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Nickel-Catalysed Pyrolysis/Gasification of Biomass Components

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Abstract: Hydrogen and syngas production have been investigated from the pyrolysis /gasification of biomass components (cellulose, xylan and lignin) in the presence of Ni-based catalysts by using a two-stage fixed-bed reaction system. Biomass samples were pyrolysed at the first stage and the derived products were gasified at the second stage. The Ni-Mg-Al and Ni-Ca-Al catalysts, prepared by co-precipitation, were applied in the gasification process. The lignin sample pyrolysed with more difficulty (56.0 wt.% of residue fraction) compared with cellulose and xylan at 500 °C, and therefore resulted in the lowest gas yield (42.7 wt.%) for the pyrolysis/gasification of lignin. However, the highest H_2 concentration from the three types of feedstock (55.1 vol.%) was collected for the lignin sample in the presence of steam and catalyst. Carbon deposition was barely observed from the TPO and SEM analysis of the reacted Ni-Mg-Al catalyst. The investigation of reaction conditions showed that water injection rate (0.02 and 0.05 g min^{-1}) had little influence on the gas production from the pyrolysis/gasification of lignin in the presence of the Ni-Ca-Al catalyst; however, the increase of gasification temperature from 700 to 900 ˚C resulted in a higher gas and hydrogen production due to the promotion of secondary reactions during the gasification process. Furthermore, coking was highest for the reacted Ni-Ca-Al catalyst at the gasification temperature of 800 °C (7.27 wt.%), when the temperature was increased from 700 to 900 °C. This work shows that the components of biomass have a significant influence on the catalytic gasification process related to hydrogen and syngas production.

Key words: Biomass; Cellulose; xylan; Lignin; Gasification; Hydrogen

1. Introduction

Hydrogen has been considered as an important clean energy for the future, since its combustion only generates water and it can be produced from renewable resources such as biomass. Biomass is a carbon-neutral material, which has drawn extensive attention to reduce the effect of greenhouse gases on climate change, and to reduce the dependence on the use of fossil fuels.

Thermal processing via pyrolysis/gasification has been shown to be an effective method to convert biomass into hydrogen [1,2]. The process of biomass gasification has been reported to be largely influenced by its main components: cellulose, hemicellulose and lignin [3-5]. Although there are several studies researching the influence of the biomass components on the process of pyrolysis, there are few studies investigating the steam catalytic gasification of different biomass components for hydrogen production.

Additionally, catalysts play an important role in the promotion of hydrogen production from biomass gasification. Introducing catalysts has been reported to increase hydrogen production and tar reduction during biomass gasification [6,7]. Ni-based catalysts have shown catalytic activity related to hydrogen production during biomass gasification process [8-10]; in addition, Ni-based catalysts are cost effective.

Co-precipitated Ni catalysts have been reported to perform better compared with catalyst prepared by impregnation, in relation to hydrogen production and prevention of coke formation during the gasification process [11]. In this work, co-precipitated catalysts, Ni-Mg-Al and Ni-Ca-Al, were investigated for the biomass component gasification experiments; this is because Mg has been reported to increase hydrogen production from gasification of plastics and biomass [11,12] and Ca has been reported to improve the stability of nickel phases during the reforming of hydrocarbons [13]. The purpose was to investigate the influence of the biomass main components on hydrogen production. In addition, the reaction conditions such as gasification temperature and water injection rate were also studied to determine their influence on the gasification process.

2. Experimental

2.1. Materials

Cellulose purchased from Research Chemicals Ltd., xylan produced from beech wood as a representative hemicellulose and lignin purchased from Sigma-Aldrich were used as received. The element analysis (CE Instruments CHNS-O analyser) of cellulose and xylan showed that C, H, O and S content was about 41, 5.5, 52 and 0.01 wt.%; N content was 0.41 wt.% for cellulose and 2.7 wt.% for xylan. Different element analysis results were obtained for lignin, which had C, H, O, N and S content of about 61.3, 5.2, 31.7, 1.1 and 0.7 wt.%, respectively. The thermogravimetric analysis of the biomass component showed that cellulose and lignin had the highest and lowest volatiles respectively, with 93.4 wt.% and 60.4 wt.% . From TGA mass loss at around 100 ℃, it was deduced that the moisture for the biomass sample was around 5 wt.%. Fixed carbon fractions for cellulose, xylan and lignin were 1.9, 12.8 and 32.6 wt.%, respectively. Cellulose had the lowest ash content (0.07 wt.%) and the ash content for xylan and lignin was around 3.6 wt.%.

The Ni-Ca-Al catalysts were prepared by a co-precipitation method with an initial Ni-loading mole ratio of 20 mol.% from $Ni(NO_3)_3 \cdot 6H_2O$ (≥97.0%), $Ca(NO_3)_2 \cdot 4H_2O$ (≥99%), $Al(NO_3)_3 \cdot 9H_2O$ (≥99%), and $NH_4(OH)$ (≥98%) (Sigma–Aldrich). Precursors with the desired Ca/Al molar ratio (1:1) were prepared by dissolving the required amount of the metal salts in deionized water. The precursor mixture was precipitated with the basic solution of $NH_4(OH)$ drop by drop in order to adjust the pH of the suspension between 6 and 9. After precipitation, the suspension was aged under agitation for an hour and then filtered under vacuum. The filter cake obtained was rinsed with deionized water for several times and followed by drying at 80 °C overnight. Finally, the solids were calcined at 800 °C for 4h with a heating rate of 1 °C min^{-1} in static air.

The Ni-Mg-Al catalyst was also prepared by a co-precipitation method. $Ni(NO_3)•6H_2O$, $Al(NO_3)_3•9H_2O$ and $Mg(NO_3)_2•6H_2O$ were dissolved into de-ionized water and $NH_4(OH)$ solution (Ni/Mg/Al molar ratio of 1:1:1) was added to the nitrate solution until the pH reached 8.3. The precipitates were filtered with water, followed by drying at 105 °C overnight, and then were calcined in an air atmosphere at 750 °C for 3h.

2.2. Experimental system

The schematic diagram of the experimental system has been reported in our previous work [14]. N_2 gas with a flow rate of 80 ml min^{-1} was used as carrier gas for each experiment. Around 0.5 g biomass sample was placed in a first stage reactor, where pyrolysis occurred at a temperature of 500 °C. The derived gaseous products were further gasified in the presence of steam and catalyst at the required gasification temperature. The produced gaseous products were cooled using condensers (air and dry ice) to collect the condensable liquid products. The non-condensed gases were collected by a Tedlar™ gas bag, and further analyzed by gas chromatography (GC). Gases were continued to be sampled for a further 20 min into the gas sample bag to ensure complete collection of the gases. Experiments were repeated insure the reliability of the results.

2.3. Characterization of gases, oil and catalysts

Non-condensed gases (H_2, CO and N_2) were analysed with Varian 3380 gas chromatograph on a 60-80 mesh molecular sieve column with argon carrier gas, whilst CO_2 was analysed by a second Varian 3380 GC on a Hysep 80-100 mesh column with argon carrier gas. Hydrocarbon gases (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10}) were analysed using a further Varian 3380 gas chromatograph with a flame ionisation detector, with a 80-100 mesh Hysep column and nitrogen carrier gas.

A higher resolution scanning electron microscope (SEM) (LEO 1530) was used to obtain the surface morphology of the reacted catalyst.

The temperature-programmed oxidation (TPO) of the reacted catalysts was carried out to obtain the degree of coke deposition, by using a Stanton-Redcroft thermogravimetric analyser (TGA and DTG). About 20 mg of the reacted catalyst was heated in an atmosphere of air at 15 °C min^{-1} to a final temperature of 800 °C, with a dwell time of 10 minutes.

3. Results and discussion

3.1. Pyrolysis/gasification of cellulose, xylan and lignin with Ni-Mg-Al

The three main components of biomass were investigated for hydrogen production through two stage pyrolysis/gasification in the presence of the Ni-Mg-Al catalyst. During each experiment, water was injected to the gasification stage with a flow rate of 0.05 g min^{-1}, while the weight of catalyst and gasification temperature was 0.25 g and 800 °C, respectively.

Table 1 shows that, gas yield (mass of gas products divided by the mass of the biomass sample) was 73.0 wt.% for the cellulose, 55.0 wt.% for the xylan, and 42.7 wt.% for the lignin. The residue fraction after biomass pyrolysis in the first reactor (weight of residue divided by the weight of biomass) was 18.0, 28.0 and 56.0 wt.% for the cellulose, xylan and lignin, respectively. It seems that lignin is the most difficult sample to decompose and the cellulose is readily pyrolyzed to mainly gas. Similar results have been reported by other researchers [4,15]. For example, Wang et al [18] reported that the highest yield of char residue was found for lignin (40.33 wt.%) and lowest for cellulose (6.44 wt.%), when the three biomass components were pyrolyzed at a temperature of around 540 °C [15].

Hydrogen production is also presented in Table 1, and showed that the highest hydrogen production was obtained for the pyrolysis/gasification of cellulose (22.6 mmol g^{-1} of biomass sample) whereas the pyrolysis/gasification of lignin generated the lowest hydrogen yield (14.0 mmol g^{-1} biomass). In addition, the gas and hydrogen production derived from the pyrolysis/gasification of biomass components in the presence of the Ni-Mg-Al catalyst was higher than the experiments conducted without catalyst as shown in our previous work, where we reported that non-catalysed hydrogen yield for cellulose was 5.8 mmol g^{-1} biomass, 4.6 mmol g^{-1} biomass for xylan and 1.8 mmol g^{-1} biomass for lignin [14].

Gas concentrations from the pyrolysis/gasification of cellulose, xylan and lignin are also shown in Table 1. Highest concentrations of hydrocarbons were obtained for the catalytic steam pyrolysis/gasification of lignin. Concentrations of H_2 were higher than 50 vol.% (N_2 free), which is much higher compared with the hydrogen concentration from non-catalytic experiments reported previously [14]. The influence of the biomass components showed that lignin produced the highest H_2 concentration (55.1 vol.%), while the H_2 concentration for the cellulose and xylan was 54.7 and 52.9 vol.%, respectively. This observation is consistent with our previous work [14], where the lignin sample produced the lowest concentration of hydrogen compared to cellulose and xylan for uncatalysed experiments, but the highest for catalysed gasification using a Ni-Zn-Al (1:1) catalyst. The lowest gas yield from the catalytic pyrolysis/gasification of lignin was related to the lignin producing the highest residue fraction, compared with cellulose and xylan. Here, the hydrogen concentration was found to be less influenced by the gas yield since the highest H_2 concentration was obtained for the lignin sample which produced the lowest gas yield. It is suggested that lignin pyrolysis generates chemical compounds which are more desirable for hydrogen production, compared with the cellulose and xylan.

3.2. Pyrolysis/gasification of lignin with Ni-Ca-Al at various conditions

Pyrolysis/gasification of lignin was carried out using the Ni-Ca-Al catalyst (0.5 g) at various reaction conditions such as gasification temperature (700, 800 and 900 °C) and water injection rate (0.02 and 0.05 g min^{-1}). The yields of products and hydrogen production are shown in Table 2.

As shown in Table 2, the increase of the water injection rate from 0.02 to 0.05 g min^{-1} resulted in negligible influence on the gas yield and hydrogen production. Since, the gas yield was 48.4 and 48.8 wt.%. The hydrogen production was 13.2 and 12.9 (mmol g^{-1} biomass) for the water injection rate of 0.02 and 0.05 g min^{-1}, respectively, when the gasification temperature was kept at 800 °C. The maximum hydrogen yield from lignin steam gasification is around 66.8 (mmol g^{-1} biomass) if all the carbon in the lignin was converted into CO_2 and all the hydrogen in the lignin and required water was converted into H_2. Therefore, around

20 % of potential hydrogen production (produced hydrogen divide by maximum hydrogen production) was obtained. The low potential hydrogen production for the cellulose gasification mainly due to the presence of 50 wt.% of sample residue after pyrolysis at the first stage. If only carbon sources entering into second gasification stage was considered for maximum hydrogen production, the potential hydrogen production could be more than 40 %. It is suggested that the water injection of 0.02 g min^{-1} is close to the steam saturation point during the catalytic pyrolysis/gasification of lignin in this work. The existence of a saturation point of steam during the catalytic gasification process has been reported [16,17].

The gasification temperature showed significant influence on the gas yield and hydrogen production, when the pyrolysis/gasification of lignin was conducted with the water injection rate of 0.02 g min^{-1}. For example, the gas yield was increased from 42.8 to 55.1 wt.% and the hydrogen production was increased from 10.5 to 17.8 (mmol g^{-1}), when the gasification temperature was increased from 700 to 900 °C (Table 2). The increase of reaction temperature resulting in an increase in the gas yield has been reported previously [18-20]. It is suggested that more hydrocarbon compounds were cracked into non-condensed gases through secondary reactions, and therefore, generates a higher gas yield, when the gasification temperature was increased. In addition, more hydrogen was produced through the steam reforming of hydrocarbons.

The gas concentrations produced are also presented in Table 2. The increase of the water injection rate also showed little influence on the gas concentrations. With the increase of gasification temperature from 700 to 900 °C at the water injection rate of 0.02 g min^{-1} for the pyrolysis/gasification of lignin in the presence of the Ni-Ca-Al catalyst; the H_2 concentration increased from 48.0 to 54.6 vol.%; the CO concentration increased from 11.1 to 14.6 vol.%; CO_2 concentration decreased from 32.6 to 24.1 vol.%; CH_4 concentration decreased from 9.6 to 6.4 vol.%; and the concentration of C_2-C_4 hydrocabron gases reduced from 1.1 to 0.3

vol.% . A similar change of gas concentration has also been reported by Yan et al. [19] For biomass gasification in relation to increasing gasification temperatures. For example, they reported that H_2 and CO concentrations were increased and CO_2, CH_4 and C_2H_4 gases were reduced when the gasification temperature was increased from 600 to 850 °C for the steam gasification of biomass char in a fixed bed reactor [19]. It seems that the water gas shift reaction was inhibited with the increase of gasification temperature in the presence of the Ni-Ca-Al catalyst used in this work, since the CO concentration was increased and the CO_2 concentration was decreased. This is due to the endothermic properties of the water gas shift reaction. However, H_2 concentration is suggested to be reduced by the prohibition of the water gas shift reaction, but the H_2 concentration was found to be increased with the increase of gasification temperature. We suggest that the production of hydrogen was dominated by the reactions of steam reforming of hydrocarbons since the hydrocarbon gases have been found to be reduced in concentration (Table 2).

3.3. TPO analysis of the reacted catalysts

3.3.1 TPO analysis of the reacted Ni-Ca-Al catalysts

The amount of coke deposition on the surface of the reacted catalyst is important to evaluate the catalytic stability of the catalyst during the catalytic gasification process. Therefore, the reacted Ni-Mg-Al and Ni-Ca-Al catalysts were analyzed by the TPO method. As shown in Figure 1, a certain degree of weight loss for the reacted Ni-Ca-Al catalysts was observed from the TGA-TPO results.

The TPO-DTG results from Figure 1 show that there are two oxidation peaks for the reacted Ni-Ca-Al catalysts. It is suggested that two types of carbons were deposited on the surface of the reacted catalyst after the catalytic pyrolysis/gasification of lignin. The first oxidation occurred at around a temperature of 410 °C and is suggested to be due to the oxidation of amorphous carbons, which are reported to be oxidised at lower temperature (around 450 °C) [11]. The second oxidation peak occurred at a temperature of around 640 °C and has been ascribed to the oxidation of filamentous carbons [11,21]. As shown in Figure 1, the reacted Ni-Ca-Al catalysts derived from the various reaction conditions all showed the presence of amorphous and filamentous carbons. However, it is interesting to find that the temperature of the oxidation peak for the filamentous carbons was moved to lower temperature, when the gasification temperature in the pyrolysis/gasification reactor system was increased from 700 to 900 °C. It is indicated that the deposited carbons are more active for regeneration/oxidation, when the catalyst was used at higher gasification temperature.

The amount of coke deposition for the reacted Ni-Ca-Al catalyst was 5.7 wt.% for the experiments carried out at a water injection rate of 0.05 g min^{-1} and gasification temperature of 800 °C (Figure 1b). Additionally, the coke deposition for the reacted Ni-Ca-Al catalyst at gasification of 700, 800 and 900 °C was 5.85 wt.% (Figure 2d), 7.27 wt.% (Figure 2c) and 3.71 wt.% (Figure 1a), respectively, when the water injection rate was reduced to 0.02 g min^{-1}.

The amount of coke deposition was calculated as the weight loss percentage from TPO experiments. The results indicate that the coke deposition was reduced from 7.27 to 5.7 wt.% with the increase of the water injection rate from 0.02 to 0.05 g min^{-1}, when the gasification was carried out on the Ni-Ca-Al catalyst at 800 °C. It is suggested that the reaction rate of carbon with steam was accelerated with the increase of water injection rate during the gasification process. The reduction of coke deposition on the surface of a catalyst has been reported when more water was injected into the gasification of plastics [22].

For the investigation of gasification temperature, carbon deposition was found to be increased when the gasification temperature was increased from 700 to 800 °C; however, the amount of coke was reduced with a further increase of the gasification temperature to 900 °C in the presence of the Ni-Ca-Al catalyst. Carbon conversion to gases (CO, CO_2, C_1-C_4 hydrocarbon gases) was increased from 24.9 to 32.0 % when the gasification temperature was increased from 700 to 900 °C for the lignin steam gasification. It is suggested that the coke formation rate was higher than the coke gasification rate although more carbons were converted into gases, when the gasification temperature was at 800 °C compared with 700 °C.

3.3.2. TPO analysis of the reacted Ni-Mg-Al catalysts

TGA-TPO results of the reacted Ni-Mg-Al catalysts from the pyrolysis/gasification of cellulose, xylan and lignin are shown in Figure 2. The results show that there is a large increase of catalyst mass during the TPO experiment. It is suggested that a large amount of Ni particles are present in the reacted Ni-Mg-Al catalysts; this is due to that the NiO particles in the fresh Ni-Mg-Al catalyst being reduced by reducing agents such as CO and H_2 during the gasification process. The weight increase of the reacted catalyst during the TPO analysis has also been reported in our previous reports [2,11].

In addition, except for the weight loss of moisture in the reacted sample, it is difficult to observe any weight losses from the reacted Ni-Mg-Al catalysts resulting from the oxidation of coke. Therefore, the Ni-Mg-Al catalyst is efficient in relation to the inhibition of carbon deposition for the steam catalytic pyrolysis/gasification of the biomass components.

3.4. SEM analysis of the reacted catalysts

The reacted Ni-Mg-Al and Ni-Ca-Al catalysts used in the pyrolysis/gasification of lignin, were analyzed by SEM. Two typical SEM micrographs for the reacted Ni-Mg-Al and Ni-Ca-Al catalysts are shown in Figure 3. From the SEM analysis, filamentous carbons could not be observed for the reacted Ni-Mg-Al catalyst; this is consistent with the TPO analysis of the reacted Ni-Mg-Al catalyst (Figure 2) where no oxidation of filamentous carbons was observed. However, the filamentous carbons were found for the reacted Ni-Ca-Al catalyst from the pyrolysis/gasification of lignin. The observation of filamentous carbon from the SEM analysis further confirms that the oxidation peak which occurred at a temperature of around 610 °C in the TPO analysis (Figure 2) could be ascribed to filamentous carbons.

4. Conclusions

In this work, the main biomass components (cellulose, xylan and lignin) were investigated in relation to hydrogen production from catalytic steam pyrolysis/gasification using a two-stage reaction system. The main conclusions are:

(1) Cellulose produces the lowest residue fraction, while the lignin pyrolysis generated the highest residue fraction. In addition, the highest gas yield (73.0 wt.%) was obtained for the pyrolysis/gasification of cellulose and the lowest gas yield (42.7 wt.%) was produced for the pyrolysis/gasification of lignin in the presence of the Ni-Mg-Al catalyst, when water was injected with a flow rate of 0.05 g min^{-1} and gasification temperature of 800 °C. H_2 concentration obtained for the catalytic steam pyrolysis/gasification of the biomass components was between 53 and 55 Vol.%. However, lignin was found to produce the highest concentrations of hydrocarbon gases (CH_4 and C_2-C_4).

(2) The change of water injection rate from 0.02 to 0.05 g min^{-1} showed a negligible influence on gas and hydrogen production from the catalytic pyrolysis/gasification of lignin with the Ni-Ca-Al catalyst; however, a reduction of the amount of coke deposition was obtained with the increase of the water injection rate.

(3) The increase of gasification temperature (from 700 to 900 °C) was found to increase the production of gas and hydrogen during the biomass pyrolysis/gasification process. However, gasification temperature of 800 °C was not suggested to be used in this work, as highest coke deposition was obtained compared with 700 and 900 °C gasification temperature (4) Ni-Mg-Al catalyst is recommended to be used for the hydrogen production from steam pyrolysis/gasification of biomass, due to its negligible coke deposition. Cellulose, xylan and lignin showed lower coke deposition as observed from the TPO and SEM analysis of the reacted Ni-Mg-Al catalyst.

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Table 1. Experimental results with the Ni-Mg-Al catalyst

Sample	Cellulose	Xylan*	Lignin
Catalyst	Ni-Mg-Al	Ni-Mg-Al	Ni-Mg-Al
Catalyst weight (g)	0.25	0.25	0.25
Water injection (g ml^{-1})	0.05	0.05	0.05
Gasification temperature (°C)	800	800	800
Gas yield (wt.%)	73.0	55.0	42.7
Residue (wt.%)	18.0	28.0	56.0
Hydrogen production (mmol g^{-1} biomass)	22.6	15.2	14.0
Gas concentrations (vol.%)			
CO	19.8	13.2	16.2
H_2	54.7	52.9	55.1
CO_2	24.8	31.6	23.3
CH_4	0.5	1.8	4.9
C_2-C_4	0.2	0.5	0.6

* as a representative hemicellulose

Table 2. Experimental results with the Ni-Ca-Al catalyst

Sample	Lignin	Lignin	Lignin	Lignin
Catalyst	Ni-Ca-Al	Ni-Ca-Al	Ni-Ca-Al	Ni-Ca-Al
Catalyst weight (g)	0.5	0.5	0.5	0.5
Water injection (g ml^{-1})	0.02	0.05	0.02	0.02
Gasification temperature (°C)	700	800	800	900
Gas yield (wt.%)	42.8	48.4	48.8	55.1
Residue (wt.%)	50.0	46.0	46.0	48.0
Hydrogen production (mmol g^{-1})	10.5	13.2	12.9	17.8
Gas concentrations (vol.%)				
CO	8.6	9.0	11.1	14.6
H_2	48.0	50.9	49.4	54.6
CO_2	32.6	30.4	29.4	24.1
CH_4	9.6	8.8	9.1	6.4
C_2-C_4	1.1	1.0	0.9	0.3

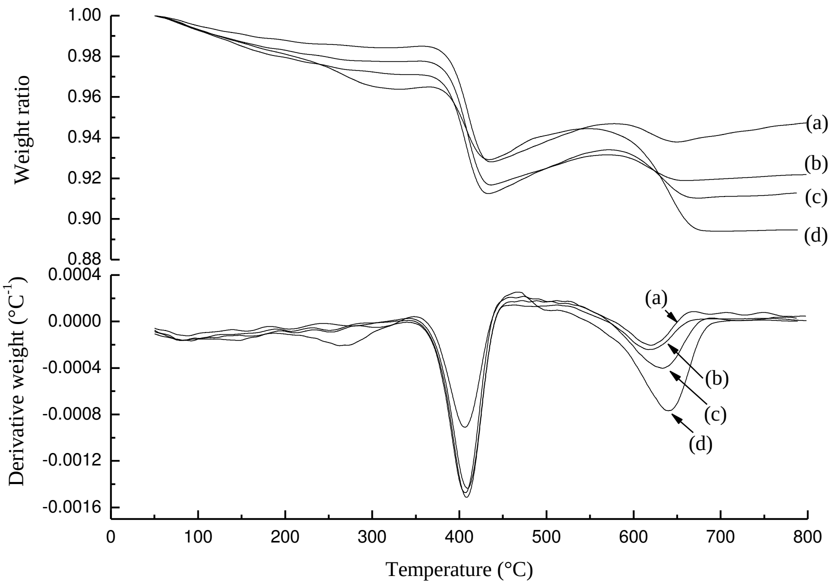


Figure 1. TGA-TPO and DTG-TPO thermograms of the reacted Ni-Ca-Al catalyst at various water injection rates and gasification temperature: (a) 0.02 g min^{-1} and 900 °C; (b) 0.05 g min^{-1} and 800 °C; (c) 0.02 g min^{-1} and 800 °C; (d) 0.02 g min^{-1} and700 °C

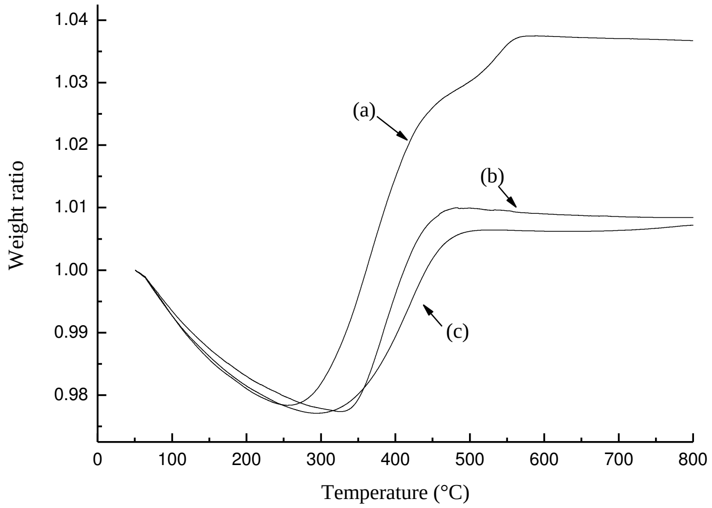
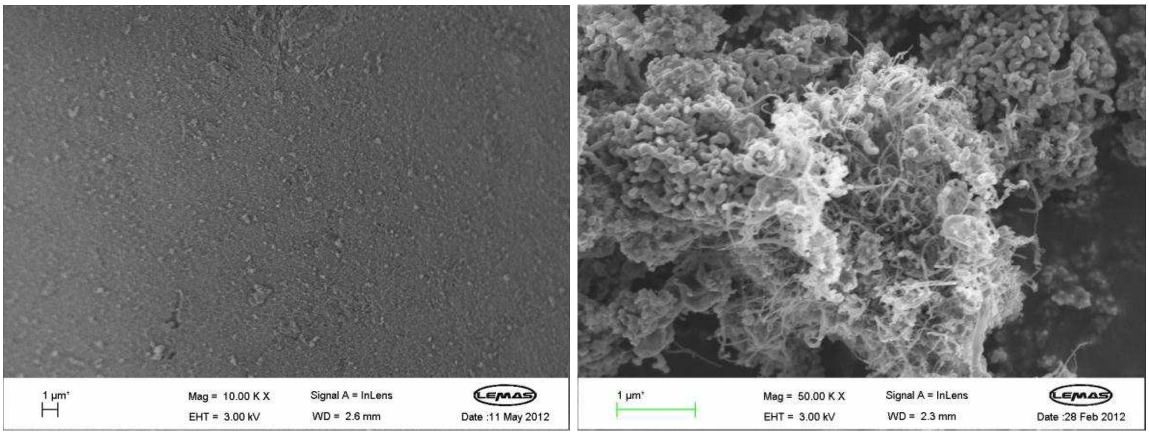


Figure 2. TGA-TPO thermograms of the reacted Ni-Ca-Al catalyst with (a) cellulose; (b) xylan (as a representative hemicellulose); (c) lignin



(a) (b)

Figure 3. SEM micrographs of the reacted catalysts, (a) Ni-Mg-Al catalyst and (b) Ni-Ca-Al catalyst