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Pyrolysis/gasification of cellulose, hemicellulose and lignin for hydrogen production in the presence of various nickel-based catalysts

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Abstract: Cellulose, hemicellulose and lignin are the main components of biomass. This work presents research into the pyrolysis/gasification of all three main components of biomass, in order to evaluate and compare their hydrogen production and also understand their gasification processes. A fixed bed, two-stage reaction system has been used employing various nickel-based catalysts. Gas concentration (CO, H_2, CO, CO_2 and CH_4) was analysed for the produced non-condensed gases. Oil byproducts were analysed by gas chromatography/mass spectrometry (GC/MS). Various techniques such as X-Ray Diffraction (XRD), scanning electron microscopy (SEM) coupled to an energy dispersive X-ray spectroscopy (EDXS), temperature-programmed oxidation (TPO) were applied to characterize the fresh or reacted catalysts. The experimental results show that the lignin sample generates the highest residue fraction (52.0 wt.%) among the three biomass components. When Ni-Zn-Al (1:1) catalyst was used in the gasification process, gas yield was increased from 62.4 to 68.2 wt.% for cellulose, and from 25.2 to 50.0 wt.% for the pyrolysis/gasification of lignin. Hydrogen production was increased from 7.0 to 18.7 (mmol g^{-1} sample) when the Ni-Zn-Al (1:1) catalyst was introduced in the pyrolysis/gasification of cellulose. Among the investigated catalysts, Ni-Ca-Al (1:1) was found to be the most effective for hydrogen production from cellulose pyrolysis/gasification.

Key Words: Biomass; Cellulose; Hemicellulose; Lignin; Gasification; Hydrogen

1. Introduction

Hydrogen is regarded as one of the most promising energies of the future; it can be generated from various resources, it can be easily stored and the combustion of hydrogen is non-polluting. In addition, the use of renewable resources instead of fossil fuels, has been encouraged to reduce greenhouse gas emission which mainly contributes to global warming and climate change. For example, the EU has endorsed an integrated approach for energy sustainability, with a target for 2020 of producing 20% of energy consumption from renewable resources and a reduction in greenhouse gas emissions of at least 20% below 1990 levels [1]. Recently, extensive interest has been drawn to biomass gasification for the production of hydrogen [2-5]. Since biomass is largely available as a carbon-neutral resource [6] and a key renewable feedstocks to respond to the vital societal need for the sustainability of energy production [7].

Biomass materials can be quite different according to the composition of their main components (cellulose, hemicellulose and lignin). For example, wood bark contains a large amount of lignin (~43 wt.%) and little cellulose (~24 wt.%), while grass contains large quantities of cellulose (~58 wt.%) and very little lignin (~4 wt.%) [8]. The investigation of thermal stability has shown that lignin has the highest thermal resistance [9]. In addition, the chemical structures of these three main components are different. Fourier transform infrared (FTIR) spectroscopy of cellulose has shown the highest IR absorbance of OH and C-O chemical groups, hemicellulose has been shown to contain a higher amount of C=O compounds, while lignin was reported to be rich in meth-oxyl-O-CH_3, C-O-C and C=C chemical groups [10].

Numerous of studies have been carried out on the pyrolysis of cellulose, heicellulose and lignin using thermogravimetric analysis (TG) [11-13], pyroprobe reactor [14] and supercritical reactor [15]. It was concluded that pyrolysis of biomass was significantly dependent on the main components of cellulose, heicellulose and lignin. For example, hemicellulose and lignin started to decompose at lower temperatures compared with cellulose during TGA analysis; however, lignin was found to be decomposed over the whole investigated temperature (from ambient to 900 °C) and produced the highest residue after the TGA experiment [10, 11]. In addition, lignin was reported to be more strongly affected by steam partial pressure than that of cellulose and hemicelluloses (xylan), when these three biomass components were investigated using TGA [16]. However, few studies have been carried out in relation to the gasification of cellulose, hemicellulose and lignin at high temperature in the presence of catalyst using a practical reaction system. An assessment of the processes that generate hydrogen from biomass, through studies on the catalytic pyrolysis/gasification of cellulose, hemicellulose and lignin will promote an understanding of biomass gasification and further enable the selection of suitable biomass resources for the generation of desired products.

Nickel-based catalysts have been commonly used to increase hydrogen production and reduce tar production in the gasification process, due to their effective catalytic performance and the comparative low cost [17-19]. Ni-Al catalysts, prepared by co-precipitation, have been widely used in the gasification of biomass and other hydrocarbon materials [20-23]. Additionally, metals such as Mg [24, 25], Cu [24, 26], Ca [4, 27, 28] and Zn [26] have been added to the Ni-Al catalyst system to improve the catalytic performance such as promotion of hydrogen production and prevention of coke deposition during the gasification process.

The purpose of this work was to investigate the influence of the biomass components, cellulose, hemicellulose and lignin, on hydrogen and gas production from a pyrolysis/gasification process. Furthermore, the Ni-Al catalysts doped with Zn and/or Ca were applied in the pyrolysis/gasification, and their catalytic properties were evaluated in terms of hydrogen production from cellulose, hemicellulose and lignin.

2. Experimental

2.1. Materials

Cellulose (Research Chemicals Ltd.), Xylan (commonly representative of hemicelluloses, from beech wood) (Sigma-Aldrich) and Lignin (Sigma-Aldrich) were used as raw samples. Results of the ultimate analysis (thermogravimetric analyser) and element analysis (CE Instruments CHNS-O analyser) of the biomass samples were shown in Table 1. Lignin shows the highest C content (61.33 wt.%), highest content of fixed carbon (32.66

wt.%) and lowest volatiles content (60. 37 wt.%). In addition, cellulose shows the lowest ash content (0.07 wt.%). A significant amount of sulphur (0.69 wt.%) was found in the lignin sample (Table 1). The low ash content in the cellulose and high sulphur content of lignin have been reported by other researchers [8, 16].

The catalysts were prepared by a co-precipitation method with an initial Ni-loading mole ratio of 20 mol.%. $Ni(NO_3)_3 \cdot 6H_2O$ (≥97.0%), $Ca(NO_3)_2 \cdot 4H_2O$ (≥99%), $Zn(NO_3)_2 \cdot 6H_2O$ (≥99%), $Al(NO_3)_3 \cdot 9H_2O$ (≥99%), and NH_4OH (≥98%) were purchased from Sigma–Aldrich. Precursors with the desired Ni-Ca-Al (1:1) (Ca/Al molar ratio 1:1), Ni-Zn-Al (1:1) (Zn/Al molar ratio 1:1), Ni-Ca-Al (Ca/Al molar ratio 1:9) or Ni-Ca-Zn-Al (Ca/Zn/Al molar ratio 1:1:2) were prepared by dissolving a certain amount of metal salts in deionized water. The precursor mixture was precipitated with a basic solution of $(NH_4)_2CO_3$ 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 several times followed by drying at 80 °C overnight. The solid products were calcined at 800 °C for 4h with a heating rate of 1 °C min^{-1} in static air.

2.2. Pyrolysis/gasification process

Pyrolysis/gasification of cellulose, xylan and lignin were carried out with a fixed-bed, two-stage reaction system (Fig. 1). The reaction system was composed of a pyrolysis reactor, gasification reactor, water injection (if steam was required in the reaction), liquid collection system and gas collection stages.

During the experiment, N_2 (80 ml min^{-1}) was used as carrier gas. 0.5 g of biomass sample was placed inside a crucible and held in the first pyrolysis reactor. 0.25 g of sand/catalyst was placed in the second reactor. The temperature of the second reactor was initially heated to the set point (800 °C). Then the first reactor was heated to the pyrolysis temperature (500 °C) at a heating rate of 40 °C min^{-1} and kept at that temperature for 30 min. Water for steam reaction was injected between the two reactors with an injection rate of 0.05 g min^{-1} when the temperature of the pyrolysis reactor reached 150 °C.

The products from the pyrolysis/gasification were cooled using air and dry ice to collect the condensed liquid. The non-condensed gases were collected using a Tedlar™ gas bag, and further analyzed off-line using packed column gas chromatography (GC). Around 20 min more time was allowed to collect the non-condensed gases to ensure complete reaction. The amounts of injected water and the condensed liquid were calculated by weighing the syringe and condensers before and after the experiment, respectively. Experiments were repeated to ensure the reliability of the results.

2.3. Products analysis and characterization

Non-condensed gases collected in the Tedlar™ bag were analysed off-line by GC. H_2, CO and N_2 were analysed with a Varian 3380 GC on a 60-80 mesh molecular sieve column with argon carrier gas, whilst CO_2 was analysed by another Varian 3380 GC on a Hysep 80-100 mesh column with argon carrier gas. C_1 to C_4 hydrocarbons were analysed using a Varian 3380 gas chromatograph with a flame ionisation detector, with a 80-100 mesh Hysep column and nitrogen carrier gas.

The selected liquid products from the condensers were collected using dichloromethane (DCM). The water content in the liquid mixture was eliminated by filtering with a bed of anhydrous sodium sulphate, and the oil was further diluted with DCM to a detectable level. The oil samples in DCM were analysed using gas chromatography/mass spectrometry (GC/MS, Hewlett Packard 5280 gas chromatograph coupled to a HP5271 ion trap mass selective detector).

BET surface area of the fresh catalyst was analyzed by N_2 adsorption and desorption isotherms on a Quantachrome Autosorb-1. The BET surface area of the Ni-Zn-Al (1:1), Ni-Ca-Al (1:1), Ni-Ca-Al (1:9) and Ni-Ca-Zn-Al (1:1:2) was 38.6, 84.7, 136.0 and 21.4 $m^2\ g^{-1}$, respectively.

X-Ray Diffraction (XRD) analysis was carried out on the fresh catalysts by using a SIEMENS D5000 in the range of 1.5-70° with a scanning step of 0.02° using Cu Kα radiation (0.1542 nm wavelength).

A high resolution scanning electron microscope (SEM) (LEO 1530) coupled to an energy dispersive X-ray spectroscope (EDXS) system was used to investigate the surface morphology and the element distributions of the reacted catalysts.

Temperature-programmed oxidation (TPO) of the reacted catalysts was carried out using a Stanton-Redcroft thermogravimetric analyser (TGA and DTG) to determine the properties of the coked carbons deposited on the reacted catalysts. About 10 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. Mass balance and hydrogen production

3.1.1. Products yields from the pyrolysis/gasification of biomass components

Experimental results from the pyrolysis/gasification of cellulose, xylan (hemicelluolose) and lignin are shown in Table 2 and Table 3. The mass balance was calculated as the weight of outputs (liquid, gas and residue) divided by the weight of inputs (injected water and biomass sample). Gas yield was obtained by the mass of non-condensed gases (calculated from the GC analysis) divided by the mass of biomass sample (0.5 g). The residue fraction was calculated by the weight of residue after pyrolysis in the first reactor divided by the weight of biomass sample. Oil yield for the pyrolysis of cellulose, xylan and lignin in the presence of sand was calculated as the weight of the collected liquid from the condensers divided by the weight of the biomass.

As shown in Table 2, lignin shows the highest residue fraction (52.0 wt.%) from the non-catalytic pyrolysis/gasification, indicating the lowest conversion of feedstock to volatile products, and resulted in the lowest oil yield (20 wt.%). The data is in agreement with the ultimate analysis of the biomass samples (Table 1), where lignin exhibited the lowest content of volatiles among the three main biomass components. Additionally, pyrolysis/gasification of cellulose in the absence of catalyst showed the highest yield of gas (55.3 wt.%), whereas the gas yield for the xylan and lignin were 44.2 and 21.5 wt.%, respectively. A low residue yield (34 wt.%) has been reported by Rutkowski et al. [29] for the pyrolysis of cellulose, compared with the pyrolysis of xylan (42 wt.%) and the pyrolysis of lignin (51 wt.%). The high content of volatiles from the decomposition of cellulose and lowest volatiles from the decomposition of lignin were also reported using TGA [10, 16]. The low production of volatiles from lignin may be ascribed to the chemical structure of lignin which is full of aromatic rings with various branches. Furthermore, exothermic reactions were observed from the TGA-DSC (differential scanning calorimetry) analysis, when hemicellulose and lignin were used [10]. These exothermic reactions favor the charring process [30] and therefore, result in a high yield of solid residue for the decomposition of hemicellulose or lignin. For the decomposition of cellulose, only endothermic reactions were observed [10], and therefore produced the highest amount of volatiles among the three biomass components.

With the introduction of steam into the pyrolysis/gasification, gas yield was slightly increased compared with the non-catalytic pyrolysis/gasification of biomass (Table 2). For example, gas yield was increased from 55.3 to 62.4 wt.% when water was injected with 0.05 g min^{-1} for the pyrolysis/gasification of cellulose.

When the nickel-based catalysts were introduced to the process of pyrolysis/gasification in the presence of steam, the gas yield was significantly increased. For example, gas yield was increased from 62.4 to 68.2 wt.% for the pyrolysis/gasification of cellulose, when the Ni-Zn-Al (1:1) catalyst was used (Table 2). Using this catalyst also increased gas yield from 25.2 to 50.0 wt.% for the pyrolysis/gasification of lignin (Table 2). It can be seen that significantly increased gas yield (around two fold) has been obtained for the lignin sample with the addition of the Ni-Zn-Al (1:1) catalyst; this might be due to the effective reforming of oil compounds derived from lignin pyrolysis, thus resulting in a large production of gases. For the catalytic steam pyrolysis/gasification process, a similar trend was obtained when comparing the different biomass components; as cellulose gave the highest gas production and lignin produced the lowest gas fraction.

When the catalyst was changed from the Ni-Zn-Al (1:1) catalyst to the Ni-Ca-Al (1:1) catalyst for cellulose pyrolysis/gasification, the gas yield showed a similar amount (68.8 wt.%); however, as shown in Table 3, relatively lower gas yield was obtained for the Ni-Ca-Al (1:9) (53.4 wt.%) and the Ni-Ca-Zn-Al (1:1:2) (62.9 wt.%) catalysts.

3.1.2. Hydrogen production from pyrolysis/gasification of biomass components

The production of hydrogen in mmol per gram of biomass sample is shown in Table 2 and Table 3. 5.8 (mmol g^{-1} sample) was obtained for the pyrolysis/gasification of cellulose without catalyst and steam, whilst 4.6 and 1.8 (mmol g^{-1} sample) were obtained for the xylan and lignin, respectively. The hydrogen production was slightly increased when steam was presented in the non-catalytic process of biomass components. For all the investigated three biomass components, hydrogen production was dramatically increased from around 7 to more than 15 (mmol g^{-1} sample), when a catalyst was introduced to the experiment. Hydrogen production was also reported to be increased when ZSM-5 and MCM-41 based catalysts were mixed with lignin for pyrolysis at 600 °C [31]. The production of hydrogen was also reported to be increased with the addition of a Ni-based catalyst to biomass pyrolysis/gasification [32-34].

The influence of the type of catalyst on hydrogen production from the pyrolysis/gasification of the cellulose was also investigated in this work. As shown in Table 3, Ni-Ca-Al (1:9) gave the lowest hydrogen production (10.7 (mmol g^{-1} sample)). With the increase of Ca content in the catalyst (Ni-Ca-Al (1:1)), the hydrogen production was increased to 22.2 (mmol g^{-1} sample) for cellulose pyrolysis/gasification.

For the pyrolysis/gasification of lignin with the Ni-Zn-Al (1:1) catalyst, carbon conversion to oils containing aromatic compounds is suggested to be dominant; therefore, lower concentrations of CO and CO_2 (Fig. 2) were obtained compared with cellulose and xylan, resulting in the lowest gas yield for lignin. However, the highest hydrogen production was obtained for lignin gasification with the Ni-Zn-Al (1:1) catalyst (Table 2); this might be due to the effective steam reforming with the Ni-Zn-Al (1:1) catalyst for the derived compounds such as aromatics from the lignin pyrolysis.

It seems that the increase of Ca or Zn content (reduction of Al content) in the catalyst system, changing from the Ni-Ca-Al (1:9) to Ni-Ca-Al (1:1) or Ni-Ca-Zn-Al (1:1:2), increased the production of gas and hydrogen. The lowest hydrogen production with the Ni-Ca-Al (1:9) catalyst was suggested to due to the lower availability of effective NiO particles for catalysis for hydrogen production. XRD analysis (Fig. 3) showed that NiO of the Ni-Ca-Al (1:9) has a smaller particle size (larger peak width indicates small particle size according to the Scherrer Equation) compared with other catalysts; thus suitable crystal size of NiO is suggested to be important for the catalytic gasification of biomass Additionally, ZnO crystals observed in the Ni-Zn-Al (1:1) catalyst from the XRD might improve the hydrogen production, compared with the Ni-Ca-Al (1:9) catalyst; since Zn metal has been reported as an effective catalytic site during the gasification of biomass [35].

Additionally, the production of hydrogen from the catalytic pyrolysis/gasification of the biomass samples seems to have little relation to the BET surface area of the introduced catalysts. As the Ni-Ca-Al (1:9) catalyst has the highest BET surface (136.0 m^2 g^{-1}), but the lowest production of hydrogen was obtained. Therefore, the catalytic pyrolysis/gasification of the biomass components is suggested to be dominated by the catalytic metal sites of the catalyst instead of the surface area of the catalyst used in this work.

3.1.3. Gas concentrations from pyrolysis/gasification of biomass components

Gas concentrations in the non-condensed gas product from the pyrolysis/gasification of the cellulose, xylan and lignin are shown in Fig. 2. CO, H_2, CO_2 and CH_4 were found to be the main gases from the non-catalytic pyrolysis/gasification process (30.4 - 44.4 Vol.% of CO, 15.0 - 27.3 Vol.% CO_2, 19.7 - 23.9 Vol.% H_2 and 10.7 - 19.9 Vol.% of CH_4). High concentrations of CO, CO_2 and CH_4 have been reported from pyrolysis/gasification of biomass samples in the absence of catalyst [36-38].

As shown in Fig.2, the highest CO concentration (44.4 Vol%) was found for the cellulose pyrolysis/gasification without Ni catalyst, and the lowest CO concentration (30.4 Vol.%) was obtained for the xylan; furthermore, the lowest CO_2 concentration (15.0 Vol.%) was obtained for the cellulose sample whist the highest CO_2 (27.3 Vol.%) concentration was observed for xylan. Similar results were reported when biomass components have been investigated for their pyrolysis behaviour in a fixed-bed reactor at a temperature of 540 °C [38]. Additionally, the highest CO_2 concentration was also obtained for xylan pyrolysis at 950 °C, compared with cellulose and lignin pyrolysis [8]. Yang et al [10] observed the highest IR absorbance of C-O was obtained for the cellulose, and the highest IR absorbance of C=O was found for the hemicellulose sample, when the biomass components were analysed by FTIR [10]. The presence of large amounts of C-O chemical groups in the cellulose might promote the production of carbon monoxide during the pyrolysis process. Additionally, the abundant presence of C=O chemical groups in the hemicellulose is suggested to favor the production of carbon dioxide. It is interesting to point out that Yang et al [10] obtained the highest CO production from the pyrolysis of cellulose in a fixed-bed reactor (consistent with the observation from our work); however, they found lowest CO release during the TGA experiment with cellulose [10]. The authors suggested that long residence time in the fixed-bed reactor promoted secondary cracking of the pyrolysis volatiles and thus increased the CO production. Fig. 2. shows that when the Ni-Zn-Al (1:1) catalyst was introduced in the catalytic experiment, the highest CO concentration was still found for the cellulose sample, and highest CO_2 concentration was observed for the xylan sample.

From Fig. 2, the highest CH_4 concentration was obtained for the pyrolysis/gasification of lignin in the absence of the catalyst, among the investigated biomass components. Lignin showed highest CH_4 production from the pyrolysis process with TGA [10]; this was suggested to be due to the larger amount of O-CH_3 chemical groups present in the lignin. Concentration of CH_4 was reduced to around 3 Vol.% from nearly 20 Vol.%, when the Ni-based catalyst was introduced in the pyrolysis/gasification process (Fig. 2).

H_2 concentration was significantly increased, CO concentration was reduced and CO_2 concentration was increased with the introduction of the catalyst (Fig. 2). It is suggested that the water gas shift reaction (Equation 1), methane steam reforming (Equation 2) and tar steam reforming (Equation 3) reactions were possibly promoted in the presence of the Ni-based catalyst [18, 25, 39]. Furthermore, concentrations of CH_4 and C_2-C_4 hydrocarbon gases were reduced significantly with the introduction of Ni catalysts.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{1}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{2}$$

$$C_nH_m + nH_2O \leftrightarrow nCO + (n + m/2)\ H_2 \tag{3}$$

The increase of H_2 concentration for the catalytic pyrolysis/gasification of lignin with the Ni-Zn-Al (1:1) catalyst was found to be the most significant, compared with cellulose and xylan (Fig. 2). The introduction of the Ni-Zn-Al (1:1) catalyst might promote steam reforming reactions of hydrocarbon oils such as aromatics (Equation 3) and also reforming of oxygenated compounds such as alcohol (Equation 4). Lignin has been found to be rich in methoxyl-O-CH_3 containing compounds, while cellulose and hemicellulose are rich in C-O and C=O compounds which contribute to the production of CO and CO_2 gases.[10] Therefore, we suggest that oxygenated compounds are more dominant in the derived hydrocarbons from the lignin pyrolysis at the first reaction stage, compared with the cellulose and xylan samples; this is further observed by the GC-MS analysis (Table ~~3~~4). Furthermore, the large amounts of oxygenated compounds were reformed to produce hydrogen when the Ni-Zn-Al (1:1) catalyst was added into the lignin pyrolysis/gasification. Thus the hydrogen concentration and production was significantly increased for the pyrolysis/gasification of lignin with the Ni-Zn-Al (1:1) catalyst, compared with the non-catalytic experiment where most of the oxygenated compounds were condensed into liquid.

$$C_nH_mO_k \leftrightarrow CO + H_2 \tag{4}$$

High hydrogen concentration was also obtained for the catalytic steam pyrolysis/gasification of cellulose in the presence of other catalysts except the Ni-Ca-Al (1:9) catalyst which gave a H_2 concentration of around 41 Vol.%. The low concentration of H_2 in the presence of Ni-Ca-Al (1:9) catalyst was ascribed to the poor ability of steam reforming of hydrocarbons; since the largest production of hydrocarbon gases (C_2-C_4) was found for the Ni-Ca-Al (1:9) catalyst (Fig.2).

3.2. Characterization of reacted catalysts

Reacted catalysts after the catalytic steam pyrolysis/gasification of cellulose, xylan and lignin were analysed by temperature programmed oxidation (TPO). The results of the TGA-TPO are shown in Fig. 4. From Fig. 4, mass-gaining curves were observed. This is due to the oxidation of Ni of the reacted catalyst; which was reduced from NiO to Ni in the reducing environment during the pyrolysis/gasification process [17, 19, 24]. The highest increase of the weight of the reacted catalyst (~4 wt.%) was found for the Ni-Zn-Al (1:1) used during the lignin pyrolysis/gasification. As shown in Fig.2, the highest H_2 concentration was produced from the pyrolysis/gasification of lignin in the presence of the Ni-Zn-Al (1:1) catalyst. Therefore, we suggest that the largest weight increase of the reacted Ni-Zn-Al (1:1) catalyst during TPO experiments was because most of NiO particles in the fresh Ni-Zn-Al (1:1) catalyst were reduced by the H_2 which produced the highest concentration of H_2 among the investigated catalysts.

As shown in Fig. 4, it is interesting to note that there is almost no carbon oxidation (weight loss between 400 and 700 °C) occurring for the reacted catalyst, indicating that the coke deposition on the reacted catalyst was negligible. In addition, the results of the EDXS analysis of the reacted catalysts are shown in Fig. 5. Carbon peaks from the EDXS analysis were very small for the reacted catalysts. This further demonstrates the low coke deposition on the reacted catalyst from the catalytic steam pyrolysis/gasification of cellulose, xylan and lignin. Large amounts of coke deposition was reported for Ni/SiO_2, Ni/ZSM-5 and Ni/mordenite catalysts when cellulose was catalytically gasified at 600 °C [40]. Significant coke deactivation has also been extensively reported for nickel-based catalysts in relation to biomass gasification [21, 41, 42]. Therefore, in this paper, Ni-Zn-Al and Ni-Ca-Al catalysts prepared by co-precipitation has the potential to significantly reduce the coke deposition for hydrogen production from the process of biomass gasification.

From the EDXS analysis (Fig. 5), the composition of the catalyst was identified and aligned with the original design of the catalyst preparation. For example, all the Ni, Ca, Al and Zn metals were found for the reacted Ni-Ca-Zn-Al (1:1:2) catalyst. Additionally, the intensity for the Ca metal was increased for the Ni-Ca-Al (1:1) catalyst, compared with the Ni-Ca-Al (1:9) catalyst. From Fig.4, it is also interesting to point out that sulphur was observed for the reacted Ni-Zn-Al (1:1) catalyst from the pyrolysis/gasification of lignin, whilst sulphur was hardly identified for the catalyst used for the cellulose and xylan samples. The presence of sulphur in the reacted catalyst is likely to be due to the relatively high sulphur content in the lignin sample (Table 1).

Morphologies of the reacted catalyst were investigated by SEM analysis. It is difficult to observe carbon deposition from the SEM analysis. Selected results of the reacted Ni-Zn-Al and Ni-Ca-Al catalysts are shown in Fig. 6, a difference between the two types of catalysts was observed from the SEM results. Filamentous carbons were easily found on the surface of the reacted Ni-Ca-Al catalyst, compared with the reacted Ni-Zn-Al catalyst. However, the oxidation of the filamentous carbons is not observed with the TPO experiment, probably due to the low amount of coke.

3.3. Oil analysis using GC-MS

Selected oil samples were analysed using GC-MS. Possible identified chemical compounds are shown in Table ~~3~~4, where the higher concentration was assigned to a higher number of stars. For example, the highest concentration of naphthalene was obtained for the pyrolysis/gasification of lignin without catalyst. The comparative concentration of chemicals was obtained according to the peak area shown in the total ion chromatogram (TIC) (e.g. Fig. 7). From Table ~~3~~4, the most abundant compounds identified were toluene, styrene, indene, and naphthalene etc. These chemical compounds have also been identified by others from the pyrolysis of cellulose, lignin and biomass samples [43, 44].

As shown in Table ~~3~~4, pyrolysis/gasification of lignin without the catalyst shows the highest total concentrations of the identified chemical compounds; in addition, more peaks could be found from Fig. 7 for the lignin sample. In addition, the oil sample obtained from the pyrolysis/gasification of lignin in the presence of sand was observed to be darker in colour compared with the oil from cellulose and xylan. The higher concentration of oxygenated compounds such as phenol in the oil derived from lignin pyrolysis/gasification is suggested to be reformed for increased hydrogen production when the Ni-Zn-Al (1:1) catalyst was added in the experiment; therefore, the hydrogen production was significantly increased for the lignin sample compared with cellulose and xylan with the Ni-Zn-Al (1:1) catalyst.

With the addition of the Ni-Ca-Al (1:1) catalyst, the concentrations of identified chemical compounds were lower than in the oil from the pyrolysis/gasification of cellulose without catalyst (Table ~~3~~4). Additionally, the dominant compound (naphthalene) from the pyrolysis/gasification of cellulose without catalyst becomes minor in the oil with the Ni-Ca-Al (1:1) catalyst (Fig. 7). Therefore, it seems that the presence of Ni-Ca-Al (1:1) catalyst was effective for reforming/cracking of aromatic compounds.

4. Conclusions

In this work, the main components of biomass, cellulose, hemicellulose (xylan) and lignin, were investigated for their hydrogen production potential in the gasification process, by using a two-stage fixed bed pyrolysis/gasification reaction system. The main conclusions were:

(1) Cellulose produces the highest amount of hydrogen (5.8 mmol H_2 g^{-1} sample) in the absence of steam and catalyst, where only 1.8 mmol H_2 g^{-1} sample was obtained for the lignin.

(2) Highest CO concentration (44.4 Vol%) was found for the cellulose pyrolysis/gasification. This is suggested to be due to the abundance of C-O chemical compounds in the cellulose sample. Furthermore, the highest CO_2 concentration (27.3 Vol.%) was observed for the xylan

sample; this is attributed to the highest content of C=O chemical compounds in the xylan sample.

(3) The introduction of Ni-based catalyst significantly increased the hydrogen production, which was increased from 7.0 to 18.7 (mmol H_2 g^{-1} sample) in the presence of the Ni-Zn-Al (1:1) catalyst. Additionally, Ni-Ca-Al (1:9) catalyst showed the lowest hydrogen production among the catalysts investigated.

(4) Coke deposition on the reacted catalyst after the gasification process was found to be negligible from the TPO analysis. In addition, sulphur was observed in the reacted Ni-Zn-Al (1:1) catalyst after the pyrolysis/gasification of lignin; this is suggested to be due to the large presence of sulphur in the lignin sample.

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Table 1

Element and proximate analysis of the cellulose, xylan and lignin samples (wt.%)

		Ultimate analysis					Proximate analysis		
	C	H	O	N	S	Moisture	Volatiles	Fixed carbon	Ash
Cellulose	41.66	5.71	52.20	0.41	0.02	4.67	93.37	1.89	0.07
Xylan	40.26	5.49	51.55	2.70	0.00	5.83	77.79	12.78	3.61
Lignin	61.33	5.14	31.71	1.13	0.69	3.41	60.37	32.60	3.62

Table 2 Experimental parameters and mass balance for the pyrolysis-gasification of various samples[a]

Sample	Cellulose	Xylan	Lignin	Cellulose	Xylan	Lignin	Cellulose	Xylan	Lignin
Catalyst	Sand	Sand	Sand	Sand	Sand	Sand	Ni-Zn-Al (1:1)	Ni-Zn-Al (1:1)	Ni-Zn-Al (1:1)
Water injection (g min^{-1})	0	0	0	0.05	0.05	0.05	0.05	0.05	0.05
Gas yield (wt.%)	55.3	44.2	21.5	62.4	45.4	25.2	68.2	67.1	50.0
Oil yield (wt.%)[b]	32.0	24.0	20.0	-	-	-	-	-	-
Residue (wt.%)	18.0	28.0	52.0	16.0	26.0	50.0	18.0	28.0	52.0
Mass balance* (wt.%)	105.3	96.2	93.5	101.1	99.4	101.0	92.0	96.8	92.3
H_2 yield (mmol g^{-1} sample)	5.8	4.6	1.8	7.0	7.4	6.2	18.7	17.5	19.4

[a] Mass balance was calculated as the weight of outputs (liquid + gas + residue) divided by the weight of inputs (injected water + biomass sample); [b]: oil yield for the catalytic pyrolysis/gasification was not identified due to the mixture of the tar and non-reacted water.

Table 3 Experimental parameters and mass balance for the pyrolysis-gasification of cellulose with various catalysts

Sample	Cellulose	Cellulose	Cellulose
Catalyst	Ni-Ca-Al (1:9)	Ni-Ca-Zn-Al (1:1:2)	Ni-Ca-Al (1:1)
Water injection (g min^{-1})	0.05	0.05	0.05
Gas yield (wt.%)	53.4	62.9	68.8
Oil yield (wt.%)[b]	-	-	-
Residue (wt.%)	18.0	18.0	20.0
Mass balance* (wt.%)	94.9	96.8	95.0
H_2 yield (mmol g^{-1} sample)	10.7	18.0	22.2

Table ~~3~~ 4

GC-MS results of the selected oil samples from pyrolysis/gasification of biomass[a]

RT (min)	Name	CAS No.	Cellulose, Sand	Xylan, Sand	Lignin, Sand	Cellulose, Ni-Ca-Al (1:1)
5.742	Toluene	108-88-3	***	***	***	-
8.715	p-Xylene	106-42-3	-	-	**	-
9.41	Styrene	100-42-5	**	*	**	-
8.715	Phenol	108-95-2	-	-	***	-
12.92	Benzofuran	271-89-6	-	-	**	-
14.56	Indene	95-13-6	*	*	***	-
16.55	Benzofuran, 2-methyl-	4265-25-2	-	-	**	-
19.17	Naphthalene	91-20-3	**	**	****	*
22.55	Naphthalene, 2-methyl-	91-57-6	-	*	**	-
22.99	Naphthalene, 1-methyl-	90-12-0	-	*	**	-
24.9	Biphenyl	92-52-4	-	-	**	-
26.85	Acenaphthylene	208-96-8	**	*	***	*
28.1	Butylated hydroxytoluene	128-37-0	*	*	**	*
30.31	Fluorene	86-73-7	-	-	**	-
35.03	Phenanthrene	85-01-8	-	-	**	-
40.92	Pyrene	129-00-0	-	-	**	-
41.99	Fluoranthene	206-44-0	-	-	**	-

[a]: * indicates the scale of chemical amounts identified from the GC-MS analysis

FIGURE CAPTIONS

Fig. 1. Schematic diagram of the pyrolysis/gasification of biomass

Fig. 2. Gas concentrations from pyrolysis-gasification of various samples (Vol.%, N_2 free)

Fig. 3. XRD analysis of the fresh catalysts: ♦ NiO; ○ $Ca_{12}O_{14}Al_{33}$; ■ $NiAl_2O_4$; ● CaO; □ ZnO; Δ $ZnAl_2O_4$

Fig. 4 TPO of the reacted catalysts

Fig. 5. EDX results for the reacted catalysts

Fig. 6. SEM results of the reacted catalysts

Fig. 7. GC-MS graphic results from pyrolysis of cellulose, xylan and lignin

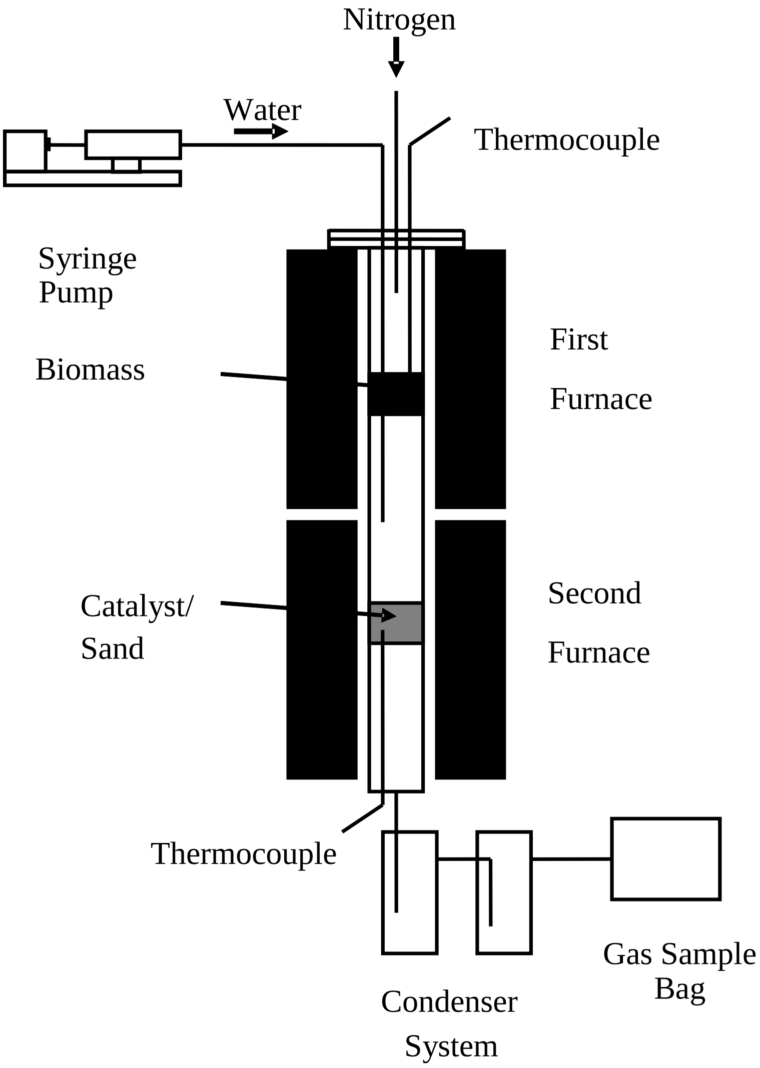


Fig. 1. Schematic diagram of the pyrolysis/gasification of biomass

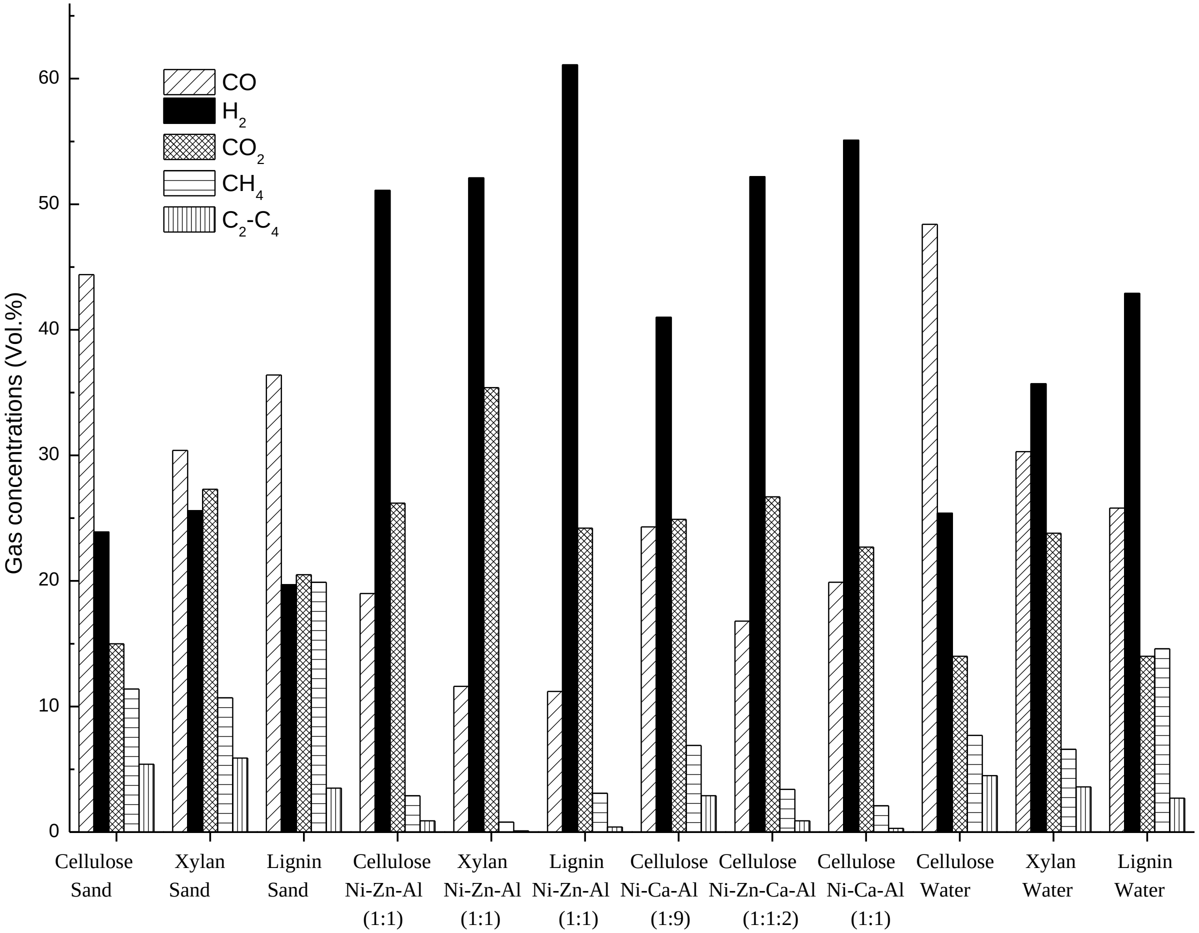


Fig. 2. Gas concentrations from pyrolysis-gasification of various samples (Vol.%, N_2 free)

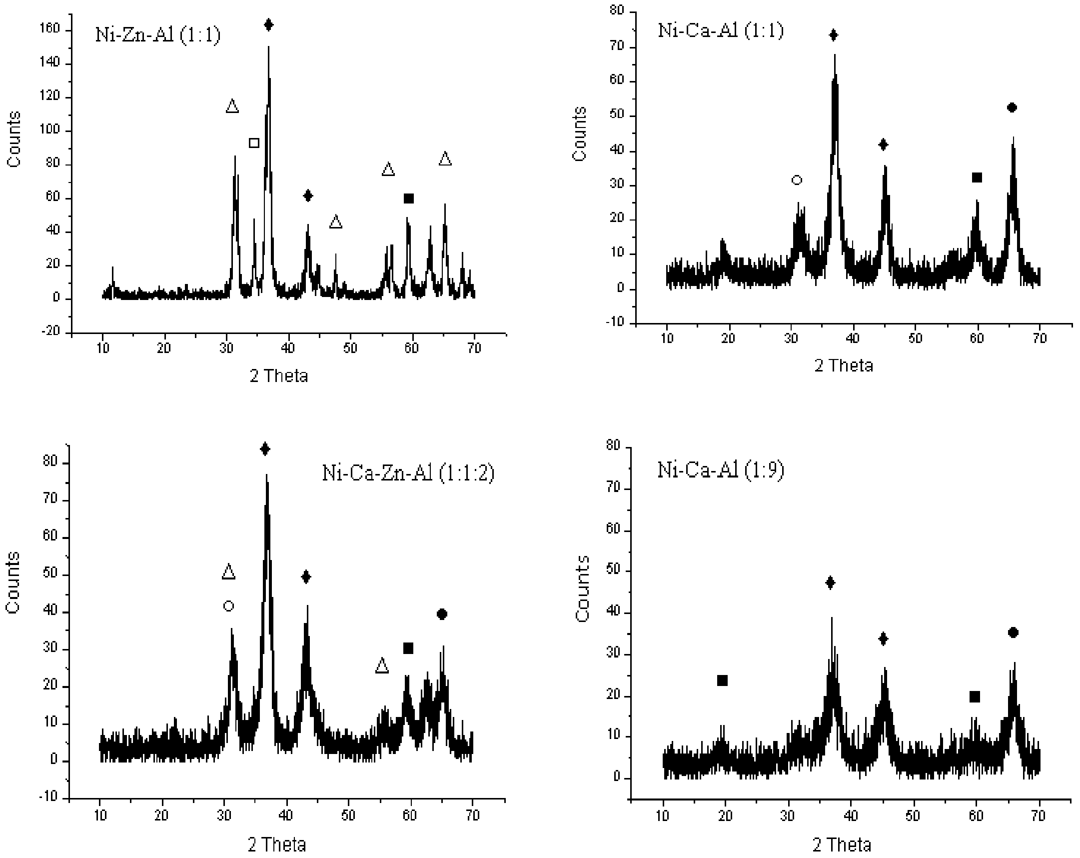


Fig. 3. XRD analysis of the fresh catalysts: ♦ NiO; ○ $Ca_{12}O_{14}Al_{33}$; ■ $NiAl_2O_4$; ● CaO; □ ZnO; Δ $ZnAl_2O_4$

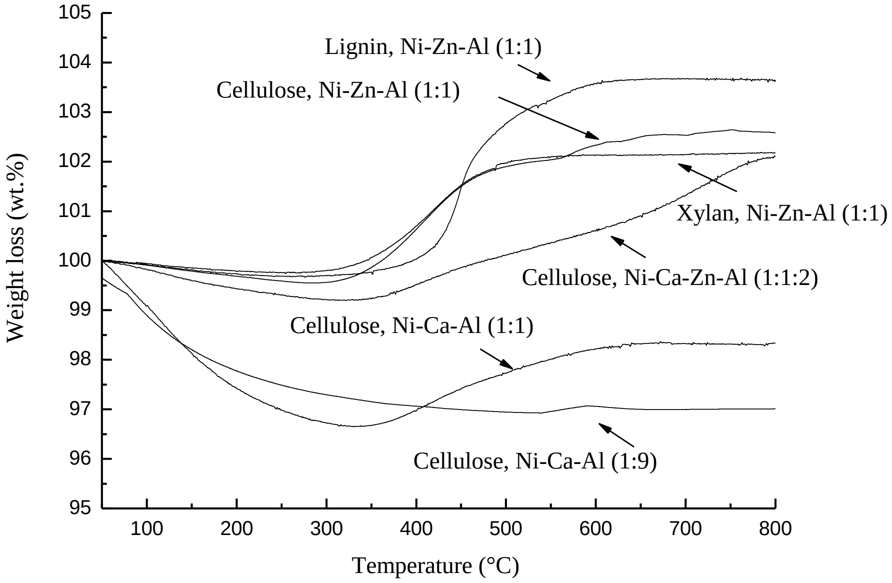
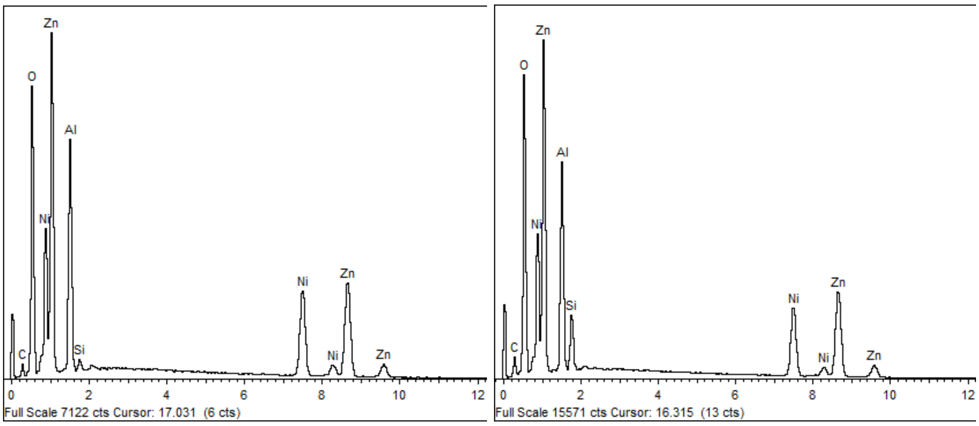
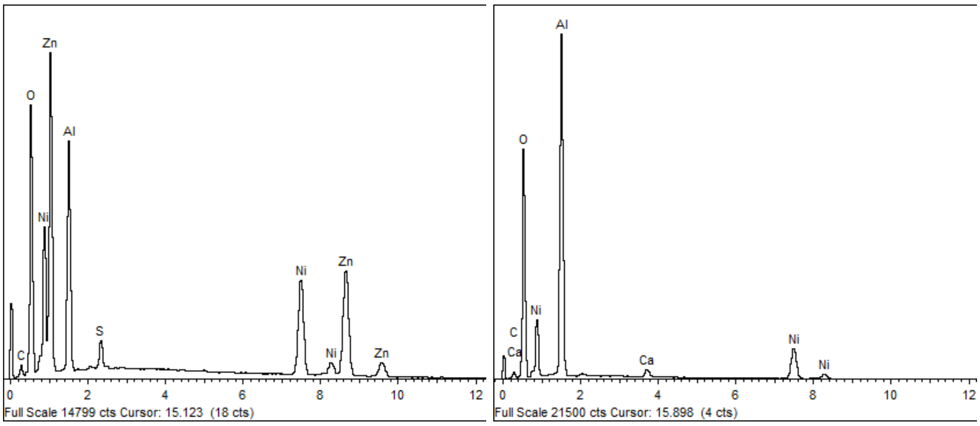


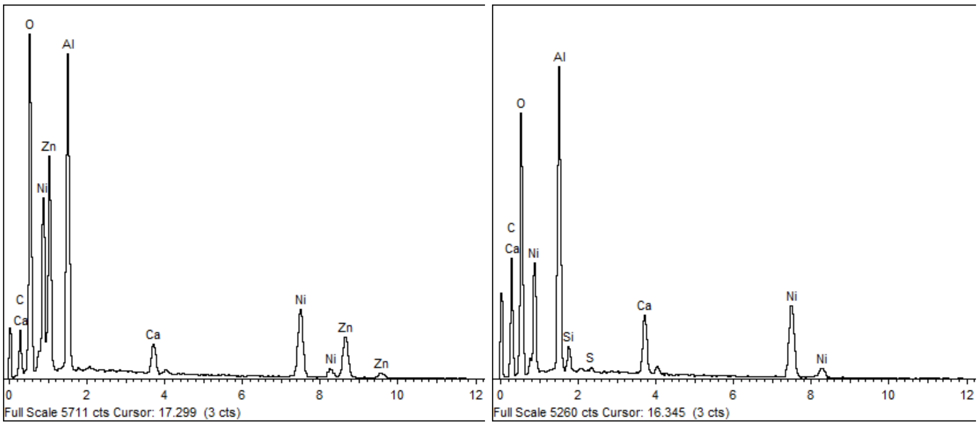
Fig. 4 TPO of the reacted catalysts



Cellulose, Ni-Zn-Al (1:1) Xylan, Ni-Zn-Al (1:1)

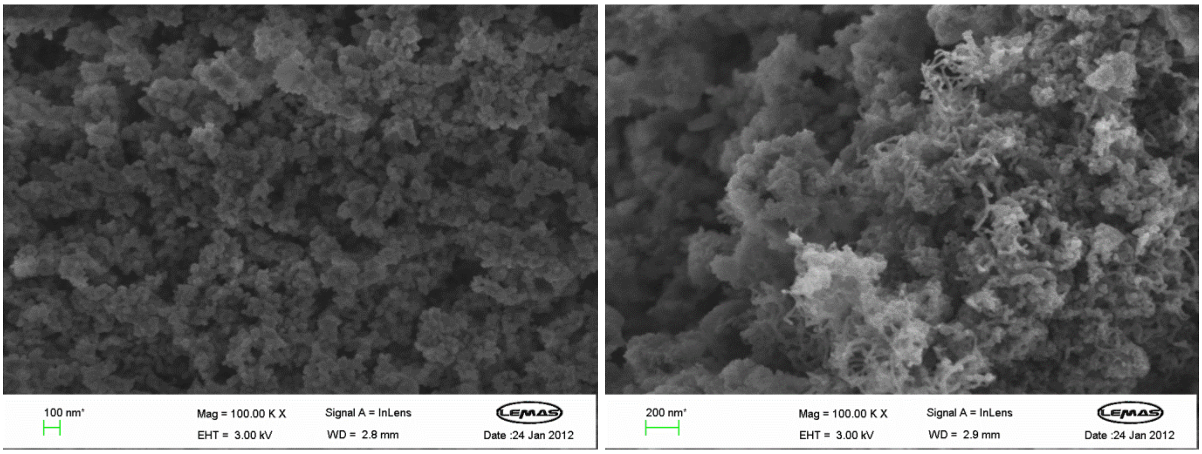


Lignin, Ni-Zn-Al (1:1) Cellulose, Ni-Ca-Al (1:9)



Cellulose, Ni-Ca-Zn-Al (1:1:2) Cellulose, Ni-Ca-Al (1:1)

Fig. 5. EDX results for the reacted catalysts



Ni-Zn-Al

Ni-Ca-Al

Fig. 6. SEM results of the reacted catalysts

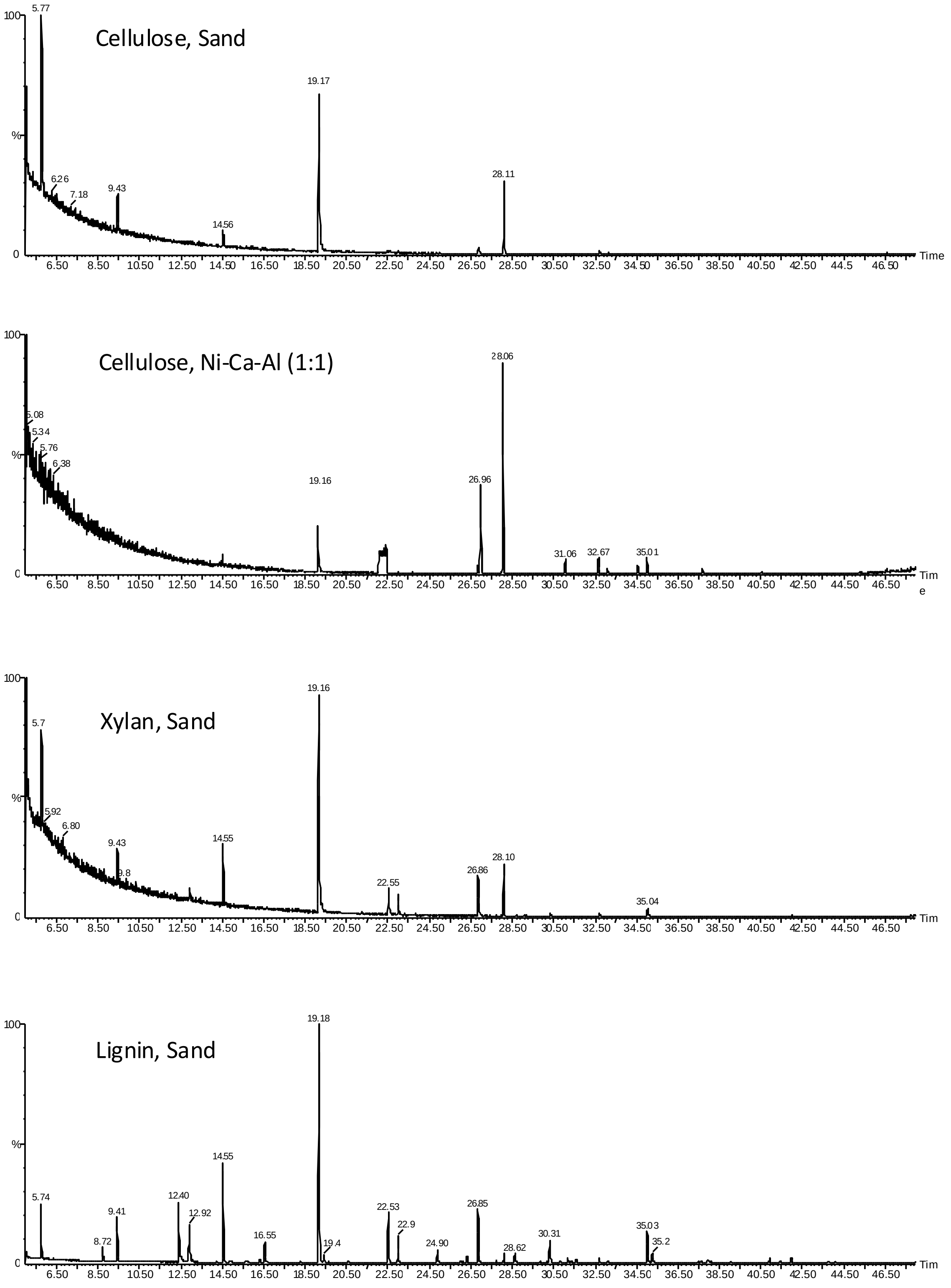


Fig. 7. GC-MS graphic results from pyrolysis of cellulose, xylan and lignin