

바이오매스의 열분해에서 니켈 촉매의 성분비에 따른 수소 수율 증대
최용근, 차토팰드히야 제이타, 이준철, 김재형, 박홍선, 손재익, 박대원[†]

서울산업대학교 에너지환경대학원

Pyrolysis of biomass in the composition of Ni-based catalyst for hydrogen-rich gases

Yongkeun Choi, Jayeeta Chattopadhyay, Juncheol Lee, Jaehyung Kim, Hongsun Park,
Jaek Son, Daewon Pak[†]

Graduate School of Energy and Environment, Seoul National University of Technology

1. Introduction:

Biomass as a term is used to describe any organic matter (excluding fossil fuels), in which energy coming from sunlight is stored in chemical bonds. This chemical energy can be released by breaking the bonds using various methods like, digestion, combustion or decomposition. Biomass is an abundantly available and renewable energy resource. Conversion of biomass to synthesis gas and hydrogen can contribute to the environmental protection by reducing CO₂ emission. This is because the synthesis gas can be converted into clean liquid fuels, such as methanol, and Fischer - Tropsch oil, and hydrogen is a promising energy carrier in the future. The main advantage of biomass to other renewable resources (e.g. solar, wind) is that it can be converted to solid, liquid and gaseous fuels[1,2]. Biomass mainly consists of hemicellulose, cellulose and lignin; each one of them degrading at different rate and with different mechanisms[3]. Generally, biomass conversion processes can be divided into two categories: biological(fermentation and anaerobic digestion) and thermo chemical (combustion, gasification and pyrolysis). Pyrolysis is a thermochemical conversion process of biomass, in which biomass getting heated at moderate to high temperatures in inert atmosphere to produce gas mixtures (H₂, CO, CO₂, CH₄), liquid tar and solid carbon residue. Now-a-days, researchers are paying their concentrations in catalytic pyrolysis of biomass to enhance the product selectivity and also to increase the total energy efficiency of the process by reducing the degradation temperature of biomass. Decrease of tar content in the hydrogen demands high reaction temperature since tar can cause some problems in the utilization of the gas to the power generation and chemical conversion. The utilization of metal catalysts in tar reducing is an effective approach to the biomass thermo chemical conversion methods. Mostly, commercially available nickel catalysts have been tested in catalytic gasification and pyrolysis methods of biomass. In the present study, we attempted to enhance the hydrogen production and

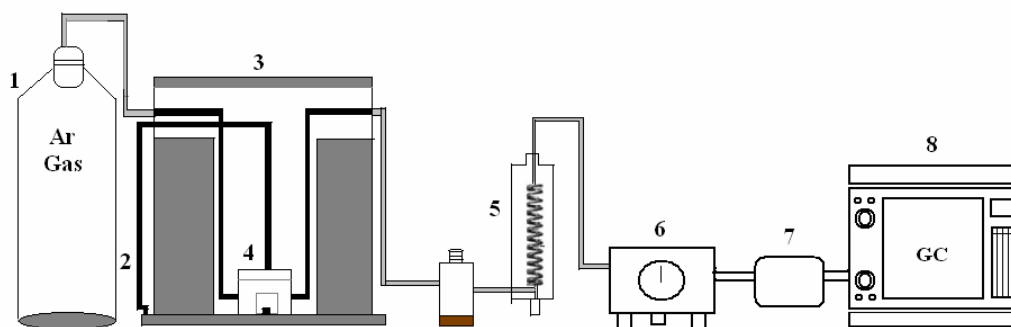
to reduce tar production in biomass pyrolysis using Ni/Al₂O₃, Ni/CeO₂ and Ni/CeO₂-Al₂O₃ catalysts having various compositions.

2. Experiment:

Catalyst Preparation: Ni/Al₂O₃, Ni/CeO₂ and Ni/CeO₂-Al₂O₃ catalysts of different compositions were prepared using co-precipitation method. Ni(NO₃)₂·3H₂O (Yakuri Pure Chemicals Co. Ltd., Osaka, Japan), Ce(NO₃)₃·6H₂O (Samchun Chemicals Co. Ltd., Korea) and Al(NO₃)₃·9H₂O (Junsei Chemical Co. Ltd., Japan) were used as precursors for nickel, ceria and alumina, respectively. The precipitates were formed using KOH (Samchun Chemicals Co. Ltd., Korea) solution. The co-precipitated mass was thoroughly washed, filtered and dried at 110°C for 12h in air followed by calcinations in furnace. In the present work, 30 and 40wt% of nickel was loaded over alumina and ceria separately. In the case of Ni/CeO₂-Al₂O₃ catalysts, 30wt% nickel was doped over the ceria - alumina support having various compositions of 40:60, 50:50 and 60:40(w/w).

Biomass Sample preparation: Papers used in the daily writing purposes was used as biomass feed stock material. The sample paper was first torn into small pieces (size less than 10mm x 10mm), followed by soaked them into water with moderate stirring for some times. The wet paper pieces were smashed properly by using mortar and piston; and kept inside an air-oven for over night at 110°C to remove extra water from the biomass.

Pyrolysis: Pyrolysis of biomass (1g) with catalysts (0.1g) was performed in a laboratory - scale fixed - bed reactor system (Fig.1). The reaction was performed in argon atmosphere with the flow rate 50ml/min from room temperature to 800°C under the heating rate of 10°C/min; then the furnace temperature was maintained at 800°C for residence time of 15min. The product gases and volatiles were collected through gas bags every after 100°C and also at 5, 10 and 15min residence time at 800°C.



- | | |
|--------------------------|----------------------|
| 1 Ar Gas Cylinder | 5 Condenser |
| 2 Thermo Couple | 6 Flowmeter |
| 3 Furnace | 7 Gas Bag |
| 4 Sample Holder | 8 GC with TCD |

Fig.1 Fixed-bed reactor system

The collected gases were analyzed by using Gas chromatograph with a thermal conductive detector (TCD). Solid residues were taken out from the reaction chamber after the pyrolysis reaction was stopped.

3. Results and discussions:

Product distributions: Pyrolysis of biomass taken place with nickel based catalysts was produced least amount of liquid tar (10 - 15wt%); whereas approx. 30wt% of solid and 55 - 60wt% of gaseous products were formed. In gas production, Ni/CeO₂ catalysts were shown best results. On the other hand, 40wt% Ni doped Al₂O₃ catalyst has produced most amount of gaseous products among the Ni/Al₂O₃ catalysts. In Ni/CeO₂-Al₂O₃ catalysts, gas production diminished in catalyst with least amount of Al₂O₃. The results are shown in Fig.2.

H₂ production: Among all the catalysts, Ni/CeO₂-Al₂O₃ (30:(50:50)) has shown the best result in hydrogen yield; whereas Ni/Al₂O₃ and Ni/CeO₂ catalysts were shown moderate activity in hydrogen production from biomass pyrolysis. At the same time, the catalytic activity was raised comparatively in the catalysts with more nickel loading (shown in Fig.3).

Residence time: All the catalysts were shown best activity in hydrogen production at 10 min of residence time at 800°C; whereas the activity diminished with residence time of 15min (presented in Fig.3).

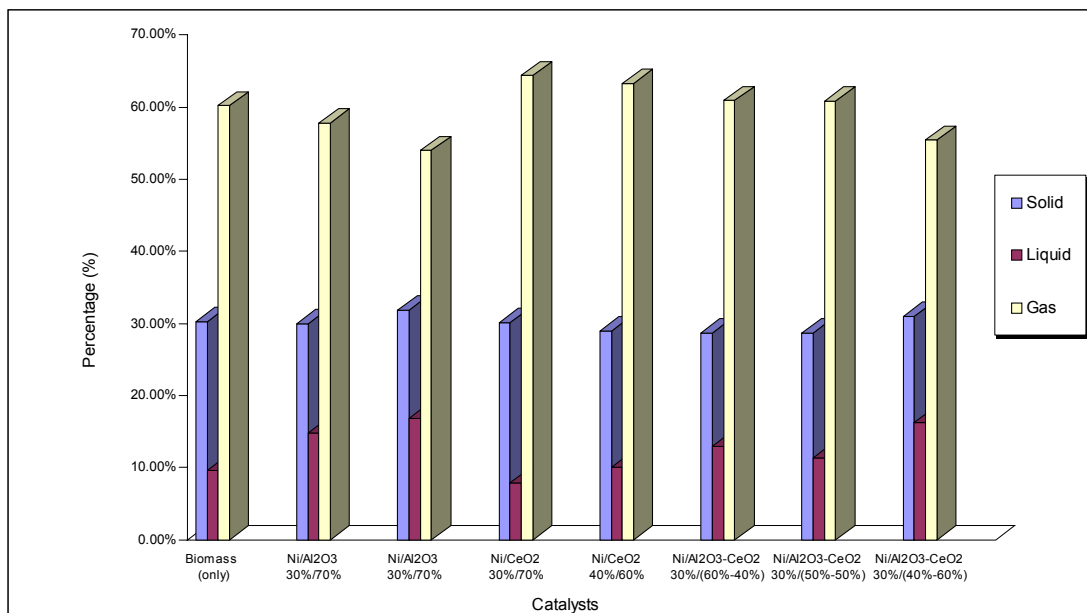


Fig.2 Distribution of solid, liquid and gas

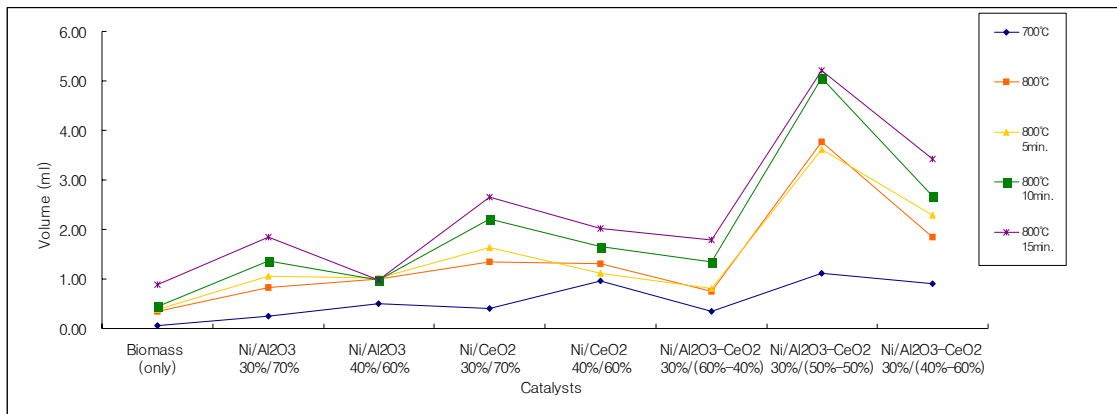


Fig.3 H₂ volume of various catalysts

4. Conclusions:

Paper used in our daily written purposes was used as biomass sample in present study. Pyrolysis of biomass was taken place in presence of Ni/Al₂O₃, Ni/CeO₂ and Ni/CeO₂-Al₂O₃ catalysts of different compositions. During catalytic pyrolysis, tar amount was reduced. At the same time, gas production was enhanced in presence of catalysts. H₂ yield was most at the residence time of 10min at 800°C.

5. Reference:

- [1] M.F. Demirbas, M. Balat, Recent advances on the production and utilization trends of bio-fuels: a global perspective, *Energy Convers. Managem.* 47 (2006) 2371 - 2381.
- [2] P. McKendry, Energy production from biomass (part 1): overview of biomass, *Bioresour. Technol.* 83 (2002) 37 - 46.
- [3] A. Demirbas, Mechanism of liquefaction and pyrolysis reactions of biomass, *Energy Convers. Managem.* 41 (2000) 633 - 646.