiers, the air flow rate was controlled at the lower end of the blower, and combustion zone temperature was around 800℃.



a. The downdraft gasifier

b. The updraft gasifier

Figure 2 Schematic diagram of the reactor system

2.5 Tar/benzene cracking

The tar cracking system included a 1-inch-diameter, 24-inch-long quartz reactor tube with a complete vacuum-sealing assembly (MTI Corporation, Richmond, CA) and a Thermolyne Economy solid-tube furnace (Fisher Scientific, Pittsburgh, PA). The furnace was equipped with a single set-point temperature controller for up to a maximum working temperature of 1,200℃. The catalyst bed was placed in the center of the tube and horizontally supported by two alumina foam blocks (MTI Corporation, Richmond, CA). In a typical experiment, the model tar or syngas flowed into the tube at one end, passed through the catalyst bed, and left at the other end. Residual tar was collected by the tar collection unit.

Table 1 shows the experimental parameters of benzene and tar cracking. In benzene cracking, temperatures were in the range of 700℃ to 900℃ at steps of 50℃. Ni loadings ranged from 0 to 21% at steps of 3%. Gas residence times were set at 0.1, 0.2, 0.3, 0.5, 0.7, 0.9, and 1.1 s. Results from benzene cracking were used to determine optimal conditions for tar cracking in biomass gasification, which were 800℃ reaction temperature, 15% Ni loading, and 0.3 s gas residence time.

Table 1 Experimental parameters of benzene and tar cracking

Parameter	Model tar (benzene) cracking	Syngas tar cracking in the downdraft gasifier	Syngas tar cracking in the updraft gasifier
Pressure/10^5 Pa	1	1.012	-
Temperature/℃	700 to 900	800	650 to 850
Initial tar concentration in the feeding gas/g • m^{-3}	22 (benzene)	2.3	7.2
Gas residence time/s	0.1 to 1.1	0.3	0.3
Gas flow rate/L • min^{-1}	3.0	5.1	9.1
Catalyst bed length/cm	3	5.1	9
Catalyst bed volume/cm^3	15.2	25.6	46.1
Ni loading in catalysts/%	0-18	15	15
Benzene flow rate/g • min^{-1}	0.066	-	-

2.6 Tar/benzene collection

The cold-trapping method was used in benzene/tar collection. The unit was composed of three 250 mL flasks dipped into an insulation box containing dry ice. Nitrogen-carried benzene or syngas-carried tars flowed into the three flasks and were quenched and collected. The amount of benzene or tar collected was measured with a high-precision analytical balance (up to 0.1 mg). Other researchers have used similar or slightly modified forms of this method[11]. A few experiments were carried out in this study by passing a known amount (0.66 g) of benzene through the cracking furnace without catalyst bed for 10 min, revealing that the collection unit captured 99.9% of the benzene. Considering that actual biomass gasification tars have even higher condensation temperatures than benzene, we expect that they will be easier to collect with the cold-trapping unit. Collected tars were dried in an oven at 105℃ for 2 h to constant weight and weighed with the high-precision analytical balance.

2.7 Syngas sampling and analysis

Syngas was collected from the sampling port or the outlet of the vacuum pump with a 500 mL Tedlar sampling bag. Molar concentrations of H_2, N_2, CO_2, CO, and CH_4 were analyzed with a SRI 8610s gas chromatograph equipped with a thermal conductivity detector (SRI Instruments, Torrance, CA).

3 Results and discussion

3.1 Effect of reaction temperature and Ni loading on benzene removal

Figure 3 shows benzene removal rate as a function of Ni loading and temperature. As expected, reaction temperature played an important role in benzene cracking. Benzene removal rate increased significantly with as reaction temperature increased up to 800℃. At temperatures higher than 800℃, the improvement in benzene removal was slight. Considering that higher temperatures require more energy input in the reaction and also may cause coking and sintering of catalysts that reduce the lifetime of the catalyst[12], it is wise to choose a lower cracking temperature with acceptable tar cracking efficiency. Thus, the reaction temperature of 800℃ was chosen to test tar cracking in the biomass gasifiers.

The effect of Ni loading on benzene removal rate can also be seen in Figure 3. Tar removal rate increased with increasing Ni loading. The biggest jump in benzene removal rate occurred from 0% to 3% Ni loading. This suggests that NiO plays a major role in the catalysis, although the Al_2O_3 support or heating of benzene might have also helped the reaction. When Ni loadings further increased, the increase in benzene removal rate slowed and remained almost unchanged after reaching 15%. Because Ni is the most expensive part of the catalyst, lower Ni loadings are always preferred for economic reasons. Therefore, 15% Ni loading was chosen to test Ni/γ-Al_2O_3 catalyst performance in the downdraft gasifier.

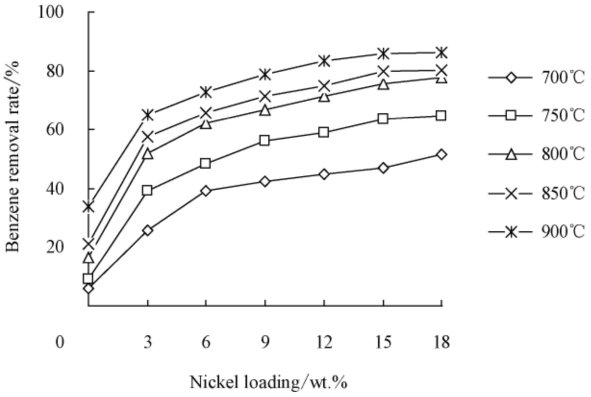


Figure 3 Benzene removal rates at various Ni loadings and cracking temperatures (gas residence time = 0.3 s)

3.2 Effect of gas residence time on benzene removal

Gas residence time refers to the length of time the model tar resides in the catalyst bed. Figure 4 shows benzene removal rate as a function of gas residence time. Benzene removal rate remained high when gas residence time was greater than 0.3 s but decreased significantly at shorter residence times. For the 0.1 s gas residence time, only around 28% of benzene was cracked. This result indicates that benzene needs sufficient time to decompose even in the presence of Ni/γ-Al_2O_3 or Ni/char catalysts. When gas residence time increased to more than 0.3 s, increase of benzene removal rate slowed gradually. Longer gas residence times require slower syngas flow rates or the use of more catalysts, so a minimal but reasonably effective time is desired. Therefore, 0.3 s was chosen as the optimum gas residence time to test catalyst performance in the removal of biomass gasification tars.

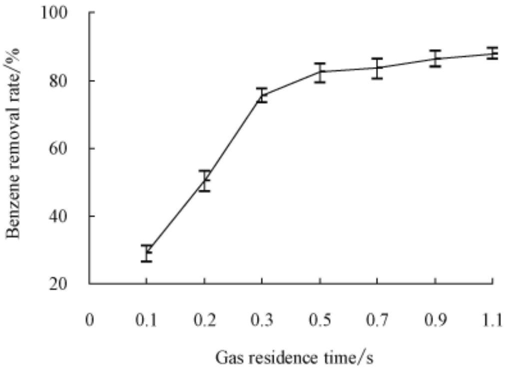


Figure 4 Benzene removal rates at various gas residence times

3.3 Removal of biomass gasification tars

Tar removal performance of the catalyst at 800℃, 15% Ni loading, and 0.3 s gas residence time was tested in a downdraft biomass gasifier. More than 99% of tars were effectively removed, from 2.25 g/m^3 in the original syngas to 0.01 g/m^3 after cracking. In addition to tar removal, gas composition of syngas from the downdraft gasifier was also improved (Table 2). Concentrations of H_2 and CO in syngas increased from 19.96% to 51.78% and from 16.26% to 21.10%, respectively. Relative changes (defined by Equation (1)) of the five major gases, H_2, CO, CH_4, CO_2, and N_2, were 159.30%, 29.8%, -84.1%, -84.4%, and -56.5%, respectively.

$$Relative\ change = \frac{Concentration\ after\ cracking - concentration\ before\ cracking}{concentration\ before\ cracking} \times 100\% \qquad (1)$$

Table 2 Comparison of syngas composition before and after reforming in gasifiers (800℃, 15% NiO loading, and 0.3 s gas residence time)

Gasifier type	Compound	Concentration before cracking	Concentration after cracking	^{a}Relative change/%
Downdraft	Tar (g/m^3)	2.25	0.01	-99.5
	H_2 (vol%)	19.96	51.78	+159.3
	N_2 (vol%)	61.65	26.81	-56.5
	CO_2 (vol%)	1.24	0.19	-84.4
	CO (vol%)	16.26	21.10	+29.8
	CH_4 (vol%)	0.88	0.14	-84.1
Updraft	Tar (g/m^3)	7.23	0.15	-98.0
	H_2 (vol%)	23.97	37.39	+56.0
	N_2 (vol%)	49.71	34.89	-29.8
	CO_2 (vol%)	1.06	0.01	-99.0
	CO (vol%)	22.95	27.21	+18.6
	CH_4 (vol%)	2.32	0.50	-78.4

Note: ^{a}Relative change = (concentration after cracking - concentration before cracking)/ concentration before cracking.

Because tar content in syngas from updraft gasifiers is usually much higher than that from downdraft gasifiers, an updraft gasifier was also studied to test performance of the Ni/γ-Al_2O_3 catalyst in a more severe condition. Similar results were obtained from the updraft gasifier. About 98% of tars were removed. However, increase of H_2 in the updraft gasifier was smaller than that in the downdraft gasifier. Only a 56% increase in H_2 was observed in the updraft gasifier versus 159% in the downdraft gasifier. Although CO concentration in the reformed syngas of the updraft gasifier was higher than that in the downdraft gasifier, relative CO increase in the updraft gasifier was also smaller. One possible reason may be that syngas from the updraft gasifier contained much higher content of tars. Therefore, different reforming conditions, such as higher temperatures, may be needed to remove all tars and achieve higher concentrations of H_2 and CO. Further studies were conducted as follows.

The effect of reforming temperature on tar removal and syngas composition was studied in the updraft gasifier. As shown in Figure 5, tar removal rate steadily increased with the increase of reaction temperature. About 99% of tars were removed at 850℃, compared with 91% at 650℃. Meanwhile, H_2 concentration increased significantly from 26.97% to 44.94%, whereas CO concentration decreased from 30.82% to 25.64% when temperature increased from 650℃ to 850℃. This suggests that when initial tar content is high, more severe cracking conditions may be needed, such as higher reaction temperatures, longer residence times, or higher Ni loadings.

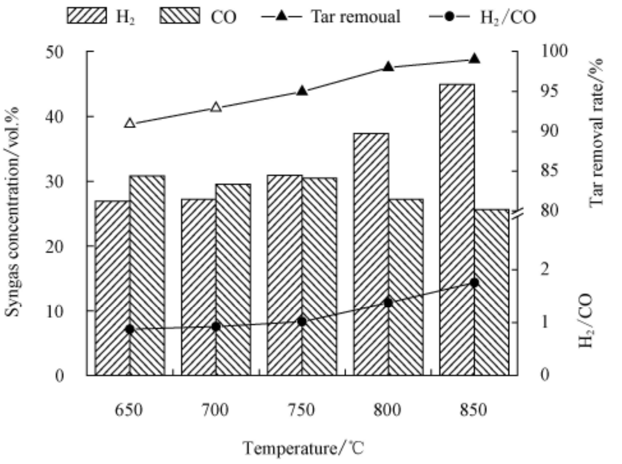


Figure 5 Effect of reaction temperature on syngas composition and tar removal rate

As seen in Figure 5, the molar ratio of H_2/CO also increased with increasing temperature. This can be explained through mechanisms of tar reforming[13-16]. It is believed that long-chain hydrocarbons (tars) are eliminated through the following reaction in the presence of Ni catalysts[17]:

$$C_nH_m + 2n\ H_2O \leftrightarrow n\ CO_2 + (2n + m/2)\ H_2 \text{Endothermi} \quad (3)$$

Meanwhile, the following reactions also take place to convert CO_2, CH_4, and H_2O into CO and H_2:

$$C_nH_m + n\ CO_2 \leftrightarrow m/2\ H_2 + 2nCO \text{Endothermic} \quad (4)$$

$$CH_4 + H_2O \leftrightarrow CO + 3\ H_2 \quad \Delta H = +210\ \text{kJ/mol} \quad (5)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41.2\ \text{kJ/mol} \quad (6)$$

Equations (2), (3), and (4) show that more H_2 than CO is produced when temperature increases. Equation (5) is usually called the water-gas shift reaction; it is an exothermic reaction, and a lower temperature favors the equilibrium to the right side. With the increase of reaction temperature, H_2/CO tends to decrease but is, however, dependent on the availability of CO_2. In this study, CO_2 in the original syngas was very low; therefore, Equation (5) was not sufficient to reduce H_2/CO in the updraft gasifier. The ratio of H_2/CO in the reformed syngas reached 2.45 for the downdraft gasifier and 1.38 for the updraft gasifier at the reaction temperature of 800°. Several syngas conversion reactions need specified ratios of H_2/CO; for example, methanol production from syngas needs a 2:1 H_2/CO ratio[14], which can be achieved by changing the reforming temperature in the presence of a Ni/γ-Al_2O_3 catalyst.

4 Conclusions

Ni/γ-Al_2O_3 catalysts were prepared by using the impregnation and calcining method. Benzene was used as the model tar to optimize catalytic reactions. The main parameters investigated were reaction temperature (700℃ to 900℃), gas residence time (0.1 s to 1.1 s), and catalyst loading (3% to 21%). On the basis of the benzene test, optimum reaction conditions of 800℃ reforming temperature, 15% Ni loading, and 0.3 s gas residence time were chosen to test catalyst performance in biomass gasifiers.

Results from the test of the catalyst in biomass gasifiers showed that tars in syngas could be effectively eliminated by catalytic cracking at the optimum conditions. More than 99% of tars were removed in the downdraft gasifier, and 98% were removed in the updraft gasifier. H_2 concentration in syngas increased significantly in both gasifiers (from 19.96% to 51.78% in the downdraft gasifier and from 23.97% to 37.39% in the updraft gasifier). CO concentration also increased in both gasifiers (from 16.26% to 21.10% in the downdraft gasifier and from 22.95% to 25.64% in the updraft gasifier). As expected, changing reforming temperature effectively adjusted the H_2/CO ratio in syngas.

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