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바이오매스의 열분해에서 촉매를 이용한 수소 생산의 수율 증대

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Catalytic pyrolysis of biomass for production of hydrogen rich gases

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1. Introduction:

Biomass is the fourth largest source of energy in the world; 15% of the world's primary energy consumption is accounting for biomass resources and about 38% of the primary energy usage in developing countries [1]. Now-a-days, the concept of using wastes, which mostly content different kinds of biomasses, as a renewable source of energy has become a priority in the field of wastes treatment. Researchers are trying to achieve new energy resources using biochemical and thermo-chemical technologies by emerging these two concepts. Different biomass components of municipal solid wastes (MSW), like paper wastes, can be efficiently achieved as an energy resource by application of various thermo-chemical conversion technologies: pyrolysis, gasification or combustion. Pyrolysis is one of the most promising thermo-chemical conversion routes; during the process biomass is thermally decomposed to H_2-rich gases, vapors, liquid tars, and carbon-rich solid residue under an oxygen absence condition.

Biomass → Gas (H_2, CO, CO_2, CmHn) + H_2O + tar + char

The selectivity of end products and gaseous components are dependent on several parameters including temperature, biomass species, particle size, heating rate, operating pressure and reactor configuration, as well as the extraneous addition of catalysts [2]. In literature, many catalysts have been used in the biomass pyrolysis process to improve overall efficiency of the system in producing high quality fuel gases, like K_2CO_3, Na_2CO_3, Fe_2O_3, $Rh/CeO_2/SiO_2$, Ni/Al_2O_3, $Rh/CeO_2/Al_2O_3$ etc. [3 - 6]. Generally, H_2-rich gas is produce data high temperature and long residence time. Although production of hydrogen from the direct pyrolysis of biomass is quite low; gas yield, especially H_2 yield could be highly improved by catalyst addition.

In the present study, nickel doped ceria and nickel doped alumina catalysts have been prepared of various compositions and catalytic pyrolysis has been performed with paper biomass samples with the presence of these catalysts. The comparative evaluation of solid, liquid and gas has been studied. At the same time, how the amount of nickel and nature of support material has influenced the hydrogen production, has also been examined.

2. Experiment:

Catalyst preparation: Ni/Al_2O_3 and Ni/CeO_2 catalysts of different compositions we reprepared using co-precipitation method. Here, 30 and 40wt% of nickel has been loaded over alumina and ceria. $Ni(NO_3)_2$. $6H_2O$, $Al(NO_3)_3$. $9H_2O$ and $Ce(NO_3)_3$. $6H_2O$ have been used as precursors for nickel, ceria and alumina, respectively. During the synthesis of Ni/Al_2O_3 catalysts, anaqueous solution containing requisite amounts of $Cu(NO_3)_2$. $3H_2O$ and $Al(NO_3)_3$. $9H_2O$ with their concentration of 0.1Neach, have been simultaneously precipitated using anaqueous solution containing 0.25N KOH (Samchun Chemicals Co. Ltd. Korea) at a pH of 9.5 to 10. The co-precipitated mass has been thoroughly washed, filtered and dried at 110℃ for 12h in air followed by calcination in furnace at 900℃ for 3h. Ni/CeO_2 catalysts were prepared applying same method using $Ce(NO_3)_3$. $6H_2O$ instead of $Al(NO_3)_3$. $9H_2O$.

Biomass sample preparation: Paper used in our daily writing purposes was employed as the biomass sample here. First the paper was torn into small pieces, and soaked them into water for some times. Then, the wet paper pieces were smashed properly by using mortar and piston; and kept inside an air oven at 110℃ for overnight.

Pyrolysis experimental set-up: The pyrolysis system consist of a sample holder, iron reaction chamber, furnace, water condenser, liquid collector, flow meter to get the volume of product gas and tedler gas bags for gas collection. Each catalyst (0.1 g) was then mixed properly with paper biomass (1 g) by smashed them together with mortar and piston. In each experiment, 1 g of biomass has been pyrolysed in furnace under argon atmosphere with flowing rate of 80 ml/min. The samples were heated from room temperature to 800℃ under the heating rate of 10℃/min; then the furnace temperature was maintained at 800℃ for residence time of 15min. The product gases were collected through gas bag every after 100℃ and also at 5, 10 and 15 min residence time at 800℃. The collected gases have been analyzed by using Gas chromatograph with a thermal conductive detector (TCD).

3. Results and discussions:

Influence of catalysts on distribution of solid, liquid and gases: The distribution of solid, liquid and gaseous products at final temperature (800℃ after 15 min residence time) has been evaluated for Ni/Al_2O_3 and Ni/CeO_2 catalysts. <Fig. 1>

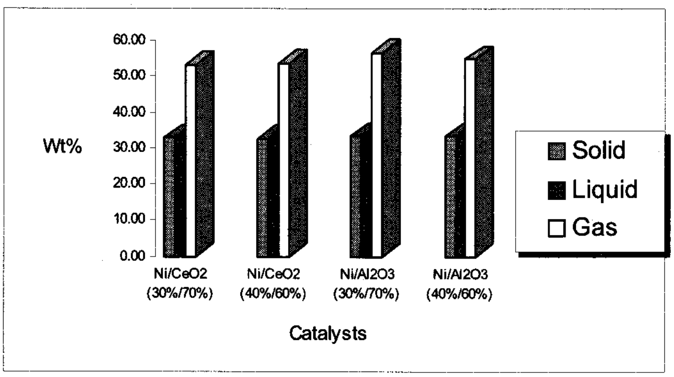

Fig. 1. The weight percentage of the distribution of solid, liquid and gaseous products

Similar product distribution trend has been noticed in all the catalysts. The average productions of solid, liquid and gaseous materials in weight percentages are 32.9, 12.3 and 54.7 for all the catalysts, respectively.

Influence of catalysts on hydrogen production: The yield of gaseous products and more specifically hydrogen has been increased with more nickel content in the catalysts. At the same time, the ceria based catalysts are more active in hydrogen production at higher ranges of temperatures. According to the GC results, 30 wt% nickel loaded ceria catalyst has shown the best results in hydrogen production at 800℃. As we know from the literature that, Ni appeared to have a stronger catalytic effect in the total gas yield and in hydrogen production [7].

Influence of residence time on hydrogen production: Biomass pyrolysis with and without presence of catalysts has shown that, residence time at 800℃ has greatly influenced the hydrogen production. In presence of all the catalysts hydrogen yield has increased considerably with rise in the residence time. 30 wt% Ni/Al_2O_3 has shown best activity at 15min. residence time at 800℃ among all the catalysts.

4. Conclusions:

Nickel based ceria and alumina catalysts have been synthesized using co-precipitation method and the catalysts have been used in pyrolysis of paper biomass species. The main products from catalytic pyrolysis of paper biomass are solid charcoal, liquid oil and hydrogen rich gas product. But the distribution of solid, liquid and gas products has not influenced differently by catalysts at higher temperature. The production of gas has reached highest value at final temperature 800℃. The results show the production of gases consisting of mainly H_2, CO, CO_2 and CH_4. The residence time at 800℃ has played an important role in hydrogen production. The residence time of 15min. 800℃has shown the best hydrogen yield for almost every catalyst; especially 30wt% nickel loaded ceria catalyst has produced highest amount of hydrogen at this condition. <Fig. 2>

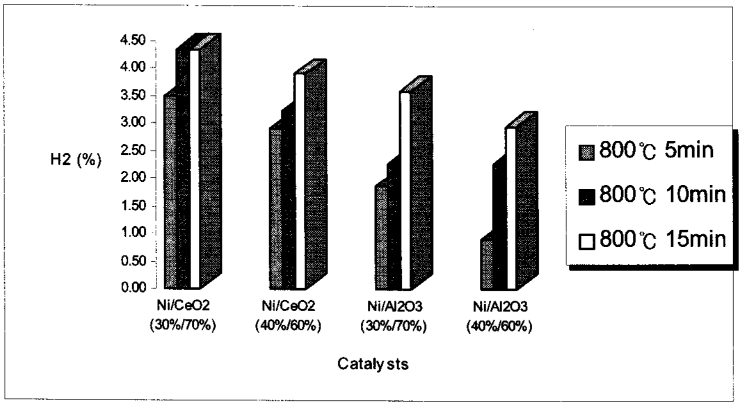

Fig. 2. The H_2 percentage of various catalysts

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