

Wang, Tiejun, Ph.D., "Biomass fuel gas to synthesis gas over highly stable nickel catalyst", Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, October, 2005.

Abstract

On account of the excessive exploitation of fossil source and seriously contaminative environmental problem, all over the world has devoted to exploit new energy, especially clean and renewable energy. Of all the renewable sources of energy, biomass is unique renewable source of carbon and named as green coal. It can be converted into liquid fuels and chemicals by the process of biomass gasification and FT synthesis. This routine can be greenhouse gas neutral. However, the production of biomass synthesis gas is the key in the whole process. In this aspect, the project presents the process of reforming biomass raw fuel gas to synthesis gas over highly stable nickel catalyst. It is very important to the production of carbon neutral fuels, status of energy shortage, threat of country safety, and rapid development of economy.

The techniques of biomass gasification have been developed extensively in the past ten years. The projects of electricity and fuel gas production from biomass gasification have come true the commercialization. However, the deep cleanup of the raw fuel gas is the bottleneck for its utilization in the FT industry. Many works reported in the recent literatures have focused on the utilization of commercial steam reforming nickel catalyst for the upgrading of biomass raw fuel gas. However, the catalysts lost their catalytic activity rapidly under the practical conditions of biomass gasification. In the present work, the highly stable NiO-MgO solid solution catalysts have been prepared by two steps co-precipitation method in order to improve the catalyst stability (anti-coking and sintering). The mechanism of biomass tar thermal and catalytic conversion and coke formation was also investigated. The effect of preparation conditions on the catalysts structure and performance was investigated by activity test and catalysts characterization. The properties and mechanisms of the reforming of raw fuel gas derived from biomass air-steam gasification and composition adjustment of synthesis gas were also investigated. We also made an evaluation to the different concepts of biomass synthesis gas production. The results obtained are listed below:

1. In the presence of H_2 and H_2O , the main reactions of thermal conversion of biomass tar are cracking, transfer hydrogenation and dehydrogenation polymerization. The tar conversion and coke formation can be inhibited by H_2 . However, the H_2O content has a neglectable affection on them. The high CO_2 content in the raw fuel gas can recarbonate the dolomite catalysts and make them lose tar-decomposing activity. Increasing H_2 content can inhibit the coke formation on the surface of Ni catalysts and improve the catalysts activity and reduction degree. The stability of tar species can be decreased by the adsorption of Ni catalysts. The H_2O and CO_2 in the fuel gas can adsorb on the surface of Ni catalyst and dissociate to O and CO or OH, and the active O attacks the tar species to produce the gas products. The NiO and basic support MgO can form solid solution structure by calcined process. The highly stable nickel catalysts fit for the reforming reactions of biomass fuel gas.

2. The 15% NiO-MgO ($(Ni/(Ni+Mg))$, atomic ratio) catalysts are prepared by two steps co-precipitation method. They show the excellent stability, activity and reducibility. No obvious

coke formation and catalyst deactivation were observed after 100h aging test. Catalysts can be reduced in-situ by biomass raw fuel gas. The two steps co-precipitation method is better than the co-precipitation and wet impregnating method. Increasing calcinations temperature can promote the formation of solid solution structure, improve the dispersion of Ni particles and inhibit carbonates formation on the catalyst surface. However, higher temperature promotes the formation of bulk solid solution structure, which is difficult to be reduced. The reducibility and activity of NiO-MgO catalyst increase as the Ni/Mg ratio increases. When Ni/Mg ratio is above 20/80, NiO-MgO catalysts lose their activity rapidly. There is a strong interaction between active centre and support surface. The NiO crystal particles can diffuse into the support and form solid solution structure at any Ni/Mg atomic ratio. The optimization of catalyst activity and stability is related to the formation of surface solid solution structures and bulk solid solution structures.

3. Increasing gasification temperature, ER ratio and S/B ratio promotes the conversion of biomass tar. The optimum gasification conditions are temperature of 750°C -800°C, ER ratio of 0.20-0.23, S/B ratio of 0.3-0.8. The reforming process upgrades the quality of synthesis gas greatly. The H₂ and CO contents increase greatly and tar conversion can be above 98%. It also increases the H₂/CO ratio and yield of synthesis gas. For 100% conversion of tar, the residence time is less than 1.0 s. Higher reforming temperature increases the tar conversion and decreases the carbon deposition on the surface of catalysts. However, in order to prevent the catalyst from sintering, the reforming temperature should not be too high. The results of 40 h aging test indicate that the stability of NiO-MgO catalyst is higher than that of Z405 catalyst. The composition of synthesis gas can be adjusted remarkably by the co-reforming of raw fuel gas derived from biomass air-steam gasification with addition of methane or biogas. The H₂/CO ratio of synthesis gas increases and the CO₂ content decreases greatly. Co-reforming concept does not require the CO₂ removal unit, which simplifies the whole process of synthesis gas production. Both efficiency and biomass carbon conversion are above 80%. No obvious carbon formation was observed after 100 h aging tests (stationary state), which indicates the high stability of NiO-MgO catalyst for the co-reforming process.

4. For the DME production from biomass synthesis gas, the “Once-through” concept combined power generation with unconverted gas has higher efficiency than 100% DME production concept. The former has simple system and little maintenance. The technology of biomass steam gasification fits for the hydrogen production. Under the optimum conditions, the technology of biomass oxygen-steam gasification fits for the synthesis gas production. With the conditions of large scale biogas production, the production of synthesis gas via co-reforming raw fuel gas derived from biomass air-steam gasification with addition of biogas will be a promising concept and developed widely in the future.