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Production of high-pure hydrogen by an integrated catalytic process: Comparison of different lignocellulosic biomasses and three major components

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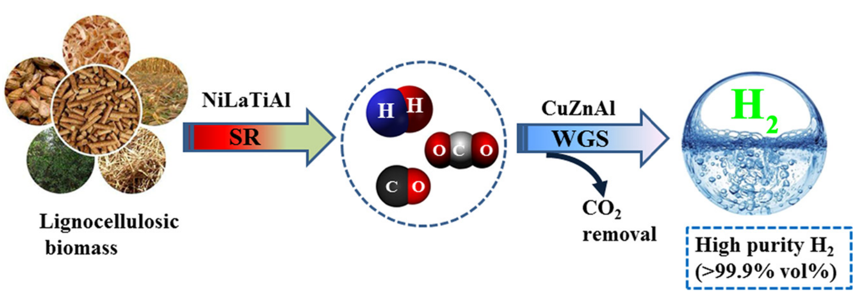
GRAPHICAL ABSTRACT

A proposed catalytic integrated process for the production of high-pure hydrogen from biomass *via* coupling the SR reaction and the WGS reaction.



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ABSTRACT

This work demonstrated an integrated catalytic process for the production of high-pure hydrogen by different lignocellulosic biomasses and three major components. The process involved in steam reforming (SR) of biomass, the water gas shift (WGS) and removal of CO_2. The results show lignin provided the highest hydrogen yield of 16.6 $gH_2/(100\ g_{biomass})$ with the H_2 purity of 99.93 vol%, which was close to theoretical yield of 17.5 $gH_2/(100\ g_{biomass})$. The actual hydrogen yields for three major components of biomasses decreased in the order: lignin > hemicellulose > cellulose. The yield of hydrogen derived from different biomass feedstocks (like rice husk, sawdust and sugarcane bagasse) mainly depended on their oxygen content, the contents of lignin, cellulose and hemicellulose and the reaction conditions. The high hydrogen yield and high purity of hydrogen obtained were attributed to that almost all of carbon-containing species were effectively converted to H_2 and CO_2 *via* coupling the SR with the WGS in the integrated process.

1. Introduction

Hydrogen is regarded as one of the most promising energies of the future due to its non-polluting and high heating value. Production of hydrogen using renewable biomass sources (like agricultural wastes or other waste streams) offers the possibility to reduce greenhouse gas emissions and expand the route of hydrogen production. Several promising approaches have been developed to produce bio-hydrogen, such

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as the gasification of biomass, the SR of biomass-derived oxygenates (like bio-oil, glycerol, polyols, alcohols, sugars, organic acids) and the supercritical water partial oxidative of biomass [1–3]. Two representative technologies, the biomass gasification [4] and the SR of biomass-derived oxygenates [5,6], have been widely investigated for producing renewable bio-hydrogen. Biomass gasification can produce hydrogen-containing syngas, typically operating in a gasifier at temperature above 800 °C in the presence of oxygen or water [7–9]. Under these conditions, biomass undergoes partial oxidation and the SR reactions, yielding bio-syngas (mainly including H_2, CO, CO_2 and CH_4), tar, char and other by-products. Generally, the biomass gasification efficiency, hydrogen yield and products distribution depend on the types of biomass feedstocks and gasifiers, gasifying agents and operating temperatures. The two major obstacles in the biomass gasification process, the formation of tar and complex gas mixtures that cause the decrease in the hydrogen content and the problem of the products separation, remain to be overcome.

Alternatively, the SR of biomass-derived oxygenates (like bio-oil) can efficiently produce bio-hydrogen with high hydrogen yield and hydrogen content in gas products, which combined the SR of organics to H_2 and CO with the WGS reaction to H_2 and CO_2 [10,11]. This process was typically conducted under medium temperature (500–800 °C) and atmospheric pressure using transition metal catalysts (especially Ni-based catalysts) or noble metal catalysts [12–14]. One of the major problems for the catalytic reforming of biomass-derived oxygenates is the deactivation of catalysts due to the deposition of coke [15,16]. Adding rare earth oxide into the Ni-based reforming catalysts or co-feeding bio-oil with methanol can partly improve the catalyst stability and prevent the deactivation of the catalyst in processes of the SR of biomass-derived oxygenates [17]. For production of pure hydrogen, another hindering is that the gas products generally contain CH_4, CO, CO_2 and other gaseous compounds, leading to the difficulty of hydrogen purification and the increase in the cost. In our previous work, a low-temperature electrochemical catalytic reforming method for efficient production of hydrogen using bio-oil was investigated [18,19].

It is well known that lignocellulosic biomasses mainly contain three main components: cellulose, hemicellulose and lignin. Yang, et al. compared the pyrolysis characteristics of hemicellulose, cellulose and lignin by TGA, FTIR and GC [20]. They found that the pyrolysis behaviors of three components were quite different. Hemicellulose is easy to be degraded in the lower temperature range of 220–315 °C. The pyrolysis of cellulose mainly occurs in the range of 315–400 °C, while that of lignin covers a wide temperature range (150–900 °C). At low temperatures ($<$ 500 °C), the pyrolysis of hemicellulose and lignin involves the exothermic reactions but that of cellulose is an endothermic process. The main gas products obtained from the pyrolysis of three components included H_2, CO, CO_2, CH_4 and other organics. Among three main components, lignin present the highest yield of hydrogen (4.2 $gH_2/100\ g_{lignin}$). More recently, Wu et al. investigated the production of hydrogen from the components of biomass by using a two-stage fixed bed pyrolysis/gasification reaction system [21]. They reported that cellulose produced the highest yield of hydrogen (1.2 $gH_2/100\ g_{cellulose}$) in the absence of steam and catalyst, but only 0.4 $gH_2/100\ g_{lignin}$ was obtained for lignin. The introduction of Ni-based catalyst significantly improved the hydrogen production, and the yield of hydrogen was increased from 1.4 to 3.7 $gH_2/100\ g_{lignin}$ in the presence of the NiZnAl catalyst. However, a large amount of by-products such as CO and solid residue were observed during the pyrolysis/gasification process. Highest CO concentration of 44.4 vol% was found for the cellulose pyrolysis/gasification, and the residue from that of lignin reached 52 wt%.

Lignocellulose is a sustainable feedstock for the hydrogen production as it is non-edible and abundant across most areas of the world. Extensive studies have shown that the hydrogen yield from biomass strongly depends on biomass feedstocks, reforming catalysts, reaction temperature, steam/biomass (S/B) ratio and reactor design [22–26]. Nickel-based catalysts, including Ni/Al_2O_3 catalyst and metals (like Mg, Cu) modified-Ni/Al_2O_3 catalysts, have been commonly used to increase hydrogen production and reduce tar production in the catalytic steam gasification/reforming of biomass, due to their effective catalytic performance and the comparative low cost [22–26]. For example, Arregi et al. reported that a maximum H_2 yield of 117 g per kg of biomass was obtained from the reforming pine wood sawdust over 14% NiO supported on Al_2O_3 at 600 °C with S/B ratio of 4 [27].

However, there are two problems that still remains a big challenge and requires further research efforts. As mention above, a large amount of CO by-product is inevitably generated during the production hydrogen by means of the gasification, SR or pyrolysis/gasification of biomass, which not only greatly reduces the yield of hydrogen but also goes against the gas purification for the production of high-pure hydrogen. Catalyst deactivation caused by the carbon deposition on catalysts also stood as another main problem for the production hydrogen through the SR of biomass. Accordingly, this work aimed to demonstrate a catalytic integrated process for the efficient production of high-pure hydrogen using different lignocellulosic biomasses and three major components of biomass. Almost all of carbon-containing species were effectively converted to H_2 and CO_2 via coupling the SR with the WGS reaction. High yield and purity of hydrogen from lignocellulosic biomasses and three components were proved, and their real hydrogen yields obtained from the catalytic integrated process are close to the theoretical values.

2. Materials and methods

2.1. Materials

The biomass of rice husk, sawdust and sugarcane bagasse was obtained from Anhui Yineng Bio-energy Co. Ltd (Hefei, China), the biomass components of lignin, cellulose and hemicelluloses were purchased from Hefei Lanxu Biotechnology Co. Ltd. (Hefei, China). Main ultimate analyses of the feedstocks are present in Table 1. All analytical reagents used were purchased from Sinopharm Chemical Reagent Company Limited (Shanghai, China).

2.2. Catalysts

The NiLaTiAl catalyst used for the SR reaction was prepared by the impregnation method [19]. For the preparation of TiO_2-γAl_2O_3 support, the solution containing tetra-*n*-butyl-titanate, cyclohexane, deionized water and aqueous ethanol was prepared. The volume ratio of tetra-*n*-

Table 1
Properties of biomass feedstocks.

Feedstock	Ultimate analysis (wt%)[a]				Biochemical analysis (wt%)		
	C	H	N	O[b]	Cellulose	HC[c]	Lignin
Sugarcane bagasse	48.90	6.10	0.22	44.78	43.86	26.24	21.82
Rice husk	44.90	6.35	0.45	48.30	44.12	21.93	25.74
Sawdust	46.20	6.02	0.48	47.30	41.94	19.33	29.63
Cellulose	45.04	6.21	0.01	48.74			
Hemicellulose	45.54	6.13	0.01	48.32			
Lignin	52.55	5.13	0.02	42.30			

[a] Dry biomass and ash free.
[b] By difference.
[c] HC: hemicellulose.