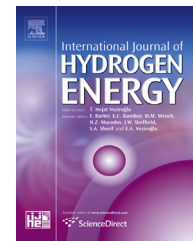


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Hydrogen production from catalytic reforming of the aqueous fraction of pyrolysis bio-oil with modified Ni–Al catalysts

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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.

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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

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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 O₂ 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/SiO₂ 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/Al₂O₃ by coprecipitation 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.	

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