Preparation and characterizations of Ni-alumina, Ni-ceria and Ni-alumina/ceria catalysts and their performance in biomass pyrolysis

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Abstract−The catalytic activity of Ni/Al_2O_3, Ni/CeO_2, and Ni/Al_2O_3-CeO_2 catalysts of different compositions were investigated over biomass pyrolysis process. Catalysts were prepared using co-precipitation method with various compositions of nickel and support materials. Surface characterizations of the materials were evaluated using XRD, SEM, and BET surface area analysis with N_2 adsorption isotherm. XRD analysis reveals the presence of Al_2O_3, CeO_2, NiO, and $NiAl_2O_4$ phases in the catalysts. Paper samples used for daily writing purposes were chosen as biomass source in pyrolysis. TGA experiment was performed on biomass with and without presence of catalysts, which resulted in the decrease of initial degradation temperature of paper biomass with the influence of catalysts. In a fixed-bed reactor, untreated and catalyst mixed biomasses were pyrolyzed up to 800 °C, with a residence time of 15 min. The non-condensable gases were collected through gas bags every after 100 °C and also at 5, 10, and 15 min residence time at 800 °C, which were analyzed using TCD-GC equipment. Comparative distributions of solid, liquid and gaseous components were made. Results indicated diminished amount of tar production in presence of catalysts. 30 wt% Ni/CeO_2 catalyst yielded least amount of tar product. The least amount of CO was produced over the same catalyst. According to gas analysis result, 30 wt% Ni doped alumina sample produced maximum amount of H_2 production with 43.5 vol% at 800 °C (15 min residence time).

Key words: Ni-alumina, Ni-ceria, Biomass, Catalytic Pyrolysis, H_2-production

INTRODUCTION

The rapid growth of population and urbanization has resulted in the continually increasing demand for energy and its resources. World energy demand is expected to rise approximately 50% above 2002 level and will increase approximately two-and-half times the present level. Biomass is the most potential candidate as a renewable energy source in the energy market worldwide. It contributes to about 12% of the world's energy supply, while in many developing countries its contribution ranges from 40 to 50%. Biomass is used to describe any organic matter (excluding fossil fuels), in which the energy of sunlight is stored in chemical bonds. This stored chemical energy can be released using biochemical and thermochemical composition methods [1]. The main advantage of biomass over other renewable energy sources (i.e., wind, solar) is its conversion to liquid, solid and gaseous fuels besides heat and power [2-5]. Nowadays, the concept of using wastes, which mostly contain different kinds of biomasses, as a renewable source of energy has become a priority in the field of waste treatment. Researchers are trying to find and develop new energy resources using biochemical and thermochemical technologies by merging these two concepts. Various biomass components of municipal solid waste (MSW), like paper wastes, can be efficiently achieved as an energy resource using different thermochemical conversion technologies, like pyrolysis, gasification or combustion. Paper wastes mostly contain cellulosic materials, consisting of mechanical pulp and a fraction of chemical pulp [6]. Thus, hemi-

cellulose and cellulose are the principal components of the paper which we use in our daily lives.

Pyrolysis is one of the most promising thermochemical 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. The selectivity of end products and gaseous components depends on several parameters, including composition and particle size of biomass species, heating rate, final temperature and residence time at final temperature during process, operating pressure, and reactor configuration, as well as the effect of extraneous addition of catalysts [7]. The main problem is to deal with the formation of tar during the thermal processes, which makes the gas unsuitable for further applications [8,9]. Tar is actually a complex mixture of condensable hydrocarbons, including single ring to 5-ring aromatic compounds along with other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbons (PAH) [9-11]. In the non-catalytic gasification with air, which is one of the conventional syngas and hydrogen production methods from biomass, high reaction temperature can be effective to remove tar in considerable amount [9]. On the other hand, the application of appropriate and suitable metal catalysts in thermal conversion methods can be a reasonable approach in reduction of tar content [9,12,13]. Extensive studies have been reported in the literature to show that iron is very efficient in reduction of hydrocarbon yield, since neutral iron containing minerals, such as dolomite $(Ca(Mg_xFe_y)(CO_3)_2)$ [8,14,15] or olivine $((Mg_xFe_y)_2SiO_4)$ [10,16,17] are known for tar cracking and reforming. Moreover, it has also been demonstrated in many studies that iron (III) is responsible for the tar cracking reactions [18,19]. Similarly, Ni-based catalysts have also shown high

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Table 1. Analysis of biomass sample

Sample	Proximate analysis (wt% dry basis)			Ultimate analysis (wt% dry ash free)					HHV* (kJ/g)
	Ash	Volatile matter	Fixed carbon[a]	C	H	N	O[a]	S	
Paper biomass	1.45	81.25	17.3	50.2	6.7	0.2	42.8	0.1	20.46

[a]By difference
*HHV, High Heating Value

effectiveness in removing hydrocarbons and in improving product gas quality [20-23].

The objective of this study was to investigate the catalytic activity of Ni-based catalysts using alumina, ceria and alumina/ceria as supporting materials during pyrolysis of paper biomass sample at high temperatures with different residence time. The main aim was to evaluate the influence of the catalysts in diminishing tar production and H_2 production during the process. The comparative influences of the nickel, ceria and alumina were also examined in quantitative distribution of solid, liquid and gaseous products and also in hydrogen gas production as pyrolysis product gas.

EXPERIMENTAL METHODS

1. Preparation of Catalysts

Ni-Al_2O_3, Ni-CeO_2 and Ni-CeO_2/Al_2O_3 catalysts having various compositions were prepared using co-precipitation method. The Ni-Al_2O_3 catalysts were prepared as follows: an aqueous solution containing requisite amounts of $Ni(NO_3)_2 \cdot 3H_2O$ (Yakuri Pure Chemicals Co. Ltd., Osaka, Japan) and $Al(NO_3)_3 \cdot 9H_2O$ (Junsei Chemical Co. Ltd., Japan) with their concentration of 0.1 N each, were simultaneously precipitated using an aqueous solution containing 0.25 N KOH (Samchun Chemicals Co. Ltd., Korea); pH was maintained between 9.5 to 10 during the process. The co-precipitated mass was thoroughly washed, filtered and dried at 110 °C for 12 h in air followed by calcination in furnace. Ni-CeO_2 catalysts were synthesized by the same method using $Ce(NO_3)_3 \cdot 6H_2O$ (Samchun Chemicals Co. Ltd., Korea) as precursor solution of ceria instead of Al$(NO_3)_3 \cdot 9H_2O$. Similarly, preparation of nickel-ceria/alumina catalysts was followed same method by using mixed aqueous solutions of metal nitrates. In the present study, 30 and 40 wt% of nickel was loaded over alumina and ceria separately. Here, these catalysts are denoted as NA-30, NA-40, NC-30, and NC-40, respectively. In the case of Ni-CeO_2/Al_2O_3 catalysts, 30 wt% nickel was doped over the alumina-ceria support having various compositions of 40 : 60, 50 : 50 and 60 : 40 (w/w); and they are represented as NAC-346, NAC-355, and NAC-364, respectively.

2. Characterizations of Ni Catalysts

Powder X-ray diffraction (XRD) for the determination of solid phases present in the nickel catalysts was measured on a D/MAX-3C equipment of Rigaku Denki Co. Ltd. by using Cu-Kα radiation with a fixed powder source (30 KV, 15 mA) in the range of 5-90° at a scan rate of 2° min^{-1}. Nitrogen adsorption-desorption experiments at 77.35 K for the determination of surface area (BET and Langmuir method), pore volume and pore size distribution (BJH method) of the samples were exhibited using Micromeritics ASAP equipment, model 2010. The thermogravimetric investigation of biomass sample, in presence and absence of catalysts, was per-

formed with a Shimadzu TGA-50H apparatus. The initial weight of the sample was close to 10 mg in all the cases. The samples were heated from room temperature to 800 °C with a heating rate of 10 °C min^{-1} under nitrogen atmosphere (30 ml min^{-1}). The morphologies of the samples were examined by scanning electron microscope (SEM) analysis performed in a JSM-6400 of Jeol, Japan.

3. Biomass Preparation

Biomass used for daily writing purposes was used as biomass feedstock material. The sample paper was first torn into small pieces (size less than 10 mm×10 mm), followed by soaking them into water for some time. 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. The dry-based weight composition is represented in Table 1.

4. Biomass Pyrolysis

Pyrolysis of biomass was carried out in a laboratory scale fixed bed reactor system consisting of a sample holder, reaction chamber, furnace, water condenser, liquid collector, flow meter to get the volume of product gas and tedler gas bags for gas collection. During the pyrolysis, 0.1 g of each catalyst was mixed properly with 1 g of biomass sample by smashing them together and placing inside the reaction chamber. A cylindrical furnace was used to supply the heat needed in the pyrolysis reaction. The samples were heated in argon atmosphere 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 15 min. The flow rate of argon was maintained at 50 ml/min, and was controlled by a rotameter. The volume of product gas was measured by an accumulative flowmeter. The product vapors were then introduced into a condenser to collect the liquid tar products. The non-condensable gases were collected through gas bags every after 100 °C and also at 5, 10, and 15 min residence time at 800 °C. The gas out-put was calculated by the total collected gas volume measured by the accumulative flowmeter and the components and their percentages determined by GC analysis with a thermal conductivity detector (TCD). After the experiment, the furnace was turned off and the argon gas flow was still maintained until the reactor cooled down to room temperature to avoid the oxidation of char, and then these were taken out from the reaction chamber. Therefore, we measured the distributions of solid, liquid and gaseous products in weight percentage parameter. The gas yield was estimated by subtraction of liquid and solid products yields from the total.

RESULTS AND DISCUSSIONS

1. Structural Properties of Catalysts

Fig. 1 shows the XRD patterns of nickel catalysts with alumina, ceria and alumina-ceria supports with various compositions. The
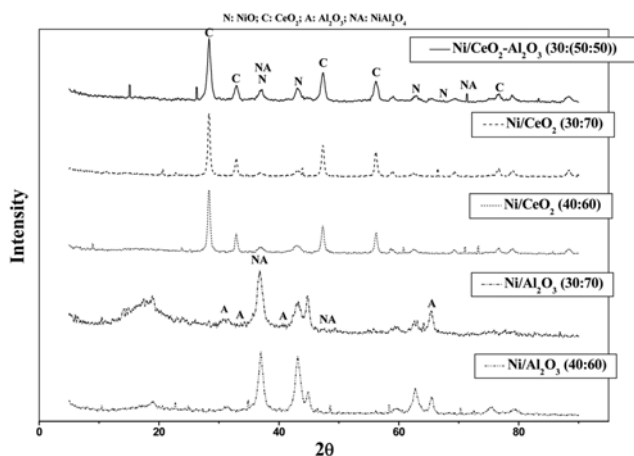
Fig. 1. XRD patterns of the Ni/Al$_2$O$_3$, Ni/CeO$_2$ and Ni/Al$_2$O$_3$-CeO$_2$ catalysts.

Fig. 2. N$_2$ adsorption isotherms of Ni/Al$_2$O$_3$, Ni/CeO$_2$ and Ni/Al$_2$O$_3$-CeO$_2$ catalysts.

results illustrate the presence of Al$_2$O$_3$, CeO$_2$, NiAl$_2$O$_4$, and NiO phases on the catalysts surface. Diffraction peaks around 27°, 33°, 47°, and 56° were found, which are ascribed to (111), (200), (220), and (311) planes of CeO$_2$ phase, respectively [24-26]; whereas the peaks for NiO were formed around 38° (111), 43° (200), and 67° (220) [27-29]. Diffraction peaks for Al$_2$O$_3$ phase were also found in the Ni/Al$_2$O$_3$ catalysts; however, they are absent in Ni/Al$_2$O$_3$-CeO$_2$ catalyst [30]. But the results show that NiAl$_2$O$_4$ structure is present in both nickel-alumina and nickel-alumina/ceria catalysts. From the patterns we can see that the peaks for NiO phase are more intense in Ni/Al$_2$O$_3$ catalysts, indicating the critical growth of that phase in the catalysts.

The nitrogen adsorption isotherms of nickel catalysts used in this study are presented in Fig. 2. The isotherms for NC-30, NC-40, and NA-30 catalysts exhibit the typical type IV, which is the characteristic of mesoporous solids [31]. A typical IV isotherm is also observed on NA-40 and NAC-346, but the adsorption volume is quite lower than that of others. The results of surface area and pore size distribution are summarized in Table 2. Among the Ni-based ceria/alumina catalysts, NAC-355 shows a specific area of 149.13 m^2 g^{-1}. But when the composition of ceria-alumina changes, the samples are showing diminished BET surface areas of 87.23 and 46.16 m^2 g^{-1} for NAC-364 and NAC-346, respectively. In Ni/Al$_2$O$_3$ catalysts, BET surface area values increased with decrease in the amount of Ni-content in the sample, whereas reverse results are exhibited for Ni/Ce$_2$ catalysts.

The SEM images of NA-30, NA-40, NC-30, NC-40, and NAC-355 catalysts are shown in Fig. 3(a)-(c), respectively. It is seen that the morphology of catalysts' surface changed with variation in their composition, although particle size was not changed in regular basis.
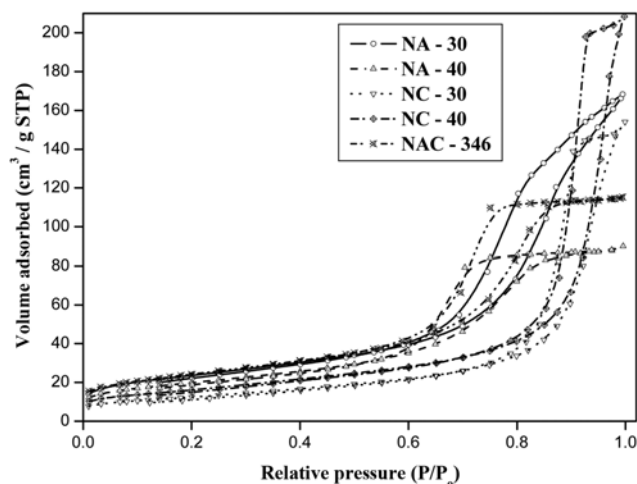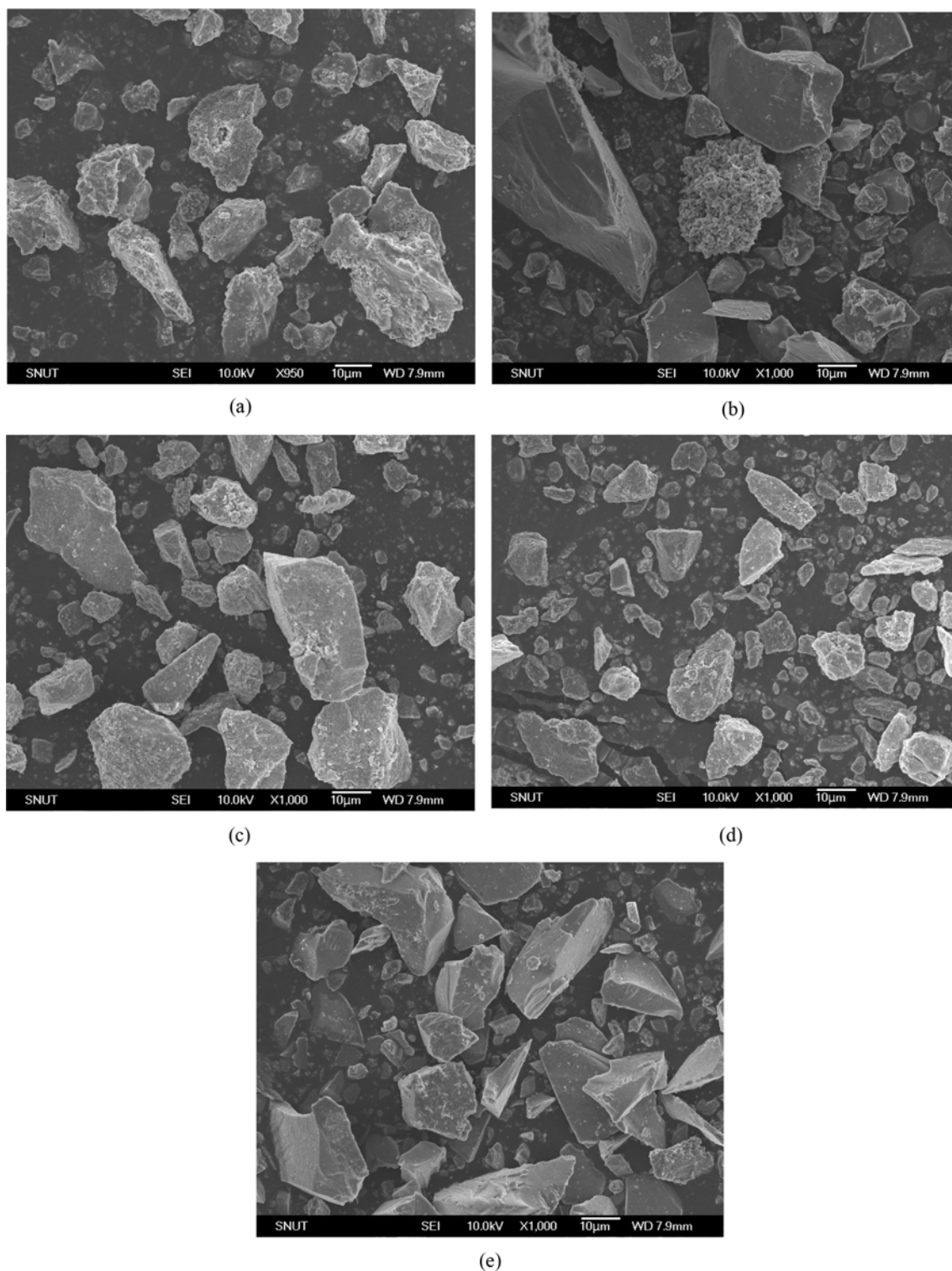
More crystal structures have been observed in the catalysts with more Ni content. At the same time, the morphological structure of NAC-355 is quite different from that of Ni-alumina and Ni-ceria catalysts, which indicates proper incorporation of each phase with others to form a new surface structure.

Thermogravimetric curves of biomass in presence and absence of catalysts are shown in Fig. 4. It is seen that biomass has started decomposing at around 270 °C without presence of catalysts; whereas the initial decomposition temperature for biomass was approximately 225 °C in presence of catalysts. Thus, it can be concluded from the results that all the catalysts influenced biomass sample to devolatilize at lower temperature. But the temperature reduction effect follows almost similar orders for all the catalysts at initial range of temperatures. It is also seen that rapid degradation of paper biomass sample (untreated with catalyst) was started from 300 °C, and it was almost finished up around 395 °C. On the other hand, the fast decomposition rate was diminished around 350 °C for the biomass samples with catalysts, but it was still degrading in medium rate till 480 °C. The trends of TG curves are almost the same for all the samples (biomass samples untreated and treated with catalysts) above 500 °C. Generally, dehydration and depolymerization reactions of cellulose are taking place during the pyrolysis process. But the dehydration reactions were expected mainly for rapid degradation of biomass samples at middle range of temperatures (300-400 °C). It is known that this water evolution process is enhanced by the presence of oxygen during biomass pyrolysis [32,33]. Thus, these catalysts might influence the rapid dehydration reaction at medium temperature range, as greater oxygen mobility was expected from these catalysts [34]. It can be concluded that the catalysts had an overall effect

Table 2. BET surface area and pore size results of catalysts

Name of the catalysts	NA-30	NA-40	NC-30	NC-40	NAC-346	NAC-355	NAC-364
BET surface area (m^2/g)	84.9405	71.7475	44.735	57.9291	46.1582	149.1304	87.2321
Langmuir surface area (m^2/g)	123.861	99.7265	62.1728	80.5226	63.9132	205.6089	120.3358
Average pore diameter (4 V/A) (A)	117.0706	75.6698	202.8645	189.7067	98.1832	64.8252	81.0316
BJH adsorption average pore diameter (4 V/A) (A)	110.1379	69.4558	176.5033	189.9921	91.8893	58.8349	74.634

(a)

(b)

(c)

(d)

(e)

Fig. 3. Scanning Electron Micrographs of (A) NA-30, (B) NA-40, (C) NC-30, (D) NC-40, (E) NAC-355 catalysts.

on biomass pyrolysis during initial and medium temperature ranges.

2. Biomass Pyrolysis

2-1. Product Distributions

Fig. 5 presents the product distributions in the form of solid, liquid and gases for the pyrolysis of biomass samples with and without presence of any catalysts. It was established from the results that

the tar yield decreases in reasonable amount with using catalysts compared to that of non-catalytic experiments. At the same time, weight percentage value of gases was enhanced during the catalytic pyrolysis of paper biomass samples in comparison to the non-catalytic experiment. The liquid tar yield was 19 wt% in the non-catalytic test, which was reduced to the least values of 7.8 and 10 wt%
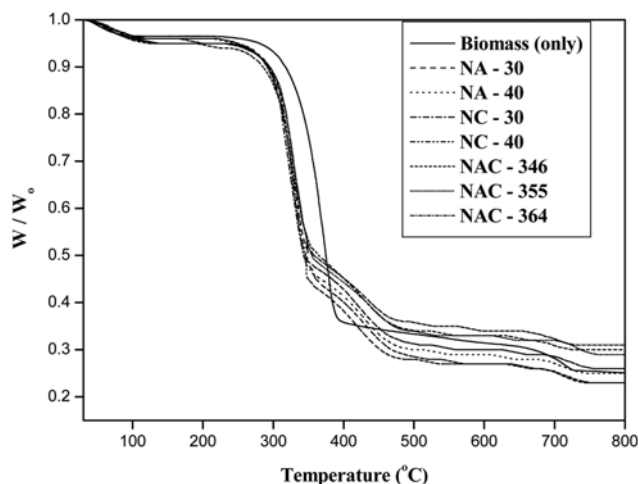
Fig. 4. TG curves of paper biomass samples with and without presence of Ni/Al₂O₃, Ni/CeO₂ and Ni/Al₂O₃-CeO₂ catalysts (heating rate 10 °C min⁻¹).
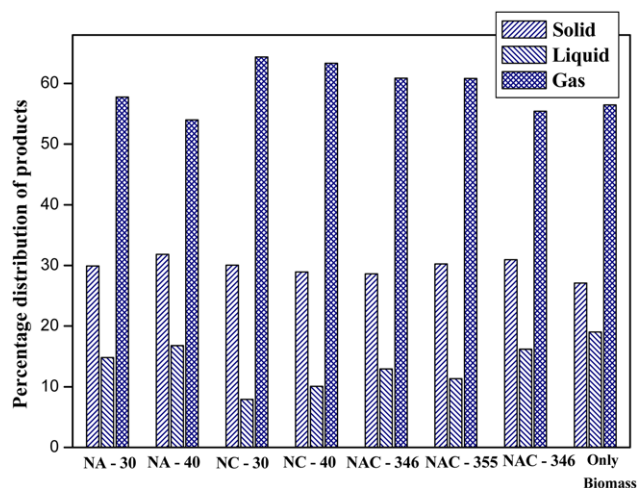

Fig. 5. Percentage distribution of solid, liquid and gaseous products at final pyrolysis temperature for biomass samples with and without presence of Ni/Al₂O₃, Ni/CeO₂ and Ni/Al₂O₃-CeO₂ catalysts.

with NC-30 and NC-40 catalysts, respectively. In presence of nickel-alumina-ceria catalysts, liquid tar amount also decreased considerably as 13.1, 11.4 and 16.1 wt% for NAC-346, NAC-355, and NAC-364 catalysts, respectively. From looking at the gas yield, the value of 56.4 wt% for the non-catalytic tests, reached 64.3 wt% with the presence of NC-30.

2-2. Gas Analysis

Figs. 6(a) to (g) show the catalytic performance in yield of important gaseous components from biomass pyrolysis process over Ni/Al₂O₃, Ni/CeO₂, and Ni/Al₂O₃-CeO₂ catalysts of various compositions. The formation of H_2, CO, CO_2, and CH_4 was observed and detected at 700 and 800 °C with 5, 10, and 15 min. of residence time at 800 °C. The experiments performed over NA catalysts have shown that CO_2 yield gradually decreased with rise in the reactor temperature to 800 °C with up to 5 min. of residence time. But CO_2 production increased suddenly for 10 min residence time at 800 °C, and

again it leveled off to some extent at residence time of 15 min. On the other hand, H_2 and CO followed complete inverse trend of production to that of CO_2 in pyrolysis process. But lesser amount of CO was found with NA-40 catalyst at 15 min residence time. In presence of NC catalysts, CO_2 production took a decreasing trend with higher temperature and also with longer residence time; and at the same time CO and H_2 showed opposite results. All the NAC catalysts exhibited a similar trend in CO_2 production as that with NC catalysts. But H_2 and CO did not completely follow an inverse pathway in their productions during the pyrolysis reaction. In the comparative activity of all the catalysts in CO gas reduction, NC-30 showed the best result (around 20 vol%) at 800 °C with 15 min of residence time. CH_4 was found in negligible amount in presence of all the catalysts.

2-3. Hydrogen Yield

In Fig. 7 comparative H_2 yield from biomass pyrolysis using Ni catalysts is presented. Two different kinds of trend were seen in hydrogen production with various catalysts. In the results, NA-30, NA-40, NAC-346, and NAC-355 catalysts produced the highest amount of H_2 at 800 °C with 10 min residence time, and then the production trend followed the inverse direction at 15 min residence time. The rest of the catalysts showed a gradual increase in the H_2 production with rise in the reaction temperature and residence time; thus, at 15 min of residence time the hydrogen yield touched the highest level. In comparison between alumina catalysts, NA-30 presented better performance in H_2 formation at every step of temperature with every residence time than that with NA-40 sample. In the comparative study between NC catalysts both the samples showed similar activity throughout the pyrolysis reaction. Although, they did not show good catalytic activity in H_2 yield; lower surface area values may be the reason behind it. Among alumina-ceria catalysts, the performance in H_2 yield had the following trend: NAC-355>NAC-346>NAC-364; which indicates the better catalytic performance with balanced composition of alumina and ceria in the sample. At the same time, NAC-355 had the highest surface area value, which makes this catalyst better in H_2 production. According to comparative performance studies of all the catalysts, NA-30 exhibited much better results in comparison to those of others, and formed the highest amount of H_2 with 43.5 vol% at 800 °C (10 min residence time).

CONCLUSIONS

Ni-doped alumina, ceria and alumina-ceria catalysts with various compositions have been synthesized using co-precipitation method and their comparative performances were evaluated in biomass pyrolysis. In the catalysts, distinct presence of NiO, CeO_2, Al_2O_3 and $NiAl_2O_4$ was seen from XRD results; whereas N_2 adsorption studies confirmed the formation of mesoporous structures in samples. In the pyrolysis process, paper used for daily writing purposes were chosen as biomass sample. Thermogravimetric analysis results of biomass with and without presence of catalysts showed that, initial degradation temperature has shifted to lower temperature in the presence of catalysts. The presence of catalysts during pyrolysis diminished tar production to a great extent. Least amount of tar was collected with NC-30, and thus gas production also reached the highest level with the same sample. According to gas analysis results, NC-30 showed the best result in CO reduction (20 vol%) at 800 °C with
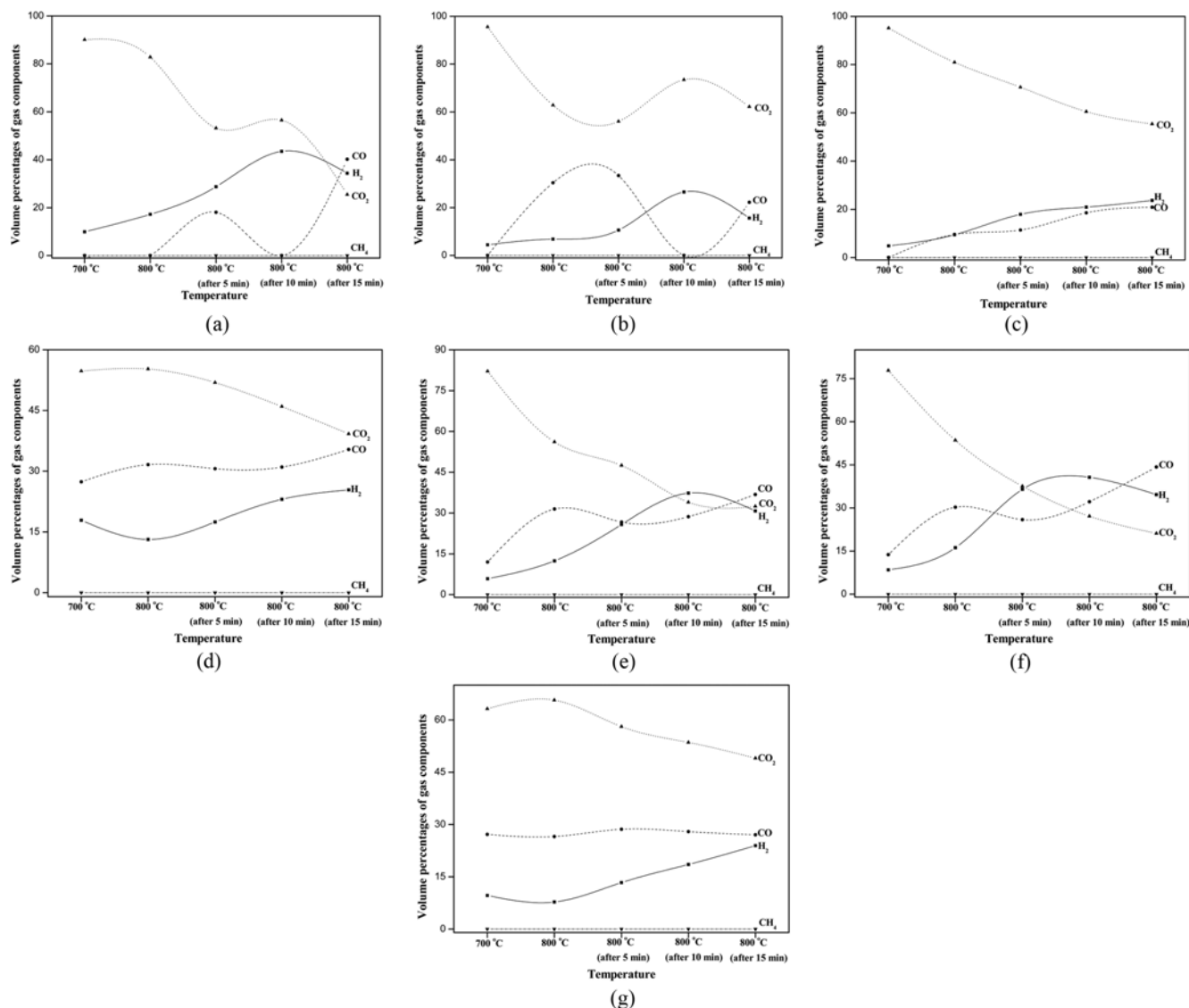
Fig. 6. Volume percentage of H₂, CO, CO₂ and CH₄ in collected product gases from biomass pyrolysis reactor using (a) NA-30, (b) NA-40, (c) NC-30, (d) NC-40, (e) NAC-346, (f) NAC-355, (g) NAC-364 catalysts.
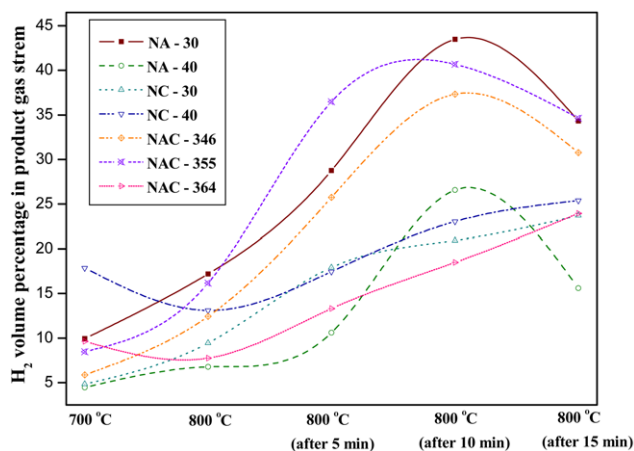

Fig. 7. Comparison of H₂ yield from biomass samples using Ni/ Al₂O₃, Ni/CeO₂ and Ni/Al₂O₃-CeO₂ catalysts of various compositions.

15 min residence time. On the other hand, NA-30 reached highest level in H₂ yield (43.5 vol%) at 800 ℃ with 15 min residence time. Among alumina-ceria samples, NAC-355 exhibited the best overall performance.

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