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Absorption-enhanced steam gasification of biomass for hydrogen production: Effect of calcium oxide addition on steam gasification of pyrolytic volatiles

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ABSTRACT

The effect mechanism of calcium oxide (CaO) addition on gasification of pyrolytic volatiles as a key sub-process in the absorption-enhanced steam gasification of biomass (AESGB) for H₂ production at different conditions was investigated using a two-stage fixed-bed pyrolysis–gasification system. The results indicate that CaO functions as a CO₂ absorbent and a catalyst in the volatiles gasification process. CaO triggers the chemical equilibrium shift to produce more H₂ and accelerates volatile cracking and gasification reactions to obtain high volatile conversion rates. Increasing the gasification temperature could improve the reaction rate of cracking and gasification of volatiles as well as the catalytic effect of CaO, which continuously increase H₂ yield. When the gasification temperature exceeds 700 °C, the sharp decrease in CO₂ absorption capability of CaO drastically increases the CO₂ concentration and yield, which significantly decrease H₂ concentration. The appropriate temperature for the absorption-enhanced gasification process should be selected between 600 °C and 700 °C in atmospheric pressure. Increasing the water injection rate (represented as the mass ratio of steam to biomass) could also improve H₂ yield. The type of biomasses is closely associated with H₂ yield, which is closely related to the volatile content of biomass materials.

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Introduction

Hydrogen, as an ideal clean energy carrier, has important functions in future energy structure. Biomass, as the only C-containing renewable resources with CO₂ neutral emission and abundant amount, has been regarded as a promising

renewable source for H₂ production [1]. Gasification, with the advantages of high efficiency, high conversion intensity and wide fuel adaptability, is one of the most intensively explored approaches for converting biomass to H₂ [2]. However, biomass, as the only hydrogen (H) source, produces considerably low H₂ yield because of its low content (generally less than 8%) [3–5]. Therefore, steam has been introduced into the

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biomass gasification process to produce extra H₂; a large number of H could be displaced from steam (H₂O) through the water–gas shift (WGS) reaction [6]. However, the H₂ yield from this conventional biomass steam gasification process is still limited by the chemical reaction equilibrium. A considerable amount of carbonaceous gases, e.g., CO, CO₂, and CH₄, and a specific amount of tar still exist in the product gas as the maximum experimental H₂ concentration is generally lower than 55 vol.% [7].

The absorption-enhanced steam gasification of biomass (AESGB) in the presence of calcium oxide (CaO) is a novel one-step technology for H₂ production. This method has recently gained increasing attention [8–16]. CaO, as a CO₂ absorbent, can effectively remove the CO₂ formed in the gasification process in situ. Thus, the limitations of chemical equilibrium of the reaction are altered, which results in the production of more H₂ [8,17]. Currently, several researchers have investigated this enhanced H₂ production process. The effect of various operation conditions, including molar ratio of CaO to C, temperature, mass ratio of steam to biomass, and so on, on the characteristics of H₂ production has been considered in thermodynamic analysis [13,18,19] and experimental studies [10,14,17,20,21]. A large increase in H₂ concentration and yield was obtained, which could be attributed to the reaction equilibrium shifts by the in situ CO₂ absorption of CaO. However, Udomsirichakorn et al. [22] found that CaO also functions as a catalyst during the AESGB process, which causes a higher H₂ production (256.81 mL g⁻¹ biomass) and a 67% reduction in tar content within the temperature of 550 °C–700 °C. The actual process of AESGB for H₂ production is a very complex multi-phase reaction process that involves a large number of reactions [2]. The detailed mechanism of this gasification process in the presence of CaO cannot be attributed alone to chemical equilibrium shift stimulated by CO₂ absorption, that is, the catalytic effect of CaO [22,23], which is still rarely studied under this new process condition (600–700 °C, high amount of CaO addition) [24]. The detailed routes of equilibrium shift and catalytic mechanism remain ambiguous because of the complexity of the multi-phase reaction system. Thus, further studies should be performed to determine the mechanism of this gasification process.

Considering that pyrolysis is the first step of gasification, biomass materials that enter into the gasifier are first pyrolyzed into volatiles and solid residues (nascent char). Nascent volatiles and char immediately react with gasification agents (i.e., H₂O) to generate a high-grade product gas [25]. Therefore,

the complex process of AESGB can be decoupled to several relatively simple processes in the presence of CaO, which include biomass pyrolysis, volatiles and char gasification, volatile–char interactions, and WGS reaction. The volatile content in biomass is generally higher than 70 wt.%; thus, volatiles gasification has an important function in the H₂ production process [26]. The present study focuses on the enhancing mechanism of CaO addition on the steam gasification of the pyrolytic volatiles of biomass. A two-stage fixed-bed pyrolysis–gasification system was used to generate nascent pyrolytic volatiles, which were subsequently gasified with steam in the presence of CaO. The effect mechanism of CaO addition at different operation conditions, including molar ratio of CaO to C (CaO/C), gasification temperature, water injection rate (representing the mass ratio of steam to biomass), and biomass feedstock, was analyzed.

Experimental

Materials

Five typical Chinese local biomasses, namely, corn stalk, cotton stalk, wheat straw, sawdust, and rice husk, with particle sizes ranging from 124 μm to 250 μm were used. Proximate and ultimate analysis of biomass materials were performed using a TGA2000 (Las Navas, Spanish) and a CHNS analyzer (EL-2, Vario Germany), respectively. The low heating value was analyzed using a bomb calorimeter (Parr 6300, Parr Instrument Company USA). The results are presented in Table 1. The five biomasses with different chemical compositions showed evident differences in volatile contents, which subsequently affect the pyrolytic volatiles gasification. The biomass samples were previously dried for 12 h at 105 °C before use.

CaO was obtained from the calcination of CaCO₃ (analytically pure, Sinopharm Chemical Reagent Co., Ltd.) in a muffle furnace at 850 °C in atmospheric pressure for 4 h.

Experimental setup and methods

The experiment was performed in a two-stage fixed-bed pyrolysis–gasification system, as shown in Fig. 1. In the first stage, the reaction tube, with an internal diameter of 45 mm and an effective heating length of 300 mm, and a hanging stainless basket loaded with the biomass materials were used for biomass pyrolysis. In the second stage, the reaction tube

Table 1 – Proximate and ultimate analysis of five biomass samples used in the experiment.

Biomass sample	Proximate analysis (wt.%, ad ^c)				Ultimate analysis (wt.%, ad ^c)					LHV ^b (MJ/kg)
	M	V	A	FC	C	H	N	S	O ^a	
Corn stalk	3.45	73.62	10.50	12.43	41.43	5.33	1.42	0.11	37.76	14.70
Cotton stalk	8.15	69.00	2.09	20.85	46.08	5.98	0.63	0.10	36.97	15.65
Wheat straw	5.03	67.36	9.50	18.15	39.69	5.49	0.53	0.18	39.58	13.91
Sawdust	4.30	78.48	1.67	15.56	48.25	5.93	0.07	0.18	39.60	16.65
Rice husk	4.29	59.90	16.19	19.62	39.47	5.26	0.34	0.07	34.38	13.70

^a Calculated by difference.

^b Low heating value.

^c Air dry basis.

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