

Catalytic Gasification of Mandarin Waste Residue using Ni/CeO₂-ZrO₂

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Catalytic gasification of mandarin waste residue was carried out using direct and indirect catalyst-contact methods for the first time. In the indirect method, non-catalytic reaction in a reactor was followed by catalytic upgrading of vapor product in another reactor. Two different catalysts, Ni/ γ -Al₂O₃ and Ni/CeO₂-ZrO₂, were employed. CeO₂-ZrO₂ support was prepared using hydrothermal synthesis in supercritical water. The catalysts were characterized by H₂-temperature programmed reduction and Brunauer-Emmett-Teller analyses. Under the condition of equivalent ratio (ER) = 0, the indirect catalyst-contact method led to a higher gas yield than the direct method. Under ER = 0.2, the yield of biogas obtained over Ni/CeO₂-ZrO₂ was higher than that obtained over Ni/ γ -Al₂O₃. Also, the coke formation of Ni/CeO₂-ZrO₂ was lower than that of Ni/ γ -Al₂O₃. Such results were attributed to the higher reducibility and better lattice oxygen mobility of Ni/CeO₂-ZrO₂, which were advantageous for partial oxidation reaction.

Key Words : Hydrogen, Waste mandarin residue, Catalytic gasification, Ni/CeO₂-ZrO₂

Introduction

Among various renewable energy sources, biomass is abundant all over the world and can be commercialized within a much shorter time than others. Biomass includes a number of different materials, such as wood, herbaceous crops, agricultural and forest residues, and organic wastes. For biomass-to-energy conversion, biological and thermochemical treatments are widely used.¹⁻⁵ Gasification is one of the thermochemical treatments, which converts biomass into syngas via partial oxidation at high temperature.⁶⁻¹² Steam or air has been used as gasifying agent.¹¹⁻¹³ The syngas can then be used to synthesize various chemicals (e.g., synthesis of methanol via Fischer-Tropsch reaction). It can also be burned in a gas turbine or in a gas engine for power production. For these applications, however, impurities contained in the syngas such as tar, acidic gases and particulates need to be removed.^{8,9,11,13,14} Among the impurities, tar is a major concern for biomass gasification due to a relatively low operation temperatures compared to coal gasification.

Tar is usually a mixture of polycyclic aromatic compounds having high molecular mass and viscosity.^{8,9,13} It causes blockage of line during the operation of gas turbines. The removal of tar is achieved by physical methods, such as filtration using a high-temperature ceramic filter, or by chemical methods, such as catalytic decomposition. Catalytic

decomposition is particularly advantageous because it can increase the production of CO and H₂. Ni/Al₂O₃-based catalysts are widely used for the removal of tar.¹³ However, the deterioration of activity due to carbon deposition is a critical problem of the catalysts. Therefore, efforts are being made to maintain or enhance the activity of Ni by using various support materials. Reportedly, CeO₂-ZrO₂ support is expected to effectively preserve the activity of Ni catalyst. Park *et al.*¹³ reported that Ni/CeO₂-ZrO₂ exhibited high activity and high resistance to coke formation in the oxidation of benzene. According to Ihm *et al.*¹⁵ CeO₂-ZrO₂ prepared by continuous hydrothermal synthesis in supercritical water exhibited higher activity, than CeO₂-ZrO₂ generated by general co-precipitation method, for wet oxidation and NO reduction.¹⁵ They attributed the higher activity of the CeO₂-ZrO₂ prepared by the hydrothermal synthesis in supercritical water to its high thermal stability and large oxygen storage capacity. Therefore, it is needed to evaluate the activity of Ni/CeO₂-ZrO₂ catalyst, synthesized by using the CeO₂-ZrO₂ prepared by the hydrothermal synthesis in supercritical water as the support material, for gasification of biomass.

In Jeju Island, Korea, about 66,000 tons per year of mandarin waste residue is produced as a byproduct of mandarin juice manufacturing.^{16,17} Although several studies have been reported on the energy conversion of mandarin waste residue, the production of syngas, in particular, the production of hydrogen by gasification of mandarin waste residue has never been reported. Therefore, research on the

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catalyst system for enhancing the production of hydrogen in the gasification of mandarin waste residue is needed at this point.

In this study, mandarin waste residue was gasified over two different catalysts, Ni/ γ -Al₂O₃ and Ni/CeO₂-ZrO₂. The hydrogen production and tar (oil) removal obtained with these two catalysts were compared with those obtained without catalyst. Air, instead of steam, was used as the gasifying agent. The effect of the catalyst-contact method on the product distribution was also investigated.

Experimental

Waste mandarin residue is composed of 1.2 wt % of moisture, 70.5 wt % of volatile matter, 14.3 wt % of fixed carbon, and 14.0 wt % of ash. The elemental analysis showed that it consisted of C (36.5 wt %), H (7.3 wt %), and N (0.5 wt %). For more detailed results of elemental and proximate analyses, one can refer to previous studies published.^{16,17} CeO₂-ZrO₂ (0.65:0.35 mass ratio) support was prepared using the method of hydrothermal synthesis in supercritical water.¹⁵ γ -Al₂O₃ was purchased from Sigma-Aldrich. The support material was impregnated with 10 wt % of Ni using the incipient wetness method. The precursor of Ni was Ni(NO₃)₂·6H₂O.

The characteristics of the Ni-impregnated catalysts were examined. Specific surface area was measured using the Brunauer-Emmett-Teller (BET) method. X-ray diffraction (XRD) patterns were obtained at room temperature by a Rigaku D/MAX-III instrument equipped with a Cu K α X-ray source. Reducibility was evaluated by BELCAT using the H₂-temperature-programmed reduction (TPR) method. For more detailed procedure of catalyst characterization one can refer to a previous study published.¹³

Catalytic gasification was conducted at 750 °C in a U-type batch reactor made of quartz. The volume, height, and inlet/outlet diameter were 50 mL, 160 mm, and 15 mm, respectively. Air was used for gasifying agent and two different equivalent ratios (ER = 0 and 0.2) were applied. The vapor-phase product was cooled in two condensers. The condenser temperature was controlled at -20 °C by a circulator for sufficient condensation of bio-oil. The product gas that passed the condensers was collected in a Teflon gas bag for further analysis.

For the contact of biomass and catalyst, two different methods were employed for gasification. In the direct contact method, catalyst and biomass were mixed with the mass ratio of 1:10 in a single reactor. The masses of catalyst and biomass were 0.5 g and 5 g, respectively. In the indirect contact method, non-catalytic reaction took place in the first reactor, followed by the catalytic upgrading of product vapor occurred in the second reactor that contained a catalyst layer. The identical mass ratio between the catalyst and biomass was maintained in the second method.

Results and Discussion

The surface areas of Ni/ γ -Al₂O₃ and Ni/CeO₂-ZrO₂ were

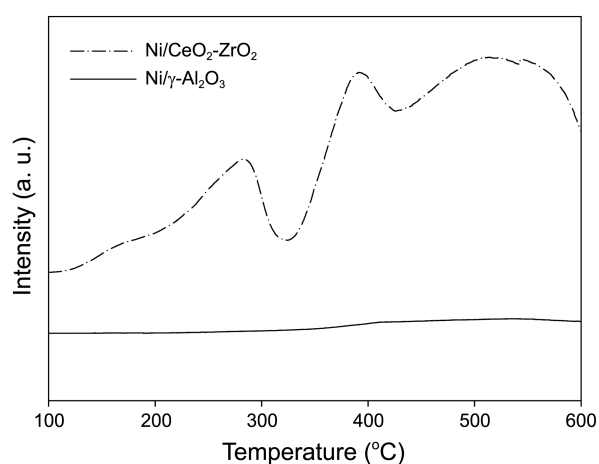


Figure 1. TPR patterns of catalysts.

71.1 m²/g and 56.6 m²/g, respectively. Figure 1 shows the TPR results. The reduction peak of Ni/CeO₂-ZrO₂ appeared at approximately 290 and 400 °C, whereas no peak was observed for Ni/ γ -Al₂O₃ until 600 °C. This indicates that the reducibility of Ni/CeO₂-ZrO₂ is much higher than that of Ni/ γ -Al₂O₃. It also implies that the lattice oxygen mobility of Ni/CeO₂-ZrO₂ is superior to that of Ni/ γ -Al₂O₃, being advantageous for partial oxidation reaction (gasification).

For the product distribution of oxygen-free (*i.e.*, ER = 0) pyrolysis-gasification reaction, the indirect catalyst-contact method resulted in higher gas and char yields and a lower oil yield than the direct method for both catalysts (data not shown). In the direct method, catalyst not only catalyzes the reaction but also facilitates heat transfer, promoting the decomposition of char. In this method, however, the vapor-phase products have limited chance to contact with catalyst. Therefore, the yield of liquid oil, containing considerable amount of tar, was not very different from that obtained from the non-catalytic reaction.

In the indirect catalyst-contact method, all the vapor-phase products pass through the catalyst layer in the second reactor and are upgraded there. Therefore, compared to the case of

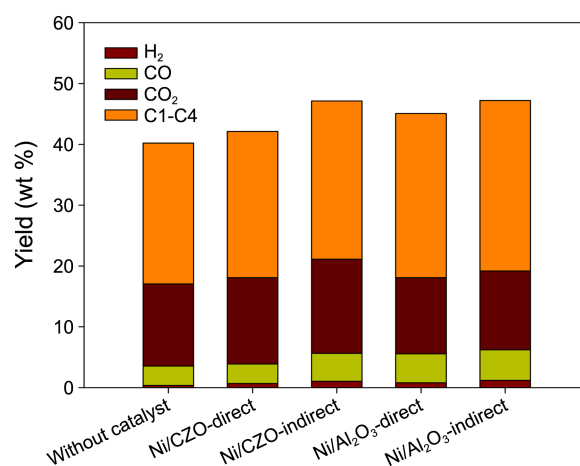


Figure 2. Yields of gas products at ER = 0.

direct method, the yield of liquid oil was significantly reduced by the conversion of tar into gaseous products within the catalyst layer. This may imply that the indirect catalyst-contact method is more advantageous than the direct method in terms of gas production and tar removal. All the yields of H₂, CO, CO₂, and hydrocarbon were enhanced by indirect method (Figure 2). It should be noted that the H₂ yields of Ni/γ-Al₂O₃ and Ni/CeO₂-ZrO₂ (Ni/CZO hereafter) were similar in the case of ER = 0.

The characteristics of catalytic gasification under a partial oxidation condition were investigated by carrying out the experiment with ER = 0.2. At this stage, only indirect catalyst-contact method was used. Similar to the case of ER = 0, the oil yield was reduced considerably by catalytic upgrading resulting in significant increase in the gas yield. In addition, increase of catalyst dose (catalyst/waste mandarin = 1/5) also increased the gas yield (Figure 3).

The effect of ER on the species distribution of product gas was significant (Figure 4). In particular, the yield of hydrocarbon (C₁-C₄), which was the most abundant species in the biogas produced under ER = 0, was reduced considerably under ER = 0.2.

Another interesting point is that the difference between the

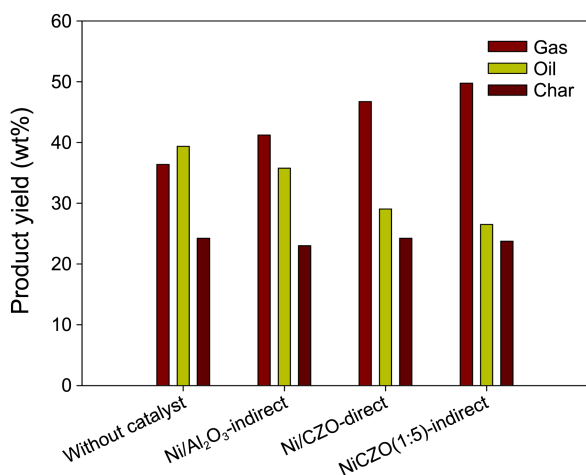


Figure 3. Yields of products at ER = 0.2.

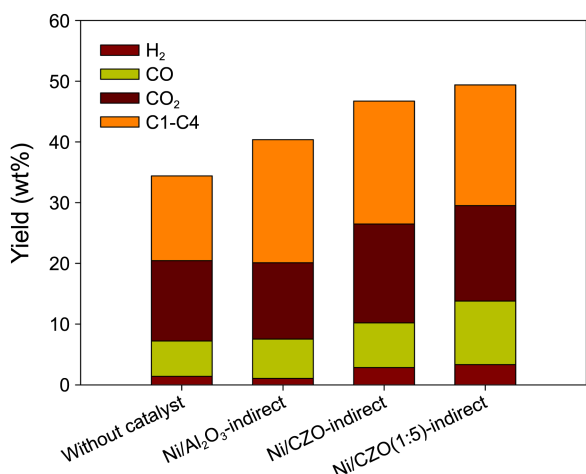
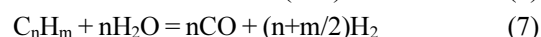
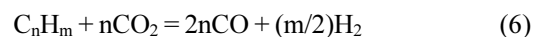
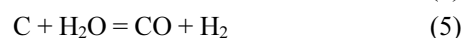
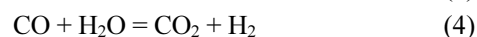
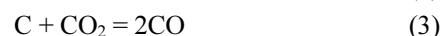


Figure 4. Yields of gas products at ER = 0.2.

two catalysts is more profound under ER = 0.2. Ni/CZO led to a higher gas yield than Ni/γ-Al₂O₃. The yields of CO, CO₂, and H₂ obtained with Ni/CZO were larger than those obtained with Ni/γ-Al₂O₃. In particular, the H₂ production by Ni/CZO (2.9 wt %) was much larger than that by Ni/γ-Al₂O₃ (1.1 wt %). This is attributed, as was shown by the TPR results, to the higher reducibility of Ni/CZO, which promotes the partial oxidation involving lattice oxygen. Reportedly,¹⁸ the following 7 reactions are expected to take place in a Ni catalyst system.



Large production of H₂ over Ni/CZO implies that the H₂-producing reactions, *i.e.*, Reactions (4)–(7), are promoted by Ni/CZO. As shown in Figure 4, doubling the catalyst dose (catalyst/waste mandarin = 1/5) increased the H₂ production (from 2.9 wt % to 3.4 wt %), which also supports that Reactions (4)–(7) are promoted by Ni/CZO.

Furthermore, Ni/CZO showed high resistance to coke deposition (4.1 wt %) than Ni/γ-Al₂O₃ (8.3 wt %) due to its lattice oxygen mobility.¹³ This implied that the catalyst stability of Ni/CZO was much higher than that of Ni/γ-Al₂O₃.

Conclusion

Two methods for catalyst-contact were compared in the catalytic gasification of mandarin waste residue. The indirect method, in which non-catalytic reaction was followed by catalytic upgrading in a separate reactor, resulted in a reduced oil yield and an increased gas yield, compared to the direct method (direct mixing of catalyst and biomass in a single reactor). The CeO₂-ZrO₂ support prepared using hydrothermal synthesis in supercritical water increased substantially the reducibility and lattice oxygen mobility of Ni, compared to γ-Al₂O₃. Under ER = 0.2, Ni/CeO₂-ZrO₂ led to a higher gas yield and, in particular, a much higher H₂ yield than Ni/γ-Al₂O₃. Ni/CeO₂-ZrO₂ also showed higher resistance to coke deposition than Ni/γ-Al₂O₃.

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