In-chamber thermocatalytic tar cracking and syngas reforming using char-supported NiO catalyst in an updraft biomass gasifier

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Abstract: The objective of this study was to evaluate the performance of an in-chamber tar cracking and syngas reforming unit. This unit was composed of a two-stage tubular reactor placed within the combustion zone of an updraft biomass gasifier. Heat generated in the exothermic combustion reactions of biomass gasification drove tar cracking and syngas reforming in the tubes, eliminating the need of external heating. The performance of the unit was evaluated using char-supported NiO catalysts and was found to be very effective in tar removal and syngas composition enhancement. A tar removal rate of 95% was achieved at 0.3 s residence time and 10% nickel loading. This condition also gave syngas high-heating value increment of 36% (to 7.3 MJ/m^3). The effect of gas residence time and Ni loading on tar removal and syngas composition of the unit was also studied. Gas residence of 0.2-0.3 s and Ni loading of 5%-10% were found appropriate to produce clean syngas with tar content appropriate for industrial applications (<0.6 g/m^3) in an updraft biomass gasifier without external heating.

Keywords: biomass gasification, tar cracking, syngas reforming, nickel catalyst, char catalyst
DOI: 10.3965/j.ijabe.20140706.011

Citation: James A, Yuan W, Boyette M D, Wang D, Kumar A. In-chamber thermocatalytic tar cracking and syngas reforming using char-supported NiO catalyst in an updraft biomass gasifier. Int J Agric & Biol Eng, 2014; 7(6): 91－97.

1 Introduction

Biomass gasification is a promising means to produce clean energy from biomass resources[1]. This thermochemical process is basically an incomplete combustion of biomass that leads to the formation of a gas mixture called syngas containing useful compounds of hydrogen and carbon monoxide[2]. Syngas can be utilized in industrial applications such as being a fuel for turbines, boilers, and internal combustion engines[3]. It can also be further converted to liquid fuels, such as diesel via the Fischer-Tropsch process[4]. However, the formation of heavy hydrocarbon species, notoriously known as tar, is a significant challenge in the implementation of biomass gasification for industrial applications. Tar is a generic term comprising all organic compounds present in syngas except gaseous hydrocarbons. Milne et al.[5] reported the following major compounds in tars: levoglucosan, hydroxy-acetaldehyde, furfurals, methoxyphenols, phenolic compounds, olefins, and alkyl tertiary and condensed tertiary products. Tars can condense to

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Received date: 2014-01-30 **Accepted date:** 2014-11-30

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more complex structures in pipes, filters, or heat exchangers of downstream equipment and processes, which may cause mechanical breakdown of the entire system. Tars may also deactivate catalysts in the refining process. It is essential to reduce the level of tars to enable widespread utilization of syngas, most of which require tar contents below 0.6 g/m^3 at normal state[5]. In order to reduce tars in syngas, methods such as physical treatment[6], thermal and plasma-assisted cracking[7], and catalytic reforming[8] have been developed, among which catalytic tar reforming is considered the most promising in large scale applications due to its fast reaction rate and reliability and also its ability to increase the quantity of useable gases such as CO and H_2 in syngas[9]. For example, Yang et al.[10] and Zhang et al.[11] evaluated different nickel-olivine catalysts, with which the highest tar removal of 98.7% was achieved. In a similar way, alumina (Al_2O_3) supported nickel catalysts were investigated with tar removal rate of 99.5%[12]. Nickel-char catalysts were also found to be inexpensive and effective to crack tars with 99% removal rate[13].

However, in order to be economically feasible, catalytic tar reforming systems need to be inexpensive, effective, and ideally they should increase hydrogen and/or carbon monoxide contents in the product gas in addition to tar removal[14]. Catalytic tar reforming generally require temperatures above 650^{o}C[15] and therefore requiring a heating source. Dayton[16] stated that the use of high temperature for tar reforming was not efficient because of the heating it required. Nevertheless, the implementation of a tar cracking system located in the gasifier combustion zone does not require an external heating source. In-chamber tar reduction might be a way to reduce tar contents and reform syngas by modifying the gasifier. The objective of this study was to evaluate an experimental catalytic tar cracking and syngas reforming unit. This unit was composed of a two-stage tubular reactor placed within the combustion zone of an updraft biomass gasifier. The heat generated in exothermic combustion reactions of biomass gasification drove tar reforming reactions in the tubular reactor.

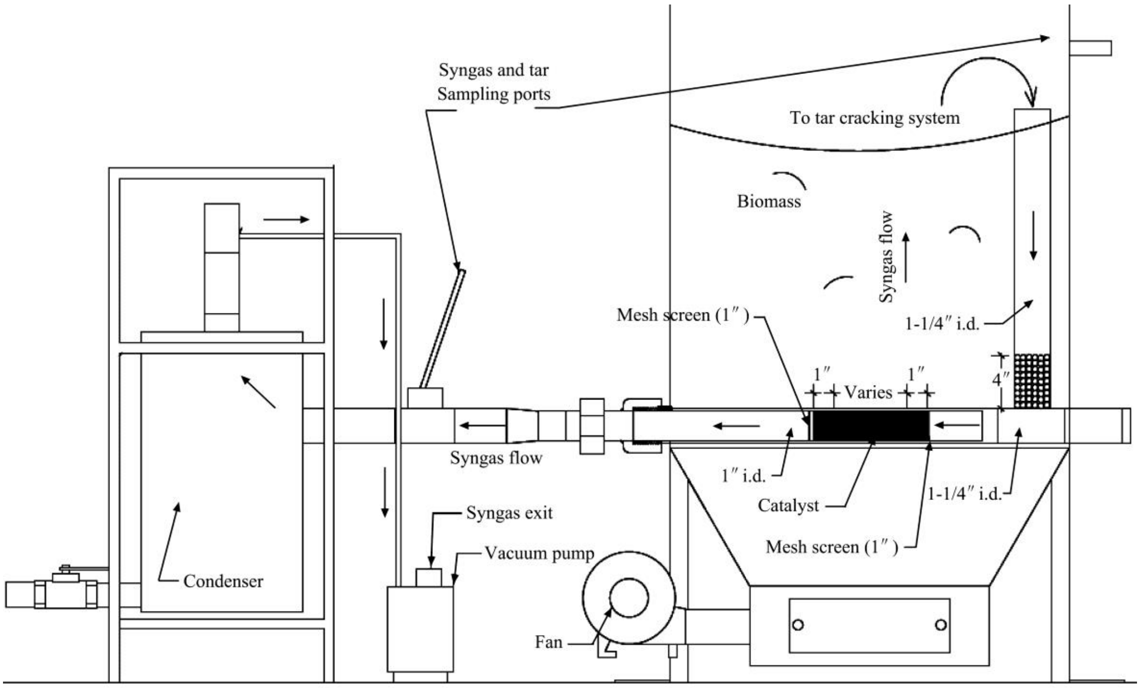
2 Materials and methods

2.1 Apparatus

Experiments were carried out on a lab-scale biomass gasification system composed of an updraft biomass gasifier, an in-chamber tar cracking unit, a water/tar condenser, and a syngas burner. Figure 1 shows a sketch of the system. The updraft gasifier was a vertical steel reactor with 0.5 m inside diameter (i.d.) by 0.96 m height. Air was provided by a centrifugal blower (510 L/min). The tar reforming unit was composed of a horizontal tube located in the middle of the combustion zone and a vertical tube above it. The horizontal tube of 31.8 mm i.d. and 508 mm length was made of black iron, where the NiO catalyst was loaded. The vertical black iron tube of 31.8 mm i.d. and 101.6 mm length was loaded with char whose particle size ranged from 6.3 mm to 9.5 mm. This vertical pipe was used as a tar pre-cracking reactor and to filter excessive particles in syngas in order to avoid blockage in the horizontal (main) catalytic bed. Syngas was drawn into the in-chamber tar cracking unit using a vacuum pump. The residence time (the duration that syngas contacts the catalyst) was calculated based on the flow rate of the syngas and the length of the catalyst bed. Tar removal rate was defined as the percentage of tars removed by in-chamber cracking from the raw syngas.

2.2 Catalyst preparation and loading

The nickel-char catalyst was prepared using nickel oxide (NiO) (Catalog number: AC41558-5000, Fisher Scientific Inc., Pittsburgh, PA) and charcoal briquettes (Grillmark®, Northbrook, Illinois). Char granules were crushed and sieved to obtain particles in the size range of 1.4 mm to 2 mm. Mechanical mixing of char and NiO was performed following the method by Wang et al.[17]. Nickel oxide loadings of 0, 5%, 10%, and 15% (weight) with a gas residence time of 0.2 s were evaluated. Evaluation of three residence times (0.1, 0.2 and 0.3 s) was carried out with nickel oxide loading of 10%. The procedure of loading the catalyst was as follows: a mesh screen was set inside the horizontal black iron tube to keep the catalyst in position. Then, a plug of refractory ceramic fiber was placed to prevent nickel oxide from blowing away. The catalyst mixture was then loaded in the middle of the catalytic bed, the length of which was determined by the gas resident time; one-inch char layer was loaded before and after the catalytic bed. Finally, a stainless steel mesh and a snap ring were used to secure the catalytic bed in place. The vertical black iron tube was simply filled with char particles. Temperatures in the chamber were measured by type-K thermocouples.



Note: Parts are not to scale; 1 inch = 25.4 mm; 1.25 inch = 31.8 mm.

Figure 1 Biomass gasification system

3 Experimental procedure

A mixture of sawdust and sawdust pellets was selected as the feedstock; 18 kg maple wood sawdust, obtained from a local landfill in Wamego, KS, was mixed with 9 kg maple wood sawdust pellets obtained from a local hardware store. Table 1 shows representative elemental and chemical compositions of maple wood sawdust[18].

Table 1 Compositions of maple wood sawdust

Analysis	Content/%
C	48.12
H	5.93
O	45.49
N	0.46
Ash	0.95
Cellulose	60.15
Hemicellulose	17.71
Lignin	11.61

The reactor was started by burning 1.8 kg of sawdust mixture for 4 minutes to create a fire-bed (100 mL of methanol was used as igniting fluid). The remaining sawdust mixture was then added on top of the fire-bed. Syngas from the gasifier was guided to the burner and burned. Once the temperature in the reaction zone reached 850°C, 14.2 L/min of syngas was drawn through the tubular tar reforming unit to test its performance using a vacuum pump; excess syngas was burned by the burner.

3.1 Syngas analysis and tar sampling

Tar samples were collected by cold trapping method both before and after passing through the tubular reactor. This tar sampling method condensed heavy tars in syngas using a two-step process[13]. First, syngas flowed through a 250 mL flask under ice-water mixture to condense heavy tars and water, and then flowed through a set of three 250 mL flasks submerged in dry ice (solid CO_2). Tars were condensed for 15 min at a gas flow rate of 3.8 L/min. After collecting, tar samples were dried overnight in an oven at 105°C and then weighed. Difference in weight before and after drying was recorded. All flasks were dried and pre-weighed too. Syngas samples were collected both before and after the tar reforming using Tedlar® polyvinylfluoride sampling bags (DuPont, Wilmington, DE). Syngas composition was measured using a gas chromatograph (SRI 8610, Torrance, CA) equipped with a thermal conductivity detector with helium as the carrier gas. Hydrogen, carbon monoxide, carbon dioxide, methane, oxygen and nitrogen were quantified. The high heating value (HHV) of syngas was calculated using the gas composition and enthalpy of combustion of reactants, hydrogen, carbon monoxide and methane using Equation (1) [19].

$$\Delta Ho = \sum(Hof)_r - \sum(Hof)_p \qquad (1)$$

where, ΔHo is high heating value; $\sum(Hof)_p$ is enthalpy of combustion of products; $\sum(Hof)_r$ is enthalpy of combustion of reactants.

4 Results and discussion

4.1 Combustion zone temperature

A number of tar cracking studies were performed by some other researchers[20-22]. However, in all cases the second stage tar cracking needed an external heating source to supply the required heat, negatively impacting the overall efficiency of the process. Heat for the tar cracking experiments in this project was supplied by the exothermic reactions in the combustion zone of the gasifier starting when the combustion zone temperatures (CZT) reached 850°C. Atypical graph of the CZT is shown in Figure 2. As shown, the CZT took approximately one hour to reach 750°C and another hour to reach 850°C. CZT stabilized at around 900°C until gasification was stopped.

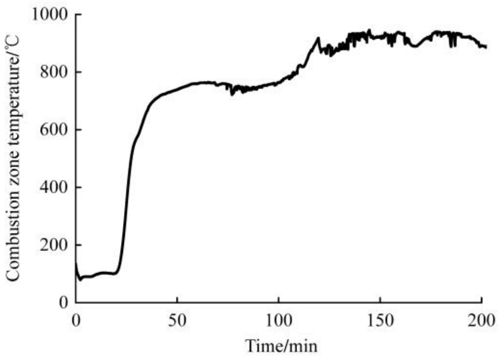


Figure 2 A typical temperature profile of the combustion zone.

4.2 The effect of residence time on tar removal and syngas reforming

The performance of the catalytic tar reforming unit was evaluated with char-supported NiO catalyst. Figure 3 shows tar cracking efficiency (or tar removal rate) for residence times of 0.1, 0.2 and 0.3 s with 10% NiO loading. It can be seen that the lowest tar cracking efficiency rate (~65%) occurred at residence time of 0.1 s, which apparently was not long enough for an effective tar cracking. Higher tar removal rates were achieved at residence times of 0.2 and 0.3 s. Tars were effectively cracked from 11.23 g/m^3 to 0.53 g/m^3 (94% removal) and from 6.32 g/m^3 to 0.35 g/m^3 (95% removal) at 0.2 s and 0.3 s, respectively. Therefore, 0.2 s and 0.3 s residence times were considered appropriate in this study. Similar results were found by Wang et al.[17] who evaluated the effect of residence time with nickel-char catalysts on tar cracking experiments in two gasification systems and found that 0.3 s residence time presented optimal performance at 800°C while 0.1 s was not long enough to yield a high cracking efficiency.

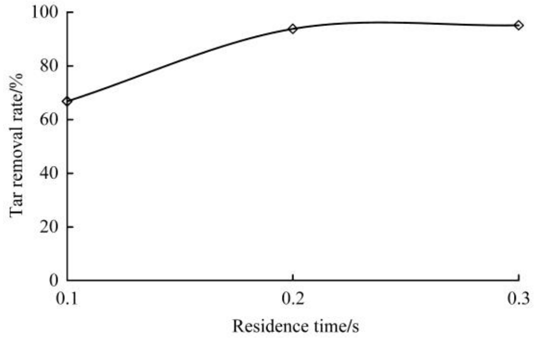


Figure 3 The effect of residence time on tar removal rate (10% nickel loading)

Table 2 shows product gas composition at the three residence times before and after catalytic reforming at 10% Ni loading. A significant increase in CO and H_2 was observed in all cases, especially at 0.2 and 0.3 s residence times, e.g., CO increase was from 19.8%, 18.1%, and 17.5% to 20.6%, 23.9% and 20.9%, and H_2 increase was from 7.4%, 8.6% and 6.1% to 10%, 14.2% and 13.7%, at 0.1, 0.2 and 0.3 s residence time, respectively. Longer residence times allowed more time for tar molecules to interact with the catalyst. This enabled a more efficient conversion of tars into H_2 and/or CO via active water shift reaction, water gas reaction and tar dehydration reaction that take place in the catalytic unit[23] since the initial and final syngas contains enough water for this reactions. CH_4 concentration either did not change or slightly increased in all cases. It is not clear why methane had an opposite behavior compared with other publications[20,24] where methane concentration generally decreased as the residence time increased. A possible explanation may be that methane production is promoted by the hydrogenation of carbon molecules when gasification temperatures exceed 700°C at 1 atm[25].

Table 2 The effect of residence time on syngas composition before and after cracking (10% nickel loading)

Catalysts	H_2/%		CO/%		CH_4/%	
	Before	After	Before	After	Before	After
Ni 10%/Char, 0.1 s	7.4	10.0	19.8	20.6	5.5	5.6
Ni 10%/Char, 0.2 s	8.6	14.2	18.1	23.9	4.0	7.3
Ni 10%/Char, 0.3 s	6.1	13.7	17.5	20.9	5.1	6.2

4.3 The effect of nickel loading on tar removal and syngas reforming

Figure 4 shows tar removal at different nickel loadings with 0.2 s residence time. Char alone (0% Ni loading) achieved a tar removal rate of 60.9%. Abu El-Rub et al[26] tested the effect of char alone as the catalyst and found that at 700°C, 81.6% of the phenols were cracked. Moreover, the tar removal rate significantly increased as Ni loading increased, suggesting that NiO played a significant role in tar removal. It is important to note that tar cracking activity also depends on reaction temperature and char particle size. Wang et al.[13,17] reported that the tar removal had a positive relationship with reaction temperature when char and nickel-char catalysts were used. It can be found from Figure 2 that the CZT was low in the first 1-2 hours of gasifier operation. Even after the temperature stabilized, it still fluctuated between 850-950°C. These variations can have adverse effects on tar cracking and reforming activities. As a result, performance of the in-chamber thermocatalytic tar reforming unit depends on gasifier design and operating conditions. Poor performance would be expected in gasifiers with low CZT (e.g., <800°C) and also in the beginning of gasifier operations due to low CZT.

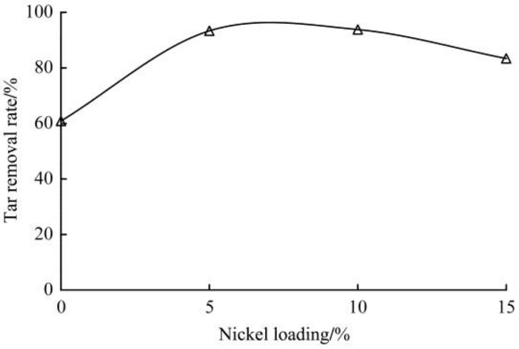


Figure 4 The effect of nickel loading on tar removal (0.2 s residence time)

Table 3 presents nickel loading effects on syngas composition at 0.2 s residence time. It was found that CO and H_2 concentrations significantly increased in most cases after syngas was reformed in the thermocatalytic tube. The highest increases of CO and H_2 concentration were 23.90% and 14.21% at the 10% Ni loading. CH_4 concentration also showed slight increases. However, decrease in CO and only slight increase in H_2 were observed at nickel loading of 15%. Similar results were reported by Wang et al.[13] who believed that when nickel loading of 15% or higher was utilized, nickel dispersion rate on char surfaces could decrease, which consequently reduced the reactivity of the catalyst.

Table 3 The effect of nickel loading on syngas composition before and after cracking (0.2 s residence time)

Catalysts	H_2 /%		CO /%		CH_4 /%	
	Before	After	Before	After	Before	After
Char only	6.0	8.5	19.9	19.7	4.2	5.3
Ni 5%/Char, 0.2 s	11.0	14.9	18.4	20.8	5.3	6.7
Ni 10%/Char, 0.2 s	8.6	14.2	18.1	23.9	4.0	7.3
Ni 15%/Char, 0.2 s	11.2	15.3	21.0	21.7	5.1	6.5

The high heating values (HHV) of syngas before and after tar cracking are summarized in Table 4. Nickel-char catalysts with 10% loading and a residence time of 0.3 s gave the highest increase in HHV (36%). The effect of gas residence time can clearly be seen, longer residence time (0.2 s to 0.3 s) gave higher HHV due to more efficient tar conversion and better syngas reforming. The effect of Ni loading is also apparent. It seemed that Ni loading of 5% was too low and that of 15% was too much, while Ni loading of 10% was found appropriate based on the increase of HHV of the produced syngas. In previous studies[12,17], Ni loading of 15% was found optimum when benzene was used as the model compound for tar cracking. However, little difference was noticed between 10% and 15%.

Table 4 High heating value of syngas before and after syngas reforming

Catalysts	HHV(±SD) before tar cracking /MJ m^{-3}	HHV(±SD) after tar cracking /MJ m^{-3}	Increment /%
Char only	5.31±0.106	6.11±1.286	14.97
10% Ni loading, 0.1 s	6.06±0.165	6.55±0.441	8.05
5% Ni loading, 0.2 s	6.26±0.308	7.69±0.415	22.88
10% Ni loading, 0.2 s	5.52±0.416	7.46±2.205	35.16
15% Ni loading, 0.2 s	6.55±0.033	7.77±0.033	18.72
10% Ni loading, 0.3 s	5.39±0.403	7.33±0.476	36.01

5 Conclusions

The performance of the tar cracking and syngas reforming unit built in the combustion zone of an updraft biomass gasifier was evaluated using char-supported NiO catalysts. The in-chamber system was found to be very effective in tar removal and syngas enhancement with performance being comparable to cracking reactors that use external heating. The highest tar removal of 95% was achieved at 0.3 s residence time and 10% nickel loading. This condition also gave the highest syngas HHV increment of 36% (7.33 MJ/m^3). The effects of gas residence time and Ni loading on tar removal and syngas composition were also studied. Gas residence of 0.2 s to 0.3 s and Ni loading of 10% were found appropriate to effectively use the heat from the combustion zone for thermocatalytic tar cracking.

Acknowledgements

This material is based upon the work supported by the U.S. Department of Agriculture and Sun Grant (Award No. 2010-38502-21836 and Subaward No. AB-5-67630. KSU11) and the startup fund of North Carolina State University. The lead author was also partially supported by the scholarship program of IFARHU-SENACYT from the Government of Panama.

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