

A comparison of catalytic and non-catalytic steam reforming of naphthalene used as biomass gasification tar model compound

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Abstract:

One of the major issues in the biomass gasification technology is how to deal with the biomass tar. Tar is an undesirable product of biomass gasification because of the various problems associated with the condensation and formation of tar aerosols, which presents significant impediment to the application of biomass gasification systems. Catalytic and non-catalytic tar steam reforming were studied in this research by using naphthalene as a model tar compound. The experiments were conducted in a lab-scale fixed bed reactor operated at 800°C. Catalytic performance on naphthalene decomposition was compared among experiment without catalyst, with 12%Fe/Al₂O₃, 3%Ni-12%Fe/Al₂O₃ and 12%Ni-3%Fe/Al₂O₃ catalysts. The results showed that low amount of Ni added, i.e. the case of 3%Ni-12%Fe/Al₂O₃ catalyst, gave the higher catalytic performance in tar steam reforming when compared with the case of 12%Fe/Al₂O₃ catalyst and with 12%Ni-3%Fe/Al₂O₃ catalyst. The carbon conversion into gas was increased to around 27% with the highest production of H₂ and CO (i.e. around 37 and 15 mmol/g feed, respectively) among all the cases. This was probably due to the presence of Ni-Fe bimetallic particles on the catalyst.

Keywords: Naphthalene; Tar; Reforming; Catalyst

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1. Introduction

Tar is an undesirable byproduct of biomass gasification because of the various problems associated with the condensation and formation of tar aerosols, which presents significant impediment to the application of biomass gasification systems. A number of research studies concerning the decomposition of tar have been undertaken mostly using catalysts such as natural dolomites, nickel-based catalysts, etc (Abu El-Rub et al., 2002). The main problems of these catalysts include fragility as in the case of dolomite or high cost as in the case of nickel-based catalysts. Among active catalysts, metallic iron was found to satisfy these two properties as performing well in cracking tar and relatively cheap. By these reasons, iron-based catalyst was interested and used in this study.

In the present work, naphthalene was used as the tar model compound because it represents the polyaromatic hydrocarbon group or tertiary tar. This tar classification group is known to be the most difficult to be thermally degraded (Abu El-Rub et al., 2002). The effects of the presence of catalyst were investigated. Catalytic performance on naphthalene decomposition was compared among experiment without catalyst, with 12%Fe/Al₂O₃, 3%Ni-12%Fe/Al₂O₃ and 12%Ni-3%Fe/Al₂O₃ catalysts.

2. Experiment

2.1 Catalyst preparations

The catalyst support material, γ -Al₂O₃, was sieved into the particle size between 0.6 and 1.0 mm. The Fe/Al₂O₃ catalyst was prepared by impregnation method using an aqueous solution of Fe(NO₃)₃·9H₂O. The loading amount of Fe was 12 wt%. For the Ni-Fe/Al₂O₃ catalyst, the mixed aqueous solution of Fe(NO₃)₃·9H₂O and Ni(NO₃)₂·6H₂O was used. Two catalysts with different Ni and Fe loading (varied by % weight) were prepared, which were 3%Ni-12%Fe/Al₂O₃ and 12%Ni-3%Fe/Al₂O₃. After the impregnation, the samples were dried at 110°C for 12 h followed by the calcination at 500°C for 3 h in air.

2.2 Experimental setup and operating conditions

The experiment using naphthalene as tar model compound was carried out in a lab-scaled fixed bed reactor. The reactor has the height of 400 mm (of which the heated zone is 300 mm) and the diameter of 10 mm. The schematic diagram of experimental setup is shown in Fig. 1. The catalyst is placed on the quartz wool in the middle of quartz reactor with the bed height of 1 cm. Before testing, the catalyst was reduced into the active form at 500°C with the 30 ml/min flow of 5% vol H₂/N₂ mixture for 2.5 hours.

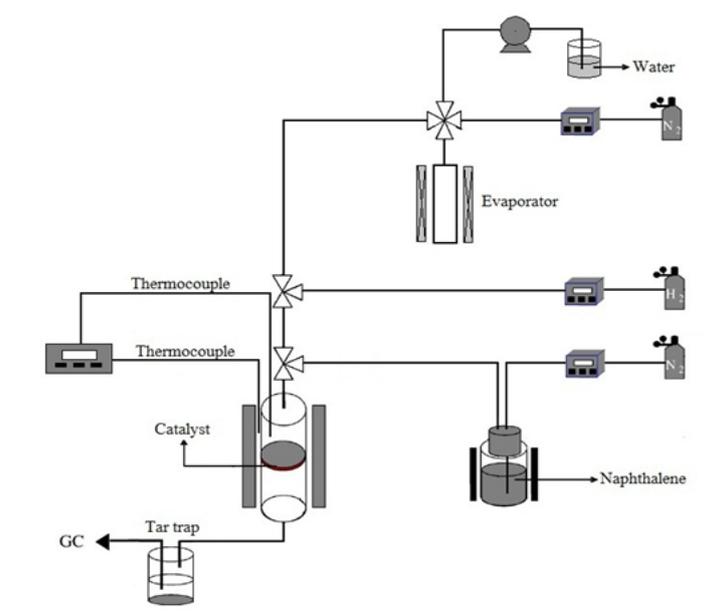


Fig. 1 Schematic diagram of experimental setup.

Naphthalene was placed in a reservoir and heated at 130-140°C before saturated in the 70 ml/min N₂ stream passed through the naphthalene reservoir. To prevent the naphthalene condensation inside the reactor system, all the pipelines were heated at 200°C by using a heating coil. For steam reforming experiments, the 300°C steam was produced by the steam generator. Deionized water was injected into the evaporator and the produced steam was saturated in the 30 ml/min N₂ stream. The steam to carbon ratio was controlled at about 0.083. The operation temperature of 800°C was used for all experiments. The gas product was collected every 20 minutes by 2L-gas bag throughout the experiment and was further analyzed by gas chromatograph (GC Shimadzu-14B and Shimadzu-2014). Tar was trapped from the gaseous stream by iced-cold traps.

The results of naphthalene reforming were reported in term of carbon conversion into gas (%), which was calculated as follow:

$$\text{Carbon conversion into gas (\%)} = \frac{[\text{CO}]_{\text{out}} + [\text{CO}_2]_{\text{out}} + [\text{CH}_4]_{\text{out}}}{10[\text{C}_{10}\text{H}_8]} \times 100 \quad (1)$$

Where; [C₁₀H₈]_{in} = The concentration of naphthalene entering the reactor
 [CO]_{out} = The concentration of carbon monoxide leaving the reactor
 [CO₂]_{out} = The concentration of carbon dioxide leaving the reactor
 [CH₄]_{out} = The concentration of methane leaving the reactor

3. Results and discussion

3.1 Catalyst characterization

The crystalline structure of catalysts was investigated by X-ray diffraction (XRD) technique. Fig. 2

shows the XRD patterns of 12%Fe/Al₂O₃ and 12%Ni-3%Fe/Al₂O₃ catalysts. The peak of Al₂O₃ at 2θ = 43.4° was taken as reference. When adding Fe metal on Al₂O₃ support, the peaks of Fe₂O₃ were observed at 2θ = 33.1° and 35.6°. For Ni-Fe/Al₂O₃ catalyst, NiO peaks were found at 2θ = 37.2° and 43.2° and the peak Fe₂O₃ was also observed.

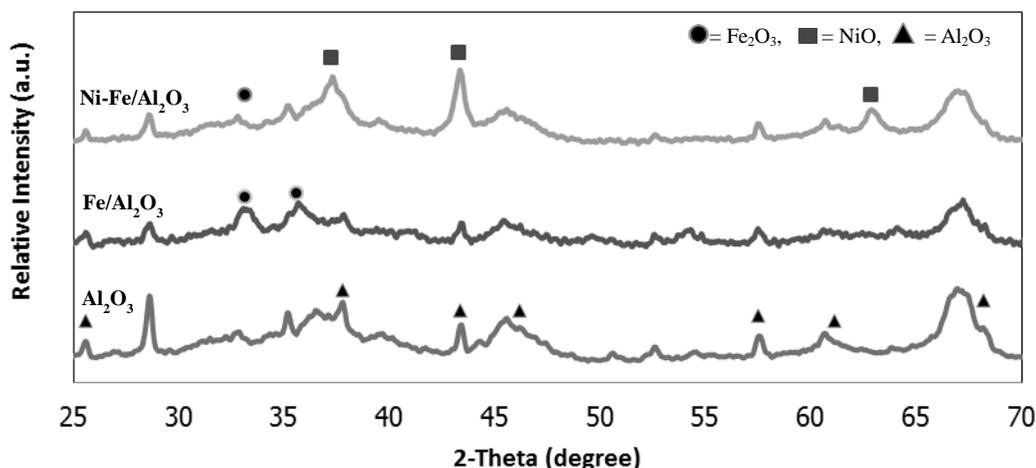
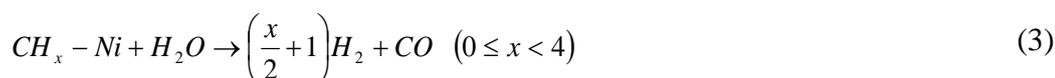


Fig. 2 XRD patterns of Fe/Al₂O₃ and Ni-Fe/Al₂O₃ catalyst.

3.2 Effect of catalyst on naphthalene reforming

All prepared catalysts including Fe/Al₂O₃ and Ni-Fe/Al₂O₃ were tested with the decomposition of naphthalene at 800°C. The reaction without catalyst was also carried out for comparison. The effect of catalyst with steam at 800°C on carbon conversion into gas is shown in Fig. 3. It was found that the carbon conversion into gas of naphthalene with the presence of catalysts were 16–30%, which was significantly higher than those without catalyst. By adding low amount of Ni, i.e. the case of 3%Ni-12%Fe/Al₂O₃ catalyst, the catalytic performance was increased by 14% when compared to the case of 12%Fe/Al₂O₃ catalyst and also higher when compared to the case with high amount of Ni, i.e. 12%Ni-3%Fe/Al₂O₃ catalyst. With regard to the product gas composition, H₂, CH₄, CO, and CO₂ were the main gaseous species from naphthalene reforming. The effect of catalyst type on gas production is shown in Fig. 4. It was found that the 3%Ni-12%Fe/Al₂O₃ catalyst also gave the highest H₂ and CO production, which confirmed the promotion of naphthalene reforming reaction by the addition of Ni. The higher activity of 3%Ni-12%Fe/Al₂O₃ could be explained by the synergy between Ni and Fe bimetallic species (Wang et al., 2011). This result was also consistent with the previous study (Oemar et al., 2013) which reported that the presence of Ni-Fe bimetallic particles in LaNi_{0.8}Fe_{0.2}O₃ catalyst had the higher performance than the LaNiO₃ catalyst for H₂ production due to the presence of Ni-Fe bimetallic particles. Moreover, Ni species has been known as the catalyst for tar cracking and steam reforming of hydrocarbon following the reaction as shown in Eqs. (2) and (3) (Yamazaki et al., 1996).



4. Conclusion

The catalytic and non-catalytic reforming of naphthalene was carried in a lab-scaled fixed bed reactor at 800°C. The iron based-catalyst had a good catalytic performance on naphthalene reforming but could be enhanced by adding a lower amount of Ni. From the results, 3%Ni-12%Fe/Al₂O₃ catalyst gave the highest carbon conversion into gas about 30% and also the highest

H₂ and CO yields. It was probably due to the presence of Ni-Fe bimetallic particles.

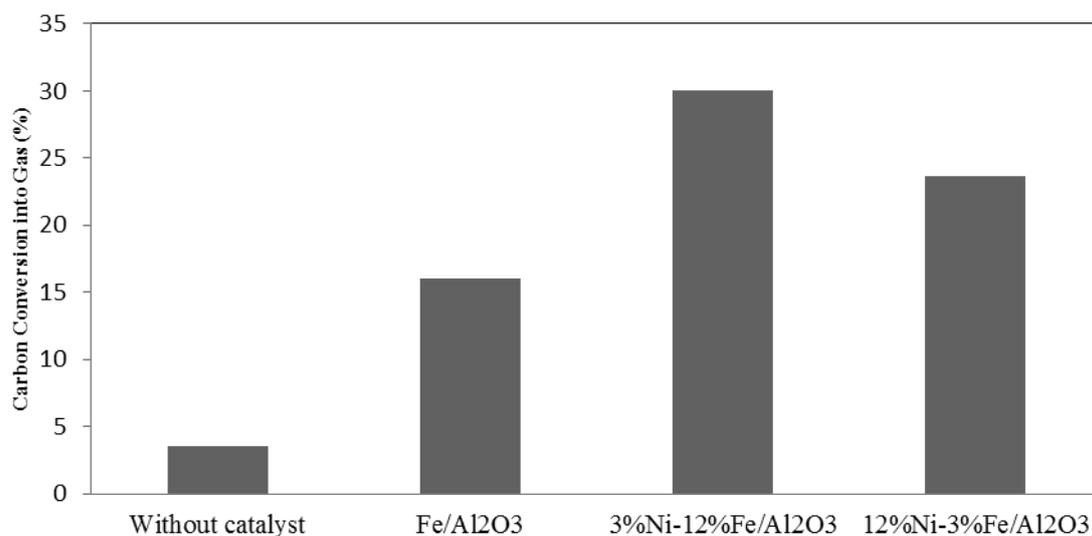


Fig. 3 Effect of catalyst on carbon conversion into gas (%) in naphthalene steam reforming at 800°C.

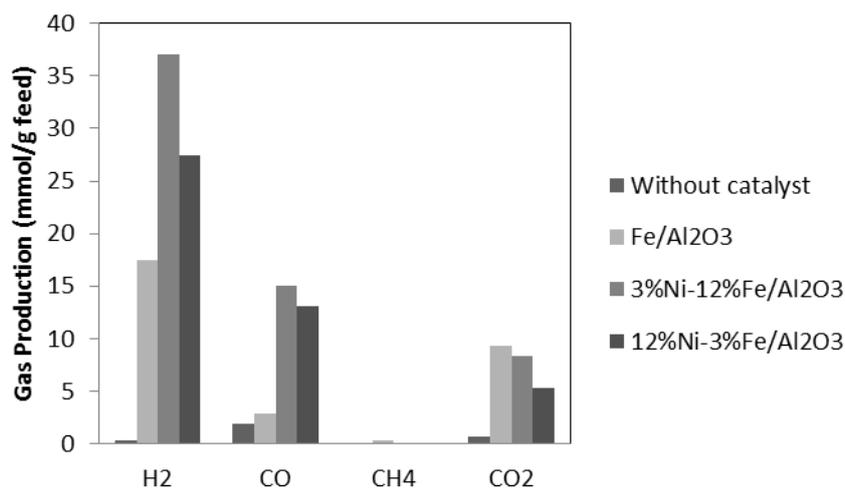


Fig. 4 Effect of catalyst on gas production yield in naphthalene steam reforming at 800°C.

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