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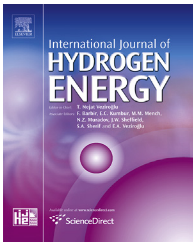

Thermodynamic analysis of syngas generation from biomass using chemical looping gasification method

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ABSTRACT

Chemical looping gasification (CLG) is a novel technology to convert carbon-containing feedstock into syngas. In the technology, lattice oxygen of oxygen carrier is used as oxygen source for char gasification, and then the reduced oxygen carrier is regenerated in air atmosphere. In this paper, the mechanism of CLG of biomass using Mn_2O_3 as oxygen carrier was discussed firstly and then thermodynamic analysis of syngas generation from biomass was performed by Gibbs free energy minimization method. Chemical equilibrium calculations were carried out to study the effects of Mn_2O_3/biomass, operation temperature, pressure, and steam/Mn_2O_3 on the gasification characteristics. The optimal thermodynamic conditions were determined to improve H_2 and CO concentrations as high as possible. The optimal Mn_2O_3/corn cob is 0.18 to obtain the highest CO and H_2 yields. The results suggest that the preferential conditions are achieved at 1000 °C and atmospheric pressure, under these conditions, the total dry concentration of CO and H_2 is 98.8% in the syngas. Steam can be used in the CLG to modify the H_2/CO in the syngas. The carbon conversion also increases under oxidizing atmosphere of steam.

Introduction

Biomass, the third largest source of energy in the world, is dominant choice for replacement of fossil fuels because of its renewability and carbon neutrality [1,2]. Biomass gasification is one of the prominent thermochemical conversion methods to produce biofuels, energy and other chemicals from biomass, and it has attracted a lot of researchers' interest in recent years [3]. During biomass gasification process, gasifying agents such as air, oxygen, steam, carbon dioxide etc. are required. Comparing with other agents, the heating value of synthesis gas produced by pure oxygen gasification is the highest. Moreover, when steam or carbon dioxide is used as

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gasifying agent, a lot of external heat is required because the gasification reaction is strong endothermic. Unfortunately, the high cost of oxygen increases the operating cost of pure oxygen gasification [4–7].

Chemical looping gasification (CLG) is a novel technology to convert carbon-containing feedstock into syngas. In this technology, lattice oxygen of oxygen carrier is used to replace pure oxygen to gasify, and the concept is derived from chemical looping combustion (CLC) [8]. The schematic of CLG of biomass is illustrated in Fig. 1. In the fuel reactor, biomass is pyrolyzed into three phase products of gas, tar, and char first and then the products of pyrolysis react with oxygen carrier. Oxygen carrier provides oxygen and the tar and char are broken down into syngas. In the air reactor, the reduced oxygen carrier is regenerated in air atmosphere. The principle of CLG is similar to the production of hydrogen via hydrolysis of hydrides [9–11]. Because the oxidation reaction is strong exothermic, the required heat of biomass gasification can be provided by the circulating oxygen carrier from the air reactor. Works have been done to investigate the feasibility and adaptability of CLG technology. Huang et al. investigated the CLG of biomass process with natural hematite as oxygen carrier in a fluidized bed reactor. Comparing with biomass steam gasification, carbon conversion and gas yield increased by 7.47% and 11.02%, respectively, and tar content lowered by 51.53% [12]. Acharya et al. studied CLG of biomass for hydrogen-enriched gas production with in-process carbon dioxide capture. Experimental results show that the use of calcium oxide not only helps to reduce the concentration of carbon dioxide to nearly zero but also increases the hydrogen concentration [13]. The NiO modified iron ore as an oxygen carrier in the CLG of biomass process was also investigated by Huang et al. Results show that the presence of spinel-type nickel iron oxide $NiFe_2O_4$ apparently improved the reaction rate of char gasification [14].

Oxygen carrier is the key issue for achieving CLG process. Cu-, Mn-, Co-, Ni-, Fe-, Ce-based oxygen carriers are greatly applied and proved to be fitted candidates in the CLC [15–18]. Among the oxygen carriers, Cu-, Mn-, Co-based oxygen carriers can release oxygen when temperatures are high [19–21]. When the three oxygen carriers are used in the CLG, the gasification rate of char can increase because the reaction between oxygen carrier and char is changed from solid–solid reaction to gas–solid reaction. Due to the low melting point of copper oxides, agglomeration may be the biggest issue of Cu-based oxygen carrier in high temperature. Comparing with cobalt oxides, the price of manganese oxides are much low. Moreover, the performances of high conversion of fuel, high temperature stability, and high oxygen transfer capacity of Mn-based oxygen carrier or manganese ore as an oxygen carrier are presented in the CLC. Additionally, some Mn-based materials show low rate of attrition, making them very promising oxygen carrier materials for applications related to CLC [22–24]. The CLC and CLG processes all refer to the conversion of fuel. The only difference is a low oxygen carrier/fuel is used in the CLG because its target product is synthesis gas rather than heat. Hence, the use of cheap Mn-based materials for CLG technology seems to be very appropriate.

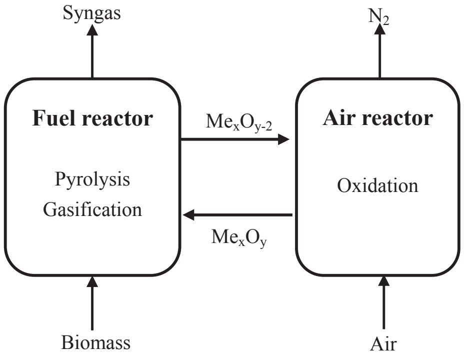

Fig. 1 – The schematic of CLG of biomass.

In the present study, the feasibility of Mn_2O_3 as oxygen carrier for CLG was investigated by thermodynamic method. An optimal mol ratio of biomass to Mn_2O_3 was determined to obtain the highest H_2 and CO yields. Besides, the equilibrium calculations employing the Gibbs free energy were used to evaluate the influence of operation temperature, pressure on gasification products. Moreover, the effect of steam on composition adjustment of the products was also analyzed.

Mechanism

Gasification is a thermochemical process in which the solid fuels are converted to combustible gases by partial oxidization. Similar to the coal gasification, the biomass gasification process is divided into two-step: pyrolysis and gasification [25]. The first step mainly produces tars and noncondensable gases at 200 °C~500 °C. The gasification process takes place at 500 °C~1200 °C. In the gasifier, the pyrolysis and gasification occur simultaneously. The chemical reactions which occur in CLG of biomass with Mn_2O_3 as oxygen carrier are presented as follows:

In the fuel reactor:

$$\text{Pyrolysis: } C_nH_mO_y \leftrightarrow \text{syngas } (H_2, CO, CH_4, CO_2) + \text{tar} + \text{char} \tag{1}$$

During gasification process, the products of pyrolysis react with Mn_2O_3 (assuming the gasification temperature 1000 °C):

$$CO + 3Mn_2O_3 \leftrightarrow CO_2 + 2Mn_3O_4 \qquad \Delta H = -192.2 \text{ kJ/mol} \tag{2}$$

$$CO + Mn_2O_3 \leftrightarrow CO_2 + 2MnO \qquad \Delta H = -101.9 \text{ kJ/mol} \tag{3}$$

$$H_2 + 3Mn_2O_3 \leftrightarrow H_2O + 2Mn_3O_4 \qquad \Delta H = -160.0 \text{ kJ/mol} \tag{4}$$

$$H_2 + Mn_2O_3 \leftrightarrow H_2O + 2MnO \qquad \Delta H = -69.7 \text{ kJ/mol} \tag{5}$$

$$CH_4 + 3Mn_2O_3 \leftrightarrow 2H_2 + CO + 2Mn_3O_4 \qquad \Delta H = 65.8 \text{ kJ/mol} \tag{6}$$