

論文 / 著書情報  
Article / Book Information

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著者(和文)	Yafei Shen
Author(English)	Yafei Shen
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## 論文要旨

THESIS SUMMARY

専攻: Environmental Science 専攻  
Department of and Engineering

学生氏名: Yafei Shen  
Student's Name

申請学位(専攻分野): 博士 (Engineering  
Academic Degree Requested Doctor of )

指導教員(主): Kunio Yoshikawa  
Academic Advisor(main)

指導教員(副): Fumitake Takahashi  
Academic Advisor(sub)

要旨(英文 800 語程度)

Thesis Summary (approx.800 English Words )

Biomass pyrolysis or gasification is considered as one of the promising technologies that can be used for power generation systems or syngas applications. During biomass gasification, the by-products including tar and char are formed. Char can be directly gasified into the additional syngas, while tar can be removed by physical and chemical methods. Many previous methods have focused on the catalytic reforming due to its fast reaction rate and reliability to increase the syngas. Among the metal catalysts, the nickel-based catalysts have been widely used for tar conversion due to its high catalytic activity and relatively low cost. Nickel-based catalysts are commonly supported by natural materials (*e.g.*, *dolomite*, *olivine*) or metal oxides (*e.g.*,  $Al_2O_3$ ,  $MgO$ ). However, these catalyst supports are generally expensive and unsustainable. Besides, the catalyst preparation steps are time and energy consuming. Therefore, these factors would limit the extensive applications of nickel-based catalysts. As an alternative, the by-product of char has been studied to be a sustainable catalyst possessing fair performance in tar removal and an excellent carbonaceous adsorbent. The char-supported catalysts with low cost could be simply gasified without the need of frequent regeneration after deactivation. Because of high content of silica and carbon, rice husk char or ash could be recycled for the fabrication of silica-based materials, carbonaceous adsorbents and catalyst supports. It should be noted that the char catalytic performance mainly depends on the pyrolysis conditions, gasifier types, tar composition and biomass sources, etc. So far, rice husk char derived from rice husk pyrolysis has never been studied as a catalyst support for tar conversion and syngas upgrading. Preliminary, an *in-situ* tar catalytic conversion has been studied for biomass gasification. By co-pyrolysis with rice husk char (RHC) or rice husk ash (RHA) supported Ni-Fe catalysts, the tar yield and the  $CO_2$  concentration were significantly decreased in biomass gasification. In particular, the condensable tar conversion efficiency could reach about 92.3% by mixing with the RHC Ni-Fe catalyst. In this study, partial metal oxides were reduced into the metallic states, thereby enhancing the catalytic reactivity. Although the bimetallic RHC/RHA supported catalysts (RHA Ni-Fe, RHC Ni-Fe) exhibited a lower tar conversion efficiency compared to the monometallic RHA Ni, the expense of the catalyst synthesis was much cheaper due to low-concentration Ni used. Moreover, omitting the calcination step, the preparation procedure of catalysts became more convenient and energy saving. Subsequently, an integrated concept of *in-situ* tar conversion has been proposed for pyrolysis of biomass, which was pretreated by nickel impregnation with sodium borohydride ( $NaBH_4$ ) modification. Significantly, it is a potential approach for *in-situ* generation of nickel nanoparticle catalysts in the carbon matrix via a facile one-step pyrolysis. The condensable tar is

transformed to the non-condensable tar or small-molecular gases by the catalytic conversion. The metallic nickel ( $\text{Ni}^0$ ) coexisted with nickel oxides is attributed to *in-situ* carbothermal reduction. Moreover,  $\text{NaBH}_4$  modification can enhance the metallic nickel ( $\text{Ni}^0$ ) generation. Compared to the catalysts preparation via the hydrogenation reduction, this approach is much convenient and energy-saving. The condensable tar derived from RH pyrolysis could be greatly removed up to 96.5% and 92.6%, by co-pyrolysis with the RHC Ni and RHC Ni-B, respectively. The synthesized RHC Ni showed high catalytic activity on tar conversion via co-pyrolysis with biomass. *In-situ* catalytic conversion can inhibit the small-molecular tars polymerization and reduce the macromolecular tar formation. Catalysts placed in contact with the feedstock inside the pyrolysis reactor (*i.e.*, *in situ*) could improve the biomass conversion, and adjust the volatilized products distribution. However, *ex situ* catalytic conversion is much feasible to be used, because the catalysts can be much easily renewed and regenerated. In addition, the syngas can be upgraded in the reformer. Metallic nickel ( $\text{Ni}^0$ ) nanoparticles are embedded in the carbon matrix via the carbothermal reduction using waste biomass as a carbon source. The RHC Ni exhibited a good performance on the tar reforming. In particular, the tar conversion efficiency could be increased with the increase of the catalyst weight and the reforming temperature. The tar reforming efficiency can reach about 50.1% by using 3 g of RHC Ni, while it was significantly increased, up to 99.8% by using 10 g of RHC Ni, maintaining a higher value of 99.3% after 5 cycles. It may be attributed to the enhancement of the catalytic reaction and residence time. Besides, if 10 g of RHC Ni employed, the tar conversion efficiency could be improved from 92.3% to 100% in the temperature range of 500-900 °C. RHC Ni showed a higher catalytic activity for the tar conversion even at lower temperatures (>500 °C). Importantly, without using the RHC Ni, more PAHs can be generated. Compared to the tertiary tars of PAHs, it is much easier to crack the nascent tars by RHC Ni. Moreover, the RHC Ni catalyst can be deactivated due to the coke deposition on the surface of the metal actives. Consequently, the waste RHC Ni could be gasified into the syngas. The presence of nickel inside the char matrix can enhance the reactivity of  $\text{CO}_2$  char gasification. After  $\text{CO}_2$  gasification at high temperatures, the metallic nickel ( $\text{Ni}^0$ ) is initially oxidized to the nickel oxide (*i.e.*,  $\text{NiO}$ ). However, the ash components are very pure, mainly composed of  $\text{NiO}$  and  $\text{SiO}_2$ . Therefore, it has a highly potential to reuse a silica-based nickel catalysts.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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