Hydrogen production from catalytic reforming of the aqueous fraction of pyrolysis bio-oil with modified Ni−Al catalysts

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ABSTRACT

Hydrogen production from renewable resources has received extensive attention recently for a sustainable and renewable future. In this study, hydrogen was produced from catalytic steam reforming of the aqueous fraction of crude bio-oil, which was obtained from pyrolysis of biomass. Five Ni−Al catalysts modified with Ca, Ce, Mg, Mn and Zn were investigated using a fixed-bed reactor. Optimized process conditions were obtained with a steam reforming temperature of 800 °C and a steam to carbon ratio of 3.54. The life time of the catalysts in terms of stability of hydrogen production and prohibition of coke formation on the surface of the catalyst were carried out with continuous feeding of raw materials for 4 h. The results showed that the Ni−Mg−Al catalyst exhibited the highest stability of hydrogen production (56.46%) among the studied catalysts. In addition, the life-time test of catalytic experiments showed that all the catalysts suffered deactivation at the beginning of the experiment (reduction of hydrogen production), except for the Ni−Mg−Al catalyst; it is suggested that the observation of abundant amorphous carbon formed on the surface of reacted catalysts (temperature programmed oxidation results) may be responsible for the initial reduction of hydrogen production. In addition, the Ni−Ca−Al catalyst showed the lowest hydrogen production (46.58%) at both the early and stabilized stage of catalytic steam reforming of bio-oil.

Introduction

Hydrogen, as a clean and high energy fuel, has attracted extensive attention in recent years for its wide applications in manufacture and the petrochemical industry [1]. In addition, there is a predicted substantial demand for hydrogen use for fuel cells in the future. Currently, the main process to produce hydrogen is from catalytic steam reforming of natural gas [2,3]. However, alternative processes for hydrogen production is urgently needed in terms of sustainability, e.g. using biomass as a renewable resource. Using biomass has been

widely accepted as an alternative way to offset greenhouse gas emissions, guaranteeing national energy security, as well as contributions to a better utilization of local natural resources, especially for those countries and regions that have plentiful supply of biomass resources [4—6].

Hydrogen can be obtained from biomass by direct thermochemical processes, biological methods and intermediate steps of oxygenates production with subsequent reforming. Since it was first proposed by NREL (USA), catalytic steam reforming of bio-oil has been an economically feasible method for hydrogen production with respect to the energy density, handling and transportation properties of bio-oil compared with raw biomass [7—10]. Additionally, up to 60—75% of crude biomass can be converted to liquid bio-oil in practical applications, demonstrating its technical maturity [11]. Steam reforming of crude bio-oil [3,7,12], aqueous fraction [13] as well as model compounds [14—16] or a mixture of them [17] for hydrogen production has been widely investigated.

Catalysts with high activity, selectivity in relation to hydrogen production and stability in terms of sintering and coke formation are of great importance to the steam reforming process [18,19]. Although, noble metals e.g. Pt and Pd are confirmed to be highly active, nickel-based catalysts have also been extensively researched, since Ni has comparatively lower cost and Ni-based catalysts are effective for O—H and C—C cracking reactions [20—22]. In addition, Ni-based catalysts have been reported to have better performance in terms of hydrogen production and catalyst deactivation, compared with other metals such as Co, Fe and Cu, for the steam reforming of acetic acid [23]. The high catalytic activity of Ni—Al catalysts was attributed to the large metallic area and high thermal stability [24]. However, Ni—Al catalysts have been reported as having problems of catalyst deactivation due to coke formation during the reforming of bio-oil [3,25]. The formation of coke on the surface of the catalyst will cause metal particle sintering and decrease the activity of the catalyst in relation to the yield and concentration of hydrogen [26].

Various strategies have been proposed to reduce coke formation during the catalytic reforming process; classified as followings: process configuration, operational parameters optimization, catalyst improvement and others such as adding O_2 to the process [27]. Thermal treatment of raw biomass before the catalytic reforming stage was reported by Valle et al. [28] in order to separate pyrolytic lignin which is mainly responsible for coke formation. The use of fluidized beds has also been reported to attenuate coke deposition on catalysts [29]. A current-enhanced catalytic steam reforming method has been proposed which reported less coke formation compared with the normal reforming method [12]. Reforming temperature and steam to carbon ratio were also found to be essential factors for coke formation as well as quality of product gas [30,31].

The modification of the catalyst via metal addition is an effective way to improve the Ni-based catalytic activity as well as carbon resistance for hydrogen production from steam reforming of crude bio-oil. It has been reported that the amount of deposited coke on Cu—Ni/SiO$_2$ was significantly reduced through the modification of the catalyst with Ca and Mg oxides [32]. Promoters including alkaline and alkaline earth metals and others such as Ce, Zn have also been known to decrease the acidity of catalyst support, prohibiting cracking and polymerization reactions, which may lead to detrimental coke formation [33—35]. The improved stability of promoted Ni—Al catalyst was probably due to the enhanced steam absorption or the production of reactive carbon formed by the promoter [35,36]. Our previous studies have shown that adding metals such as Zn and Ca to Ni/Al$_2$O$_3$ by co-precipitation are effective for biomass catalytic gasification, in relation to the reduction of coke deposition on the surface of the catalyst [6]. However, insufficient knowledge exists about their influence on bio-oil reforming; in addition, there is a lack of detailed investigation of the influence of those metals on catalytic behavior in terms of hydrogen production and catalyst deactivation, from the process of steam reforming of real-world bio-oil.

In this paper, the aqueous fraction of crude bio-oil from corn stalk pyrolysis was catalytically steam reformed in a two-stage fixed bed reactor. Process optimization in relation to reforming temperature and steam to carbon ratio were initially optimized. Then, five Ni—Al catalysts with different metal addition (Ca, Ce, Mg, Mn and Zn) were applied to the steam reforming of bio-oil. Additionally, catalyst characterization including X-ray diffraction, temperature programmed oxidization and scanning electron microscopy were also carried out for a fundamental understanding of the catalytic effects of adding metal to the Ni—Al catalyst.

Experimental material and methods

Experimental materials

The bio-oil used for catalytic steam reforming experiments was obtained from fast pyrolysis of corn stalk in a small scale tube furnace at 500 °C, more details about the pyrolysis configuration can be found in our previous report [37]. Bio-oil used in this study was the aqueous fraction, which was a brown colored liquid with an acidic odor. The properties and elemental composition of the bio-oil are shown in Table 1. The ultimate analysis of bio-oil was carried out using a CHNS/O elementary analyzer (Vario Micro cube, Germany). It was shown that the main elemental composition was carbon, hydrogen and oxygen with the average molecular formula of $CH_{1.847}O_{0.676}$ excluding water. Other impurities such as sulfur and nitrogen are minor components and not considered here.

Table 1 — Main characteristics of the bio-oil.	
Characteristics	Bio-oil
Elemental analysis (dry, wt%)	
Carbon	47.34
Hydrogen	7.29
Nitrogen	2.63
Oxygen[a]	42.70
Sulfur	0.05
Water content (ar, wt%)	71.57
Density (g ml^{-1})	1.03
pH	3.85
[a] Calculated by difference.	

Table 2 – Main composition of bio-oil determined by GC–MS (mass % of bio-oil).

No.	Species	Content	No.	Species	Content
1	Acetic acid	54.76	12	2-Cyclopenten-1-one, 2-methyl-	1.53
2	Furfural	6.53	13	1,2-Benzenediol	1.53
3	2-Methoxytetrahydrofuran	4.35	14	1,4:3,6-Dianhydro-alpha-d-glucopyranose	1.36
4	Pyridine	3.59	15	Phenol, 3-methyl-	1.35
5	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	3.31	16	1,2-Benzenediol	1.22
6	2-Propanone, 1-(acetyloxy)-	2.55	17	5-Methoxy-pent-4-enoic acid, methyl ester	1.06
7	1-Hydroxy-2-butanone	2.41	18	2-Cyclopenten-1-one, 3-methyl-	1.04
8	Butyrolactone	2.41	19	Cyclopentanone	0.95
9	2-Furanmethanol	2.30	20	Acetic acid, methoxy-	0.90
10	Phenol	2.29	21	beta-D-Glucopyranose, 1,6-anhydro-	0.71
11	2-Furanol, tetrahydro-	1.92	22	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	0.67

The pH of bio-oil was measured with an Ohaus Instrument PH meter Starter 2c and the water content was determined using Karl-Fisher titration method with TitroLine KF-10Coulometric Titrator. The bio-oil had a high oxygen content, strong acid and high water content (71.57 wt%). Light component organic compounds containing mostly carbohydrate-derived compounds were observed using gas chromatography–mass spectroscopy (GC–MS) (7890A/5975C, Agilent Technologies, USA), the main components are listed in Table 2. The components identified are mainly consisted of acids, furfural, ketones and phenols originating from thermal degradation of the cellulose, hemicellulose and lignin in biomass.

Catalyst preparation and characterization

The Ni–M–Al catalyst with molar ratio 1:1:1 (Ni loading content of 33.3 relative atomic %) was prepared by a co-precipitation method (all the five Ni–Al catalysts were prepared using same way, and M stands for the different metal addition e.g. Ce, Ca, Mg, Mn and Zn). The precipitant $NH_4(OH)$ was added to an aqueous solution containing $Ni(NO_3)_2 \cdot 6H_2O$, $M(NO_3)_2 \cdot 4H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ until the final pH (around 8.0) was obtained, while the solution was kept at 40 °C with moderate stirring during the precipitation process. The precursors were filtered and washed with water (40 °C) and then dried at 105 °C for around 12 h, followed by calcination under static air atmosphere at 750 °C (heating rate of 20 °C min^{-1}) for 3 h. The catalysts were then crushed and sieved to keep particle size between 65 and 212 μm.

It is worth noting that all the Ni–Al catalysts were not reduced, as the gases produced during the reforming process, such as H_2 and CO, possess the ability to reduce the catalyst in situ [24]. Therefore, the NiO phase would be reduced initially during the steam reforming process, and act as active sites for catalytic reactions.

The composition and physical structure of the catalysts was characterized with X-ray diffraction (XRD), scanning electron micrograph (SEM) and temperature programmed oxidization (TPO) analyzer. Species identification of fresh and reacted catalyst was performed with an XRD analyzer (X'Pert PRO, PANalytical B.V., Netherlands), with peaks being identified using High Score Plus software package. The measurement was completed in the 2θ range from 5° to 85° with a scan step size of 0.026°. Simultaneously, SEM (JSM-5610LV, JEOL, Japan) operating at 20 kV was carried out to observe the morphology of carbon deposited on the catalyst. The TPO

analyses was conducted to quantify the carbon deposition content of reacted catalyst through combustion in air (100 ml min^{-1}) in a Thermogravimetric Analyzer (TGA) (PerkinElmer Instruments, USA), with a heating rate of 15 °C min^{-1} from room temperature up to 800 °C and keep this temperature for 10 min. The differential thermo-gravimetry (DTG) results from the experiment of TPO are also discussed in this study.

Experimental setup and procedure

Catalytic steam reforming of bio-oil was conducted in a two stage fixed bed reactor shown in Fig. 1. The reaction system consisted essentially of a stainless steel tube gasification reactor with two temperature ranges (Zone I: vaporization zone (Height: 405 mm, I.D. 51 mm) and Zone II: gasification zone (Height: 257 mm and I.D. 32 mm)), a continuous feeding system, and gas condensing system with ice and water mixture and a gas cleaning section followed by gas-sampling and measurement system. The vertical stainless steel tube was designed with two stages corresponding to the furnace for bio-oil (including water) volatilizing and catalytic gasification, respectively.

During each experiment, the reactor was heated up to the preset temperature and kept stable. The volatilization zone I was set at 400 °C [13,38] to avoid excessive coke formation before catalytic reforming, while the reforming temperature (T_2) of zone II was set ranging from 600 to 900 °C. From the temperature distribution along the reactor (Fig. 1), it can be seen that the temperatures of zone I were close to the preset temperature while zone II maintained at least 120 mm length of constant temperature area corresponding to different preset conditions. The residence time through the catalyst was calculated and ranged between 0.23 and 0.46 s, which was comparable to the 0.24 s (at the optimal condition) used by Bimbela et al. [17], therefore ensuring that the catalytic reforming took place completely. Bio-oil was fed continuously into the reactor at a mass flow rate of 0.3 g min^{-1}. High-purity nitrogen was supplied as carrier gas at 150 ml min^{-1}. A thin layer of quartz wool was placed on a mesh support in the middle of the catalytic stage to hold the catalyst particles. 0.5 g of catalyst was loaded evenly between two layers of quartz wool. After pyrolysis and catalytic reforming, the gas product was passed through a two-stage ice-water condenser for condensable vapors condensing. The non-condensable gas was periodically sampled and analyzed on-line, while liquid in
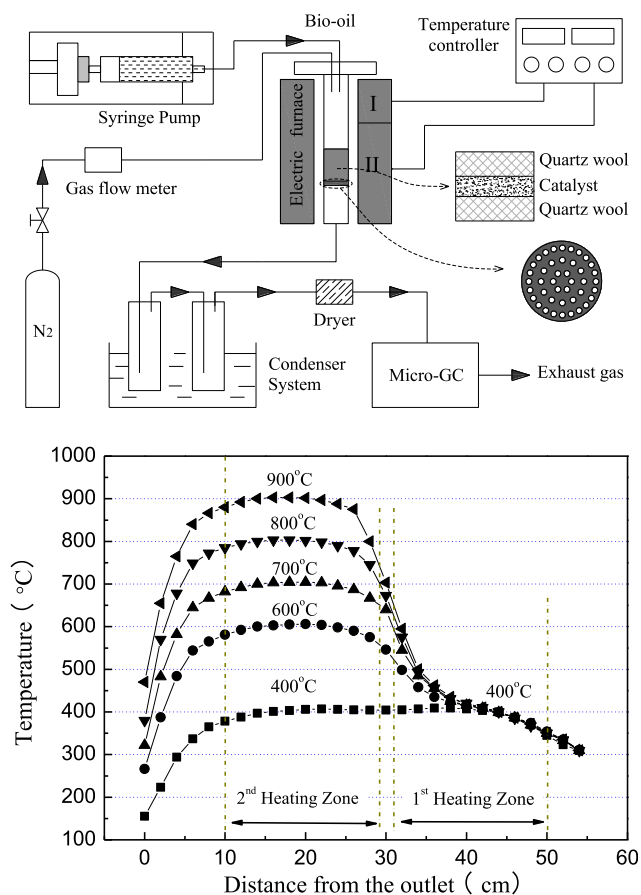
Fig. 1 – **Schematic diagram of the two staged fix bed gasifier system and the temperature distribution along the reactor.**

the condenser was collected for further analysis. Experiments were repeated twice to ensure the reliability of the results. Blank experiments were carried out with quartz sand as a control experiment.

The gas product was measured using a dual-channel gas chromatograph (GC) (Micro-GC 3000A, Agilent Technologies, USA) that was equipped with thermal conductivity detectors (TCD). Channel A (molecular sieve 5A) was used to detect H_2, CO, CH_4 at 110 °C and channel B (a chromatographic column of polystyrene) was to check CO_2, C_2H_2, C_2H_4 and C_2H_6 at 105 °C [39,40]. The average value of three times measurements of each gas sample was used.

Adding water directly into the bio-oil was adopted to investigate the influence of water content to the process, and the amount was calculated based on the specified S/C (steam/carbon) ratio, which was defined as the total mole of water in the feed to the mole of carbon in bio-oil. Initial water content in bio-oil sample (71.57 wt%) has been considered for the calculation of S/C ratio.

Calculation methods

Based on the ultimate analysis, all the organic compounds can be simplified as CH_mO_n on a carbon basis. Hence, the reactions taking place during the steam reforming process of bio-oil can

be described by Eq. (1), similar to the description of the industrial process of methanol reforming for hydrogen production [41].

$$CH_mO_n + (1-n)H_2O \rightarrow CO + (1+m/2-n)H_2 \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 + Q \qquad (2)$$
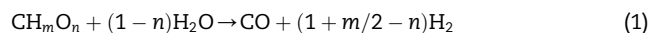
Water gas shift reaction (Eq. (2)) plays an important role for hydrogen production during the steam reforming of bio-oil. The maximum stoichiometric hydrogen yield can be achieved when the reaction of reforming occurs as follows:

$$CH_mO_n + (2-n)H_2O \leftrightarrow CO_2 + (2+m/2-n)H_2 \qquad (3)$$
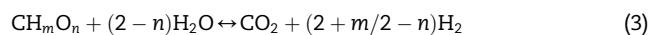
The hydrogen yield is defined as the mole ratio of H_2 in the product gas divided by H_2 in stoichiometric potential:

$$H_2\ \text{yield}(\%) = \frac{\text{moles of } H_2 \text{ obtained}}{(2+m/2-n) \times \text{moles of C in the feed}} \times 100$$

H_2 selectivity is defined as the mole fraction of H_2 in the produced gas containing H_2, CO, CO_2, CH_4 and C_2, which indicates the hydrogen purity in the gas product.

The yield of each carbon-containing gas (CH_4, CO, CO_2) is quantified by:

$$CH_4(CO, CO_2)\ \text{yield}(\%) = \frac{\text{moles of } CH_4(CO, CO_2) \text{ obtained}}{\text{moles of C in the feed}} \times 100$$

Carbon conversion shows the ability of carbon converted to gas, higher carbon conversion is corresponding to more carbon converted to gaseous product. Carbon conversion can be calculated as follows.

$$C\ \text{conversion}(\%) = \frac{\text{moles of } CH_4, CO, CO_2 \text{ and } C_2 \text{ obtained}}{\text{moles of C in the feed}} \times 100$$

Gas and liquid yields are the mass of gas or liquid divided by the feed (aqueous solution of bio-oil). While for solid product, as it is difficult to separate the deposited coke and solid residue in the second stage, the difference of the mass of solid in the second stage before and after each experiment was recorded as the weight of solid product to provide information for mass balance calculation.

Results and discussion

Optimization of process conditions for catalytic reforming of bio-oil

Ce, Mg modified Ni–Al catalysts have been reported to show higher reforming activity and significantly promote oxygenates conversion compared with pure Ni–Al catalysts [42,43]. In addition, our previous tests found that the Ni–Ce–Al has high hydrogen selectivity, so it was chosen for the optimization of process conditions. Catalytic steam reforming of bio-oil was carried out using the Ni–Ce–Al catalyst (0.5 g) at various catalytic temperatures (600, 700, 800 and 900 °C) and water to carbon ratios (S/C ratio) (3.54, 6 and 9). The effect of temperature on product gas is shown in Table 3. In addition, Table 4

Table 3 – Experimental results of catalytic steam reforming of bio-oil aqueous fraction with different catalytic temperature (T_2), S/C = 3.54, Ni–Ce–Al catalyst, 30 min reaction time.

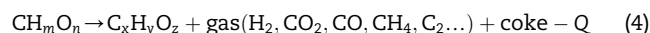| Experiment	1	2	3	4
T_1 (°C)	400	400	400	400
T_2 (°C)	600	700	800	900
Bio-oil feeding rate (g min^{-1})	0.3	0.3	0.3	0.3
Gas yield (g g^{-1} bio-oil)	0.03	0.09	0.33	0.37
Liquid yield (g g^{-1} bio-oil)	0.82	0.74	0.54	0.62
C conversion (%)	8.11	24.81	80.44	90.40
H_2 yield (%)	5.64	17.68	55.30	57.21
Gas composition (Vol%)				
H_2	60.82	61.68	62.44	60.07
CH_4	5.21	8.54	8.19	9.88
CO	11.59	15.96	9.53	8.91
CO_2	21.57	13.44	19.01	20.45
C_2	0.79	0.38	0.82	0.69

shows the influence of S/C ratio on the yield of products from catalytic steam reforming of bio-oil.

From Table 3, gas yield increased significantly from 0.03 to 0.37 g g^{-1} bio-oil (including water fraction) when the reforming temperature increased from 600 to 900 °C, and liquid yield was decreased from 0.82 to 0.61 g g^{-1} bio-oil. It indicated that more compounds in the bio-oil were converted to gas product with reforming temperature rising up. However, the WGS reaction was inhibited as the catalytic reforming temperature was increased from 600 to 700 °C due to the exothermic nature of the reaction; consequently the concentration of CO_2 decreased but CO increased. When the reforming temperature is lower than 700 °C, the process was mainly controlled by hydrocarbons reforming. And the lower carbon conversion might be due to incomplete reaction of bio-oil, and a majority of organics especially those large molecule compounds which need higher energy for cracking/reforming. As temperature increasing further (>700 °C), the concentration of C_{2+} decreased while CH_4 concentration increased from 8.19 to 9.88 Vol%. Therefore, the thermal cracking of large molecules in bio-oil might attribute to the increasing of carbon conversion at higher temperature.

Table 4 – Experimental results of catalytic steam reforming of bio-oil aqueous fraction with different S/C ratio, T_2 = 800 °C, Ni–Ce–Al catalyst, 30 min reaction time.

Experiment	3	5	6
T_2	800	800	800
S/C	3.54	6	9
Gas yield (g g^{-1} bio-oil)	0.33	0.30	0.27
Liquid yield (g g^{-1} bio-oil)	0.54	0.63	0.55
C conversion (%)	80.44	71.56	63.10
H_2 yield (%)	55.30	52.89	46.71
Gas composition (Vol%)			
H_2	62.44	64.59	64.61
CH_4	8.19	8.56	7.72
CO	9.53	6.62	6.30
CO_2	19.01	19.37	20.53
C_2	0.82	0.87	0.84

The reforming temperature showed significant influence on the hydrogen and gas yield. With the increase of reforming temperature (T_2) from 600 to 800 °C, H_2 yield increased remarkably from 5.64 to 55.30% and the carbon conversion showed similar tendency, increasing from 8.11 to 80.44%. It might be because hydrogen production was in the kinetic controlled region rather than the thermodynamic controlled region as the temperature was lower than 800 °C, and higher temperature is favorable for high H_2 yield and carbon conversion [44]. Thus, H_2 yield was increased with the increase of catalytic reforming temperature despite the exothermic reaction of the WGS. However, only a slight increase of hydrogen yield was obtained when the reforming temperature was between 800 and 900 °C, as the hydrogen production process is complex and is not only controlled by temperature, but is also influenced by many other factors, such as the CO_2 absorption enhanced reaction, WGS reaction, and steam reforming/cracking reactions. While CO_2 capture by carbonation process was thermodynamically unfavorable at higher temperature, thus the CO_2 fraction increased slightly from 19.01 to 20.45 Vol% (H_2 production was reduced at high temperature). However, the thermal cracking (Eq. (4)) and methanation reaction (Eq. (5)) of liquid oil also happened simultaneously during the reforming process [13,19], which resulted in a higher hydrogen production at higher reforming temperature:

$$CH_mO_n \rightarrow C_xH_yO_z + gas(H_2, CO_2, CO, CH_4, C_2...) + coke - Q \quad (4)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 - Q \quad (5)$$

In addition, the enhanced thermal cracking reactions at higher reforming temperature e.g. 900 °C will lead to more serious coke deposition and catalyst sintering (catalyst deactivation) [2]. Therefore, by considering the energy consumption of the process, 800 °C was selected as the optimized reforming temperature for further studies in this work.

Steam reforming of bio-oil was carried out with different S/C ratios at a catalytic temperature of 800 °C. Raw bio-oil mass flow was fixed at 0.3 g min^{-1} while the actual bio-oil (include added water) feeding rate was adjusted with S/C ratio. From Table 4, gas yield was decreased from 0.33 to 0.27 g g^{-1} raw bio-oil and C conversion was decreased from 80.44 to 63.1% when S/C ratio was increased from 3.54 to 9. A small decrease in CO and CH_4 molar fraction was also observed. H_2:CO ratio was 6.55, 9.76, 10.26 for the water to carbon ratio of 3.54, 6 and 9 respectively, and the H_2 concentration increased slightly, indicating that the Water Gas Shift reaction was favored with more steam.

However, the hydrogen yield was decreased from 55.30 to 46.71%. It is suggested that S/C ratio of 3.54 is already close to the steam saturation point for the bio oil used here. Furthermore, more water may lower the reactor temperature, which might inhibit the reforming reactions. Simultaneously, an increase of steam amount corresponds to higher flow rate and shorter residence time; thus resulting in a decrease of residence time of reactants in catalyst. The two factors might lead to the lower H_2 production at higher S/C ratio. Wang et al. [45] have proved the feasibility of hydrogen production from bio-oil catalytic reforming without steam addition. In addition, the energy consumed for evaporating and heating the

excessive steam to the specified reforming temperature may compromise the feasibility of the process. Therefore, an S/C ratio of 3.54 was selected for investigating the effect of catalyst during the steam reforming of bio-oil.

Steam reforming of bio-oil with different catalysts

Mass balance and hydrogen production
In this section, Ni−Al catalysts with different metal addition and silica sand were tested in the steam reforming of bio-oil. All of the tests were performed under the same reaction conditions: S/C ratio of 3.54, reforming temperature of 800 °C, and operation time of 30 min. Gas composition for each experiment was analyzed about every 4 min.

The profile of gas composition during catalytic steam reforming of bio-oil with Ni−Ce−Al catalyst is shown in Fig. 2. The maximum production of hydrogen (77.16 Vol%) was obtained at the beginning of the reaction process with the lowest CO_2 concentration (3.09 Vol%). The high catalytic activity at the beginning of the reforming process in terms of hydrogen production is due to the availability of abundant catalytic sites. However, with reaction extension, CO_2 content increased with the reduction of H_2 concentration until the gas concentration was gradually stabilized. Carbon conversion to gas increased from 22.68 to 47.35% mainly due to the rise in CO_2 content. It is suggested that the catalyst was deactivated with bio-oil steam reforming. In addition, the increase of C_2H_2 and C_2H_4 concentrations indicated the suppression of cracking/reforming reactions of hydrocarbons. Coke is formed when the catalyst was used for a certain time. The detailed information of coke formation and catalyst sintering will be discussed later.

As shown in Table 5, all the modified Ni−Al catalysts showed good performance for hydrogen production, the highest H_2 yield of 56.46% was obtained with the Ni−Mg−Al catalyst, followed by the Ni−Ce−Al (55.30%) and Ni−Zn−Al (52.01%) catalysts. Furthermore, the Ni−Ca−Al catalyst generated the lowest hydrogen production (46.58%) among the catalytic runs; however it still showed some catalytic activity for H_2 promotion in comparison with the controlled

Fig. 2 − Gas composition and carbon conversion during reforming process with time, Experimental conditions: S/C = 3.54, T_2 = 800 °C, Ni−Ce−Al catalyst.

experiment which produced only 38.72% of hydrogen production. Hydrogen yield showed similar trend with the hydrogen production in terms of weight of bio-oil.

Although hydrogen production showed large differences for different catalysts, the variance of gas yield was very limited. The Ni−Zn−Al and Ni−Mg−Al have relatively higher gas yield of 0.40 and 0.38 g g^{-1} bio-oil, respectively. It is around 0.32−0.34 g g^{-1} bio-oil for the left catalysts. Carbon conversion shows a similar trend with that of gas yield.

Hydrogen yield and gas composition varied greatly with different catalyst type. The high H_2 selectivity (composition) of 62.44 and 60.97 Vol%, as well as the low composition of CO_2 were obtained by the addition of Ce and Mn, respectively. It is suggested that the addition of Ce or Mn to Ni−Al catalyst may enhance the absorption of CO_2 by CeO and Mn_2O_3. The highest H_2 yield (29.02 mg g^{-1} bio-oil) was obtained for the Ni−Mg−Al catalyst, and the lowest hydrogen yield (23.94 mg g^{-1} bio-oil) was obtained with the Ni−Ca−Al catalyst, during the catalytic steam reforming of bio-oil. The benefit of Mg addition to the Ni−Al catalyst was suggested to block the active sites that were necessary for the coke formation on surface of catalyst [36]. Medrano and co-workers reported on the influence of the promoters, Mg and Ca, on Ni−Al catalysts in the catalytic steam reforming of pyrolysis liquids and reported that Ca showed poorer activity in relation to H_2 content and lower carbon conversion compared with Mg [8]; this is consistent with our results. In addition, it has been reported that steam absorption was enhanced by Mg, resulting in more hydrogen present in steam being converted into H_2 gas [18].

For the control experiment, the yield of CH_4 and C_2 gases is lower than that with Ni−Al catalysts. It indicated that thermal cracking of large molecules to small hydrocarbons e.g. C_2H_4 is dominant for bio oil gasification without catalyst compared with the steam reforming of light hydrocarbons, which are known as precursors for coke deposition on the surface of catalyst [32,43].

Life time assessment of the modified Ni−Al catalyst
Four-hour catalytic steam reforming of bio-oil with the modified Ni−Al catalysts has been carried out to evaluate the stability of the catalysts, and the result is shown in Fig. 3. The Ni−Mg−Al catalyst showed the most stability in terms of hydrogen production. For the other catalysts, hydrogen production was reduced for the first half hour. In the presence of the Ni−Ce−Al catalyst, H_2 yield was reduced from around 62% at the beginning to 50% after 30 min. It may be due to coke deposition on the catalyst surface, which could prevent the active sites being able to react with the reactants, thus the reforming process was inhibited; on the other hand, the WGS reaction was suppressed with the decrease in the capacity of CO_2 absorption, and it was not so favored for hydrogen production. Medrano et al. [8] investigated a modified Ni−Al catalyst for steam reforming of bio-oil at 650 °C in a fluidized bed, where the same tendency was observed after a 2-h stream test. The loss of activity was suggested due to carbonaceous species on the catalyst.

After 60-min test of steam reforming of bio-oil, it seems that all the modified Ni−Al catalysts were stabilized in relation to hydrogen production. Ni−Mg−Al still showed the best performance for catalytic reforming, with a H_2 yield of 52.18%
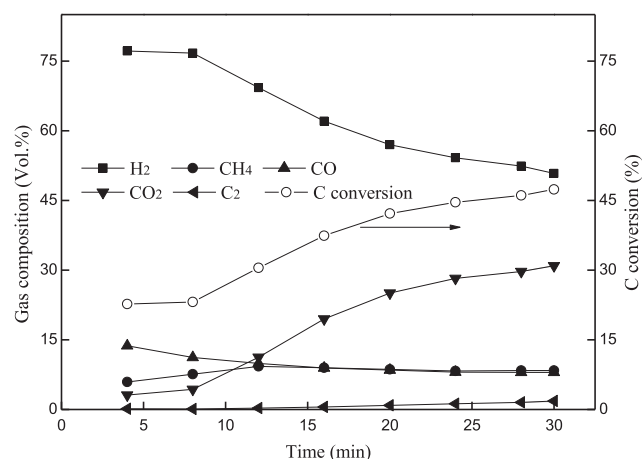
Table 5 – Experimental results of steam reforming of bio-oil aqueous fraction with or without catalysts, $T_1 = 400\ °C$, $T_2 = 800\ °C$, S/C = 3.54, bio-oil feeding rate = 0.3 ml min^{-1}, 30 min reaction time.

	Ni–Ca–Al	Ni–Ce–Al	Ni–Mg–Al	Ni–Mn–Al	Ni–Zn–Al	Sand
gas yield (g g^{-1} bio-oil)	0.33	0.33	0.38	0.32	0.40	0.36
C conversion (%)	80.20	80.44	90.42	76.04	94.05	84.74
H$_2$ yield (%)	46.58	55.30	56.46	50.98	52.01	38.72
Gas composition (Vol%)						
H$_2$	57.65	62.44	58.99	60.97	56.14	43.50
CH$_4$	9.99	8.19	8.08	8.69	8.49	10.57
CO	7.26	9.53	8.19	7.74	7.32	12.30
CO$_2$	23.55	19.01	22.94	21.58	26.16	29.99
C$_2$	1.55	0.82	1.79	1.02	1.89	3.64
Gas production (mg g^{-1} bio-oil)						
H$_2$	23.94	28.42	29.02	26.20	26.73	19.90
CH$_4$	33.25	30.57	31.00	30.06	32.41	36.23
CO	42.43	60.61	55.63	46.73	48.87	69.37
CO$_2$	223.47	207.17	251.66	213.29	276.30	217.71
C$_2$	9.48	5.87	12.54	6.60	12.75	15.05

obtained at 240 min, while other catalysts had a relatively lower yield range from 40 to 46%.

Characterization of the reacted catalyst

The XRD diffraction result of fresh and used catalyst collected after the 4 h test is shown in Fig. 4. Wide and asymmetric peaks of the fresh catalyst compared with the used catalyst indicate low crystallinity of the fresh catalyst. The main diffraction of the fresh catalyst corresponds to NiO, metal oxides, NiAl$_2$O$_4$ and Al$_2$O$_3$. The presence of NiO phase in the fresh Ni–Al catalyst (Fig. 4a) is consistent with the production of Ni phase after the reforming process, which was confirmed by the XRD pattern of the reacted catalyst (Fig. 4b). Ce, Zn, Mn modified catalysts showed high intensity of diffraction for oxide species, while no obvious signal was present for NiO on Ni–Ce–Al catalyst. High intensity of MO for the Ni–Mn–Al catalyst may account for the high selectivity of H$_2$ which resulted from CO$_2$ absorption enhanced effect at the initial phase of reforming process (shown in Fig. 3), as a large proportion of CO$_2$ could be absorbed by metal oxides (the

absorption effect of CO$_2$ gas has been observed during the experiment, not shown here). For the Ni–Ca–Al catalyst, it seems that a mainly crystal phase of NiO or Ni rather than Ni-metal could be identified; this might be related to the poor
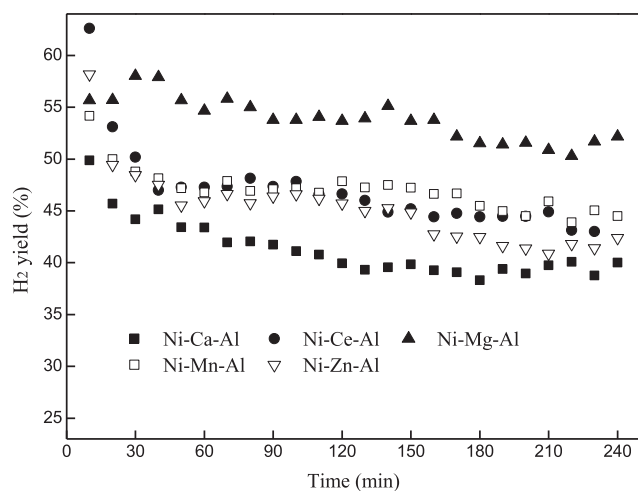

Fig. 4 – XRD analysis of fresh (a) and reacted (b) catalyst (MO refers to oxides of modified metal).

Fig. 3 – Hydrogen production from life-time assessment of Ni–Al modified catalysts. Experimental conditions: $T_1 = 400\ °C$, $T_2 = 800\ °C$, S/C = 3.54, 240 min reaction time.

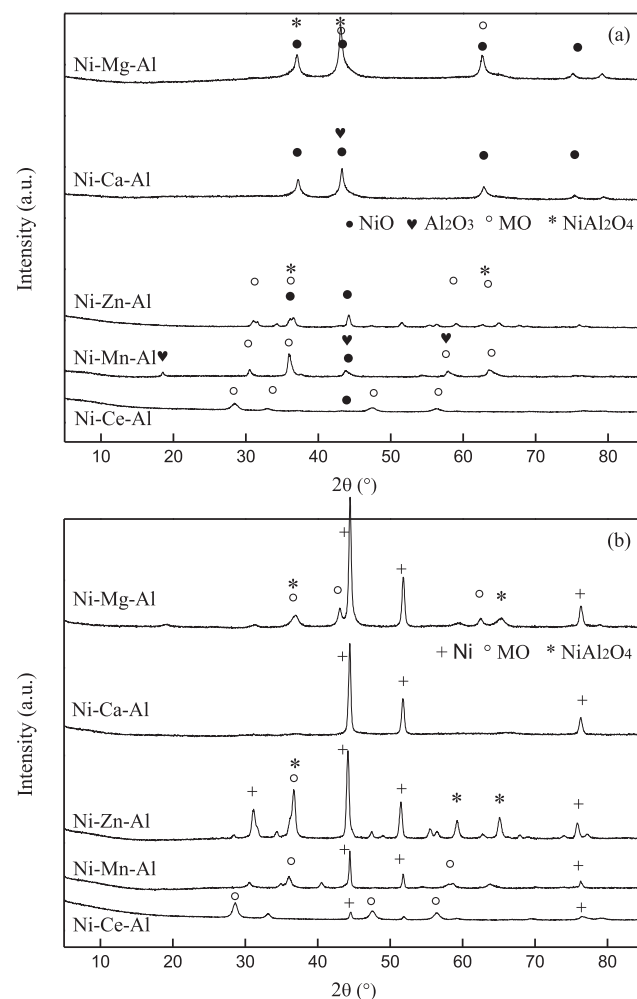performance of the Ni–Ca–Al catalyst during the catalytic steam reforming of bio-oil.

Both the fresh and reacted Ni–Mg–Al show peaks of MgO at diffraction angles 2θ of 42.9° and 62.3°, the presence of MgO was reported to enhance spillover of O and/or –OH anions from the carrier surface into the metal particles [46], which contributes to its high activity for hydrogen during the life time tests (Fig. 3). The patterns of $NiAl_2O_4$ and other compounds like NiO have very similar diffraction patterns, which make it difficult to confirm the presence of $NiAl_2O_4$ in the catalyst. The diffraction peaks at 44.5°, 51.8° and 76.3° detected in the reacted Ni–Al catalyst was attributed to metallic Ni, which resulted from the reduction of NiO by reducing gases (H_2, CO etc.) during the catalytic steam reforming of bio-oil. The diffraction peaks of carbon could be barely detected by XRD on the reacted catalysts, indicating the modified Ni–Al catalyst with good performance to carbon resistance.

Coke formation on the used catalysts was measured with TPO analysis (Fig. 5). There was a slight moisture loss peak (around 100 °C) for all Ni–Al catalysts and then the five catalysts undergo different weight loss patterns for coke oxidation.

The increasing weight peak ranging from 350 to 450 °C was regarded as the oxidation of metallic Ni in the catalyst (Fig. 4). The amount of coke can be calculated in terms of TG curves
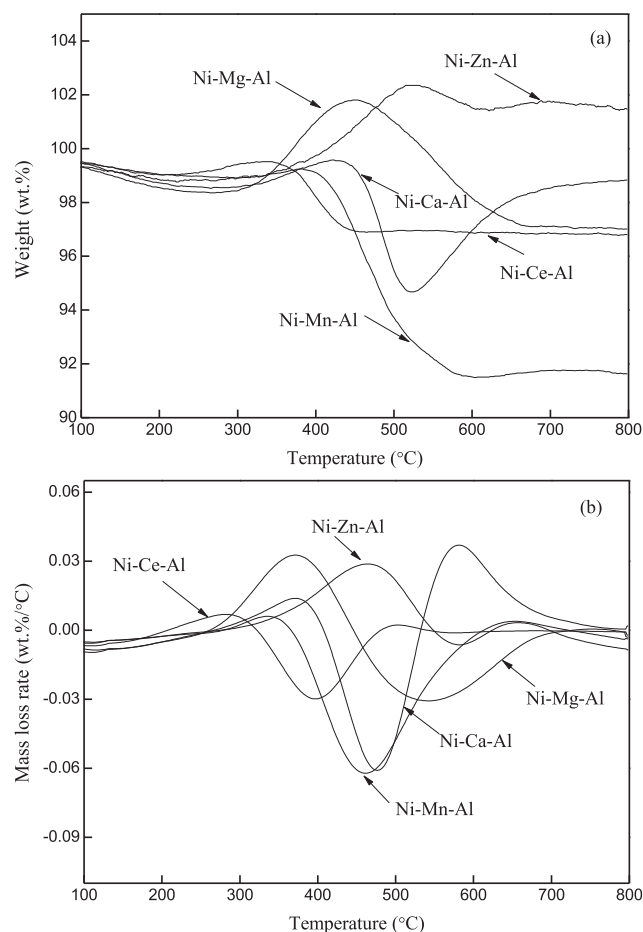
from 100 to 800 °C (the oxidation of metallic Ni was excluded), as mentioned in our previous work [47]. The calculated amount of deposited coke was 4.75, 2.62, 4.59, 7.27 and 0.73 wt % for the Ni–Al catalyst with Ca, Ce, Mg, Mn and Zn, respectively. The reacted Ni–Zn–Al shows the least coke deposition, it might illustrate the reason that Ni–Zn–Al has the highest carbon conversion (Table 5). It can be concluded that promoters Zn, Ce and Mg have less coke deposited than Mn and Ca. Wu et al. [6] also found that Ni–Zn–Al had better coke deposition resistance than Ni–Ca–Al from SEM and TPO results. The largest coke formation on the reacted Ni–Mn–Al catalyst is consistent with former reports that Ni–Mn–Al catalyst generated a large amount of carbon nanotubes during plastics gasification [48].

As shown in Fig. 5b, the lower carbon oxidation peak (350–440 °C) was ascribed to the combustion of amorphous carbon derived from the metal-support interface, while oxidation peak at higher temperature was assigned to filamentous carbon [21,49]. The generation of amorphous carbons could encapsulate the catalytic sites [21,50] during the thermal-chemical conversion process. Therefore, the presence of abundant amorphous carbons on the reacted Ni–Ce–Al, Ni–Ca–Al and Ni–Mn–Al catalysts might be responsible for the reduction of hydrogen production at the initial stage of catalytic reforming of bio-oil (Fig. 3).

More stable filamentous carbons (oxidation peak around 520 °C) were deposited on the reacted Ni–Zn–Al and Ni–Mg–Al catalyst, while the reacted Ni–Ca–Al catalyst seems to have a moderate deposition of filamentous carbons compared with other reacted catalysts. Medrano [8] found the promoter Ca and Mg to Ni–Al catalyst produced the generation of a more polymerized carbon that was difficult to be oxidized. The formation of filamentous carbons on the reacted Ni–Ca–Al, Ni–Mg–Al and Ni–Zn–Al has been confirmed from the SEM analysis (Fig. 6(a), (c) and (e)).

The average diameter of the filamentous carbon on the reacted Ni–Mg–Al was smaller than that on the reacted Ni–Zn–Al catalyst. Longer and thicker filamentous carbons were observed on reacted Ni–Zn–Al (Fig. 6); this might be responsible for the low hydrogen production during the catalytic reforming of bio-oil (Fig. 3).

In general, all the five modified Ni–Al catalysts showed good performance for bio-oil reforming. Ni–Mg–Al catalyst presented the most catalytic and stabilized performance in terms of hydrogen production, and the capillary filamentous carbon deposited had tiny influence on its activity. The good capability of CO_2 absorption contributed to the high H_2 yield and selectivity of Ni–Ce–Al at an early reaction stage. The rapid deactivation of Ce, Mn, Ca modified catalysts over the first 30 min of the experiment resulted from the amorphous carbon deposition on the catalyst. Ni–Zn–Al revealed the best carbon resistance from the TPO results. A relatively low activity for hydrogen production was obtained by Ni–Ca–Al, which was due to less interaction between Ni and Ca.

Fig. 5 – TGA analysis (a) and DTG (b) results of temperature programmed oxidation of reacted catalysts.

Conclusions

In this study, catalytic steam reforming of bio-oil aqueous fraction was carried out with Ni–Al catalysts in a two stage

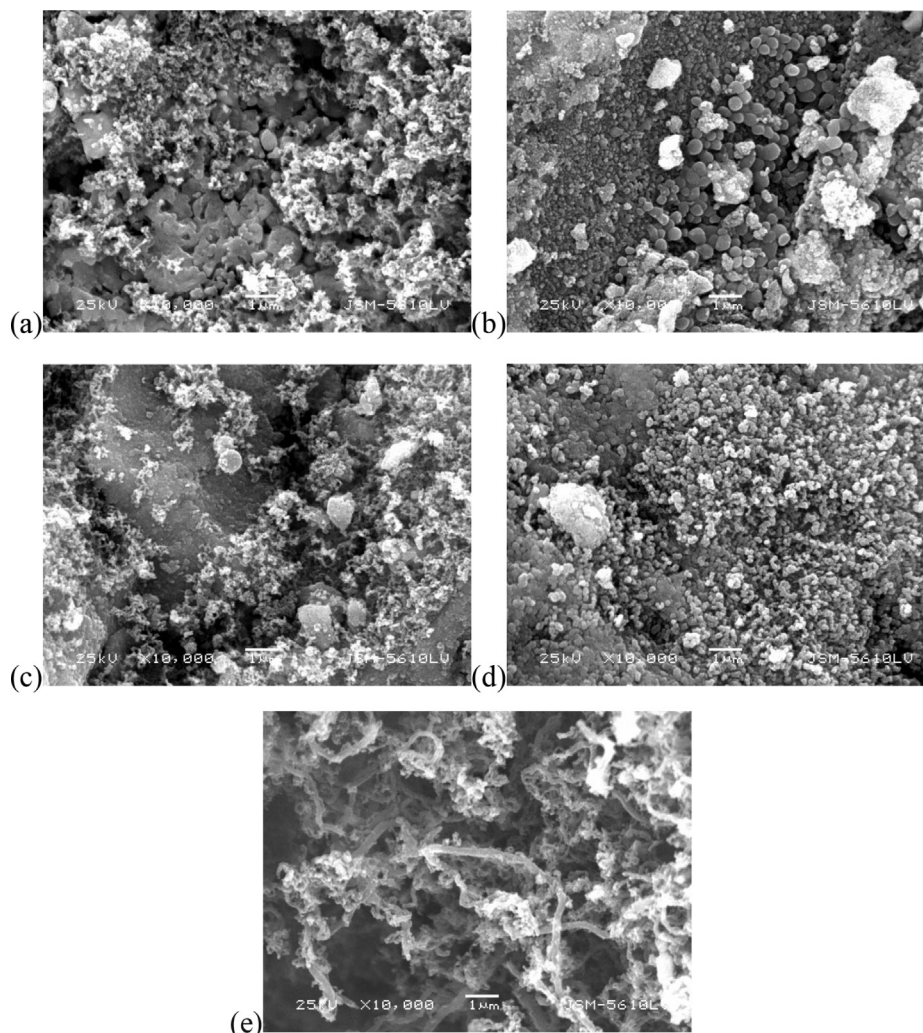**Fig. 6 — SEM images of the reacted Ni—Al catalysts: (a)Ni—Ca—Al, (b)Ni—Ce—Al, (c)Ni—Mg—Al, (d)Ni—Mn—Al, (e)Ni—Zn—Al.**

fixed bed reactor for hydrogen production. The conclusions can be derived as follows.

1) Significant influence on gas yield and composition was observed with catalytic temperature and steam to carbon ratio. High catalytic steam reforming temperature favors the reactivity of reforming reaction and thermal cracking of bio-oil compounds, thus promoting H_2 production and carbon conversion. WGS reaction and H_2 selectivity was found to be enhanced at a high S/C ratio, while excessive steam was found to be detrimental for H_2 production. An optimum reforming temperature and S/C ratio of 800 °C and 3.54, respectively, was obtained in this work.

2) The Ni—Al catalyst was modified with Ca, Ce, Mg, Mn and Zn. All the five modified Ni—Al catalysts showed high activity for H_2 production compared with non-catalytic trials. CO_2 absorption was suggested at the initial operation time of 30 min for the catalytic steam reforming process, resulting in a high H_2 yield. The Ni—Mg—Al exhibited the highest catalytic reactivity and stability with H_2 yield of 56.46%. Additionally, Ni-metal crystal phases seems to be beneficial for the catalytic activity of hydrogen production,

as the Ni—Ca—Al catalyst with mainly NiO phases and minor Ni-metal phases (XRD results) generated the lowest yield of hydrogen.

3) The modified Ni—Al catalysts exhibited excellent carbon deposition resistance. Filamentous carbons were observed on the Ni—Mg—Al and Ni—Zn—Al catalysts, which has a small effect on catalyst activity. Amorphous carbon deposited on the reacted Ni—Ce—Al, Ni—Ca—Al and Ni—Mn—Al catalysts was suggested to account for the rapid deactivation of catalytic activity in initial reforming process.

REFERENCES

[1] Parthasarathy P, Narayanan KS. Hydrogen production from steam gasification of biomass: influence of process parameters on hydrogen yield—a review. Renew Energy 2014;66:570—9.

[2] Valle B, Remiro A, Aguayo AT, Bilbao J, Gayubo AG. Catalysts of Ni/α-Al$_2$O$_3$ and Ni/La$_2$O$_3$-αAl$_2$O$_3$ for hydrogen production by steam reforming of bio-oil aqueous fraction with pyrolytic lignin retention. Int J Hydrogen Energy 2013;38(3):1307—18.

[3] Wu C, Huang Q, Sui M, Yan Y, Wang F. Hydrogen production via catalytic steam reforming of fast pyrolysis bio-oil in a two-stage fixed bed reactor system. Fuel Process Technol 2008;89(12):1306—16.

[4] Ma L, Wang T, Liu Q, Zhang X, Ma W, Zhang Q. A review of thermal—chemical conversion of lignocellulosic biomass in China. Biotechnol Adv 2012;30(4):859—73.

[5] Du S, Yang H, Wang X, Zhang S, Chen H. Effect of oxygen and steam on gasification of palm oil wastes. Proc ICE Waste Resour Manag 2014;167(1):25—34.

[6] Wu CF, Wang ZC, Huang J, Williams PT. Pyrolysis/gasification of cellulose, hemicellulose and lignin for hydrogen production in the presence of various nickel-based catalysts. Fuel 2013;106:697—706.

[7] Davidian T, Guilhaume N, Iojoiu E, Provendier H, Mirodatos C. Hydrogen production from crude pyrolysis oil by a sequential catalytic process. Appl Catal B Environ 2007;73(1):116—27.

[8] Medrano J, Oliva M, Ruiz J, García L, Arauzo J. Hydrogen from aqueous fraction of biomass pyrolysis liquids by catalytic steam reforming in fluidized bed. Energy 2011;36(4):2215—24.

[9] Wang D, Czernik S, Montane D, Mann M, Chornet E. Biomass to hydrogen via fast pyrolysis and catalytic steam reforming of the pyrolysis oil or its fractions. Ind Eng Chem Res 1997;36(5):1507—18.

[10] Wang S, Li X, Guo L, Luo Z. Experimental research on acetic acid steam reforming over Co—Fe catalysts and subsequent density functional theory studies. Int J Hydrogen Energy 2012;37(15):11122—31.

[11] Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels 2006;20(3):848—89.

[12] Kan T, Xiong J, Li X, Ye T, Yuan L, Torimoto Y, et al. High efficient production of hydrogen from crude bio-oil via an integrative process between gasification and current-enhanced catalytic steam reforming. Int J Hydrogen Energy 2010;35(2):518—32.

[13] Li H, Xu Q, Xue H, Yan Y. Catalytic reforming of the aqueous phase derived from fast-pyrolysis of biomass. Renew Energy 2009;34(12):2872—7.

[14] Rioche C, Kulkarni S, Meunier FC, Breen JP, Burch R. Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts. Appl Catal B Environ 2005;61(1):130—9.

[15] Xu W, Liu Z, Johnston-Peck AC, Senanayake SD, Zhou G, Stacchiola D, et al. Steam reforming of ethanol on Ni/CeO$_2$: reaction pathway and interaction between Ni and the CeO$_2$ support. ACS Catal 2013;3(5):975—84.

[16] Wang C, Dou B, Chen H, Song Y, Xu Y, Du X, et al. Renewable hydrogen production from steam reforming of glycerol by Ni—Cu—Al, Ni—Cu—Mg, Ni—Mg catalysts. Int J Hydrogen Energy 2013;38(9):3562—71.

[17] Bimbela F, Oliva M, Ruiz J, García L, Arauzo J. Hydrogen production via catalytic steam reforming of the aqueous fraction of bio-oil using nickel-based coprecipitated catalysts. Int J Hydrogen Energy 2013;38(34):14476—87.

[18] Liu S, Chen M, Chu L, Yang Z, Zhu C, Wang J, et al. Catalytic steam reforming of bio-oil aqueous fraction for hydrogen production over Ni—Mo supported on modified sepiolite catalysts. Int J Hydrogen Energy 2013;38(10):3948—55.

[19] Seyedeyn-Azad F, Salehi E, Abedi J, Harding T. Biomass to hydrogen via catalytic steam reforming of bio-oil over Ni-supported alumina catalysts. Fuel Process Technol 2011;92(3):563—9.

[20] Fatsikostas AN, Verykios XE. Reaction network of steam reforming of ethanol over Ni-based catalysts. J Catal 2004;225(2):439—52.

[21] Bimbela F, Chen D, Ruiz J, García L, Arauzo J. Ni/Al coprecipitated catalysts modified with magnesium and copper for the catalytic steam reforming of model compounds from biomass pyrolysis liquids. Appl Catal B Environ 2012;119:1—12.

[22] Wang S, Zhang F, Cai Q, Li X, Zhu L, Wang Q, et al. Catalytic steam reforming of bio-oil model compounds for hydrogen production over coal ash supported Ni catalyst. Int J Hydrogen Energy 2014;39(5):2018—25.

[23] Hu X, Lu G. Comparative study of alumina-supported transition metal catalysts for hydrogen generation by steam reforming of acetic acid. Appl Catal B Environ 2010;99(1):289—97.

[24] Wu CF, Williams PT. Hydrogen production by steam gasification of polypropylene with various nickel catalysts. Appl Catal B Environ 2009;87(3):152—61.

[25] Wang Y, Hu X, Mourant D, Song Y, Zhang L, Lievens C, et al. Evolution of aromatic structures during the reforming of bio-oil: importance of the interactions among bio-oil components. Fuel 2013;111:805—12.

[26] Chen P, Hou ZY, Zheng XM. Production of synthesis gas via methane reforming with CO$_2$ on Ni/SiO$_2$ catalysts promoted by alkali and alkaline earth metals. Chin J Chem 2005;23(7):847—51.

[27] Rennard D, French R, Czernik S, Josephson T, Schmidt L. Production of synthesis gas by partial oxidation and steam reforming of biomass pyrolysis oils. Int J Hydrogen Energy 2010;35(9):4048—59.

[28] Valle B, Aramburu B, Remiro A, Bilbao J, Gayubo AG. Effect of calcination/reduction conditions of Ni/La$_2$O$_3$—αAl$_2$O$_3$ catalyst on its activity and stability for hydrogen production by steam reforming of raw bio-oil/ethanol. Appl Catal B Environ 2014;147:402—10.

[29] Remiro A, Valle B, Aramburu B, Aguayo AT, Bilbao J, Gayubo AG. Steam reforming of the bio-oil aqueous fraction in a fluidized bed reactor with in-situ CO$_2$ capture. Ind Eng Chem Res 2013;52(48):17087—98.

[30] Wu CF, Williams PT. Effects of gasification temperature and catalyst ratio on hydrogen production from catalytic steam pyrolysis-gasification of polypropylene. Energy Fuels 2008;22(6):4125—32.

[31] Remiro A, Valle B, Aguayo A, Bilbao J, Gayubo AG. Operating conditions for attenuating Ni/La$_2$O$_3$—αAl$_2$O$_3$ catalyst deactivation in the steam reforming of bio-oil aqueous fraction. Fuel Process Technol 2013;115:222—32.

[32] Carrero A, Calles J, Vizcaino A. Effect of Mg and Ca addition on coke deposition over Cu—Ni/SiO$_2$ catalysts for ethanol steam reforming. Chem Eng J 2010;163(3):395—402.

[33] He L, Berntsen H, Ochoa-Fernández E, Walmsley JC, Blekkan EA, Chen D. Co—Ni catalysts derived from hydrotalcite-like materials for hydrogen production by ethanol steam reforming. Top Catal 2009;52(3):206—17.

[34] Frusteri F, Freni S, Chiodo V, Donato S, Bonura G, Cavallaro S. Steam and auto-thermal reforming of bio-ethanol over MgO and CeO$_2$ Ni supported catalysts. Int J Hydrogen Energy 2006;31(15):2193—9.

[35] Lónyi F, Valyon J, Someus E, Hancsók J. Steam reforming of bio-oil from pyrolysis of MBM over particulate and monolith supported Ni/γ-Al$_2$O$_3$ catalysts. Fuel 2013;112:23—30.

[36] Lisboa JS, Santos DCRM, Passos FB, Noronha FB. Influence of the addition of promoters to steam reforming catalysts. Catal Today 2005;101(1):15—21.

[37] Chen Y, Yang H, Wang X, Zhang S, Chen H. Biomass-based pyrolytic polygeneration system on cotton stalk pyrolysis: influence of temperature. Bioresour Technol 2012;107:411—8.

[38] Wang Y, Mourant D, Hu X, Zhang S, Lievens C, Li CZ. Formation of coke during the pyrolysis of bio-oil. Fuel 2013;108:439—44.

[39] Gao Y, Wang XH, Yang HP, Chen HP. Characterization of products from hydrothermal treatments of cellulose. Energy 2012;42(1):457—65.

[40] Xin S, Yang H, Chen Y, Wang X, Chen H. Assessment of pyrolysis polygeneration of biomass based on major components: product characterization and elucidation of degradation pathways. Fuel 2013;113:266—73.

[41] Pojanavaraphan C, Luengnaruemitchai A, Gulari E. Effect of support composition and metal loading on Au catalyst activity in steam reforming of methanol. Int J Hydrogen Energy 2012;37(19):14072—84.

[42] Sánchez-Sánchez MC, Navarro RM, Fierro JLG. Ethanol steam reforming over $Ni/M_xO_y-Al_2O_3$ (M = Ce, La, Zr and Mg) catalysts: influence of support on the hydrogen production. Int J Hydrogen Energy 2007;32(10):1462—71.

[43] Trane R, Dahl S, Skjøth-Rasmussen MS, Jensen AD. Catalytic steam reforming of bio-oil. Int J Hydrogen Energy 2012;37(8):6447—72.

[44] Lan P, Lan L, Xie T, Liao A. The preparation of syngas by the reforming of bio-oil in a fluidized-bed reactor. Energy Source Part A 2014;36(3):242—9.

[45] Wang S, Li X, Zhang F, Cai Q, Wang Y, Luo Z. Bio-oil catalytic reforming without steam addition: application to hydrogen production and studies on its mechanism. Int J Hydrogen Energy 2013;38(36):16038—47.

[46] Basagiannis AC, Verykios XE. Steam reforming of the aqueous fraction of bio-oil over structured $Ru/MgO/Al_2O_3$ catalysts. Catal Today 2007;127(1):256—64.

[47] Wu CF, Williams PT. Pyrolysis-gasification of post-consumer municipal solid plastic waste for hydrogen production. Int J Hydrogen Energy 2010;35(3):949—57.

[48] Wu CF, Nahil MA, Miskolczi N, Huang J, Williams PT. Processing real-world waste plastics by pyrolysis-reforming for hydrogen and high-value carbon nanotubes. Environ Sci Technol 2013;48(1):819—26.

[49] Wu CF, Williams PT. Investigation of coke formation on Ni—Mg—Al catalyst for hydrogen production from the catalytic steam pyrolysis-gasification of polypropylene. Appl Catal B Environ 2010;96(1):198—207.

[50] Wu CF, Williams PT. $Ni/CeO_2/ZSM$-5 catalysts for the production of hydrogen from the pyrolysis-gasification of polypropylene. Int J Hydrogen Energy 2009;34(15):6242—52.