

The Development of Ni/Dolomite Catalyst in Simultaneous Biomass Gasification and Reforming in Fluidized Bed

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Abstract: Simultaneous gasification and steam reforming of the biomass on Ni/dolomite catalyst in fluidized bed reactor were studied in the gaseous production in the one stage reactor. **Problem statement:** The parameters such as temperature, steam flow rate, biomass feed rate, gas flow rate for fluidization, oxygen flow rate and catalyst types were studied to produce the high gaseous products including tar elimination. **Approach:** The temperature at 780°C, steam flow rate of 222 mmol h⁻¹, gas flow rate for fluidization 450 mL min⁻¹ and oxygen input 50 mL min⁻¹ were found to be the suitable conditions. The Ni/Dolomite and the developed Ni/Dolomite were studied about their performance. **Results:** It was confirmed that Ni/Dolomite and newly developed Ni-WO₃/Dolomite show high performance in biomass gasification. **Conclusion/Recommendations:** It was claimed that Ni/Dolomite catalyst was the effective and give best performance for tar cracking. Newly developed Ni-WO₃/Dolomite catalyst was investigated to resist sulfur and coking. Three types of catalyst were used in the biomass gasification, which are Ni/Dolomite, Ni/Dolomite+Silica binder and Ni-WO₃/Dolomite. From the XRD analysis, structures of type 1 (Ni/dolomite) and type 2 (Ni/Dolomite+Silica binder) were similar which were in CaCO₃, MgNiO₂, NiO and MgO forms. Type 3 (Ni-WO₃/Dolomite) was CaWO₄, MgNiO₂, NiO and MgO forms. When the catalytic gasification was operated, newly Ni-WO₃/Dolomite catalyst was the best catalyst for bamboo and palm shell biomasses, which could produce the high carbon monoxide and hydrogen but low methane and carbon dioxide were found. Carbon deposition on catalyst was around 0.37 mg according to the TG analysis.

Key words: Biomass gasification, fluidized bed reactor, Ni/dolomite catalyst, tar reforming

INTRODUCTION

Biomass is the production of photosynthesis and is thought to be one of the most promising renewable energy resources. Gasification of biomass with steam has been known to produce gases (H₂, CO, CO₂ and CH₄), light and heavy hydrocarbon (tar) and char.

The biomass gasification is the primary process for producing the synthesis gas lead to the production of DME, methanol or LPG in the secondary process. Absolutely, tar and char still be the major problems in the catalytic gasification. The biomass gasification apparatus was continuously developed to the high performance in the gas production^[1-11].

Recently, Ni-supported dolomite (Ni/Dolomite) catalyst^[12-14] was studied for catalytic performance in

the tar gasification to claim that it is an effective catalyst for fixed bed gasification of tar. The Ni/Dolomite catalyst showed excellent activity for the gasification of tar and its model compounds (toluene and naphthalene) and resistance against coking.

In the present study, the new apparatus, 1-stage system of biomass gasification with fluidized bed reactor, was modified and set up with the stainless steel reactor. The main objective of this research was to find the conditions that can completely eliminated the wastes (tar and char) from the reaction lead to the useful gases. We expect that this results can lead to the further research on the biomass gasification with in-situ tar and char gasification process in a catalytic fluidized bed as the first process and then through the methanol or DME process as the second process.

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Moreover, the effects of temperature, steam rate, fluidized velocities, biomass feeding rate, oxygen input including catalysts which are the main role for biomass gasification with fluidized bed reactor by continuous biomass feeding rate were investigated the tendency of products that occurred. The result of them and the efficiency of new apparatus were described in this study. The differences of catalyst such as Ni/Dolomite, Ni/Dolomite+SiO₂ binder and the newly developed Ni-WO₃/Dolomite (Takuma Co. Ltd in Japan) were investigated the characteristic in the gasification process for eliminating tar.

MATERIALS AND METHODS

Figure 1 shows the schematic diagram of biomass gasification with fluidized bed. The cylindrical stainless steel tube reactor with inner diameter of 38.7 mm and 705 mm of height was located inside an electric furnace, which is heated by temperature programmed method. The flow of Argon and hydrogen with gasifying medium (steam) from water pump were fed into evaporator and then flowed through a gas distributor which is placed at the bottom of the reactor and contain Ni/Dolomite catalyst. Before gasification occurred, Ni/Dolomite had to reduce in hydrogen at 700°C for 2 h in order to be the effective and performance catalyst. The various amounts of biomasses were fed from the top under gravity by continuous feed and analyzed every 4 min. The gaseous products flow through the top of reactor into impinger bottles which contained isopropyl alcohol (IPA) for tar trap and were analyzed by TCD gas chromatograph. The effects of temperature at 780°C and steam flow rate at 222 mmol h⁻¹ were selected as the suitable condition to investigate the performance of Ni/Dolomite catalyst.

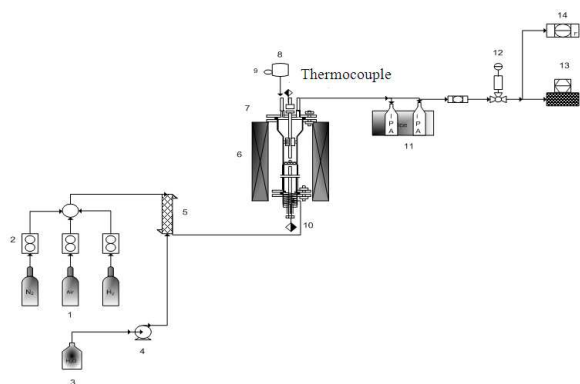


Fig. 1: Schematic diagram of the experimental set up for biomass fluidized bed gasification

RESULTS

Figure 2 showed the result of three types of catalyst on gas compositions in gasification with fluidized bed. Bamboo was used to check the products because they are so interesting and abundant in our country. According to the Fig. 2, the biomass feed rates at 30 g h⁻¹ were fed continuously at temperature 780°C, steam flow rate 222 mmol h⁻¹, gas flow rate for fluidization 450 mL min⁻¹ and Ni/Dolomite catalyst 10 g. Compare with three types of Ni/Dolomite catalysts, it may be seen that the newly Ni-WO₃/MgO-CaO catalyst can produce the synthesis gas higher than Ni/Dolomite and Ni/Dolomite+SiO₂ binder. Also, carbon dioxide and methane were decreased. Hence, this experiment can be suggested the result of Srinakruang *et al.*^[12-13], which used toluene and naphthalene as tar model, that the performance of Ni/Dolomite can be operated in the real biomass gasification for tar elimination to form the synthesis gas. Compare with the literature of Asadullah *et al.*^[2-9] who studied the cedar wood gasification on Rh/CeO₂/SiO₂ catalyst, the advantage of Rh/CeO₂/SiO₂ catalyst could play at the low temperature and also could produce the high carbon conversion but the cost of this catalyst is relatively higher than conventional catalyst, since the work was done at the laboratory level. The chemicals used for catalyst preparation were high grades and expensive. Thus, Ni/Dolomite catalyst was also another choice in biomass gasification due to the properties of cost, preparation and life time were completely the appropriate catalyst^[12-14], which can be brought in a commercial scale laboratory.

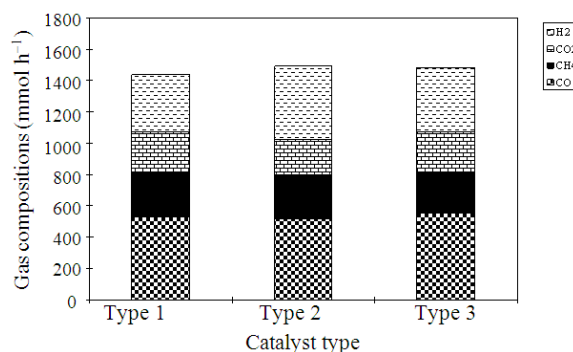


Fig. 2: The effect of Ni/Dolomite catalyst on the gas compositions in biomass gasification and reforming with fluidized bed, Type 1: Ni/Dolomite; Type 2: Ni/Dolomite+SiO₂ binder; Type 3: Ni-WO₃/MgO-CaO

In Fig. 2 the effect of Ni/Dolomite catalyst on the gas compositions in biomass gasification and reforming with fluidized bed.

DISCUSSION

The effect of Ni/dolomite catalyst: Form the previous study, Srinakruang *et al.*^[12-13] have presented the effectiveness and performance of Ni/Dolomite catalyst that can eliminate tar formation. According to XRD analysis in Fig. 3, the structure of Ni/Dolomite catalyst was observed as CaCO₃ (2θ = 29.48°). It was claimed that MgNiO₂, NiO and MgO were detected at 43.0, 43.2 and 62.8° in the same result as Srinakruang *et al.*^[12-13]. NiO was reduced with hydrogen at 700°C to be reduced nickel (Ni⁽⁰⁾) form in reaction (1). When gasification was carried on, tar has been derived to react with reduced nickel to form nickel carbide in reaction (2) and finally reacted with steam to be synthesis gas in reaction (3):

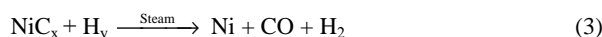


Table 1 shows the characteristics of three types of Ni/Dolomite catalyst that are used in this experiment.

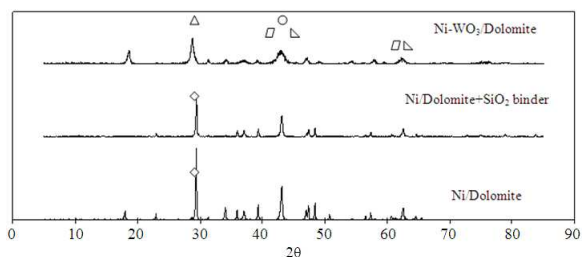


Fig. 3: XRD analysis of three types of Ni/Dolomite catalyst (a) Ni/Dolomite; (b) Ni/Dolomite+SiO₂ binder; (c). Ni-WO₃/Dolomite (◇) CaCO₃, (○) NiMgO₂, (△) NiO, (□) MgO, (Δ) CaWO₄

Table 1: The physical properties of three types of Ni/Dolomite catalysts

Type	Catalysts	Ni form ^a	BET (m ² g ⁻¹) ^b	Metallic surface area (m ² g ⁻¹) ^c
1	Ni/Dolomite	NiO, NiMgO ₂	27.0	0.5
2	Ni/Dolomite+SiO ₂ binder	NiO, NiMgO ₂	27.0	0.4
3	Ni-WO ₃ /Dolomite	NiO, NiMgO ₂	30.3	1.3

^a: Measured by XRD analysis; ^b: Calculated from N₂ adsorption isotherm; ^c: Calculated from H₂ adsorption after Ni reduction at 900°C with 20% H₂

NiO was the main structure that is the keyword in the tar gasification. Also, BET and metallic surface area are shown in the Table 1. It can be seen that Ni-WO₃/Dolomite catalyst has the highest surface area and metallic surface area because of WO₃ addition. The arrangement of nickel based on dolomite was regularly dispersed.

Ni/Dolomite + SiO₂ binder was developed because Ni/Dolomite structure might break during the process of crushing and sieving. SiO₂ binder was added to support the stronger structure.

In addition, the newly developed Ni-WO₃/Dolomite catalyst has been studied to get the highest performance by Sato *et al.*^[14]. It was found that the new catalyst exhibited higher activity at low temperature and better resistance to sulfur and coking. In the new catalyst, an added component that promotes dissociation of the combined sulfur elements accelerates the reactions as shown in Eq. 4 and 5, presumably retaining the larger part of active Ni. Ni-W catalyst is known to be highly active for hydrodesulfurization (HDS). In HDS process, WS_x on Ni catalyst promotes conversion of organic sulfur compounds to H₂S. It is also confirmed that H₂S desorbs from sulfide Ni catalyst in the presence of H₂ at high temperature. Therefore, it is possible that W promotes sulfur dissociation shown in Eq. 4 and 5.

In the Fig. 3, it is shown that XRD analysis of Ni-WO₃/Dolomite catalyst which the structure of Ni/dolomite catalyst was observed as CaWO₄ (2θ = 18.58 and 28.74°). It has been claimed that MgNiO₂, NiO and MgO were detected at 43.0, 43.2 and 62.8°:



Also, The SEM photography of three catalysts is presented to see the impregnated characterization of Ni based on dolomite as shown in Fig. 4. The dispersion of Ni based on dolomite may be seen after binder addition. Ni-WO₃/Dolomite catalyst was found that nickel is dispersed and arranged regularly more than Ni/Dolomite and Ni/Dolomite+SiO₂ binder.

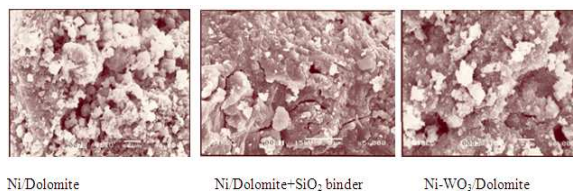


Fig. 4: The dispersion of Ni-supported on dolomite catalyst by SEM photography

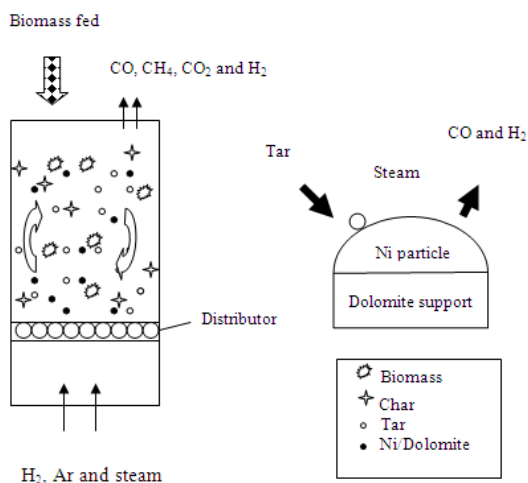
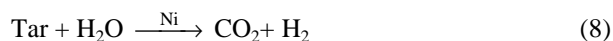
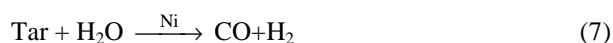
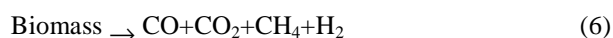


Fig. 5: The mechanism of biomass gasification in fluidized bed with Ni/Dolomite catalyst

Figure 5 could explain the mechanism that occurs in the fluidized bed after biomass was fed. Actually, the effective of biomass gasification with fluidized bed occurred as well as the suitable conditions are found. When gasification occurred, biomass was gasified with steam to produce gases, tar and char. Tar was eliminated with Ni/Dolomite catalyst lead to the synthesis gas. Char was reacted with steam to the gaseous products. Moreover, water gas shift and steam reforming which are the reversible reactions were also the important role to form gaseous products:



CONCLUSION

Simultaneous gasification and steam reforming of the biomass on Ni/dolomite catalyst in fluidized bed

reactor were studied in the gaseous production in the one stage reactor. The parameters such as temperature, steam flow rate, biomass feed rate, gas flow rate for fluidization, oxygen flow rate and catalyst types were studied to produce the high gaseous products including tar elimination. The temperature at 780°C, steam flow rate of 222 mmol h⁻¹, gas flow rate for fluidization 450 mL min⁻¹ and oxygen input 50 mL min⁻¹ were found to be the suitable conditions. The Ni/Dolomite and the developed Ni/Dolomite were also studied about their performance. It can be confirm that Ni/Dolomite and the newly developed Ni-WO₃/Dolomite show high performance in biomass gasification.

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