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Effect of torrefaction on the high temperature steam gasification of cellulose based upon the Gibbs free energy minimization

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Abtract

The steam gasification can convert biomass into syngas, which can be conveniently used as fuels or chemical raw materials. Cellulose, as an important component of biomass, has a significant effect on the gasification behavior. Steam gasification behaviors of raw and torrefied cellulose at high temperature were investigated using a non-stoichiometric equilibrium model. The effect of torrefaction severity on the high temperature steam gasification of cellulose was evaluated. With increasing of steam/cellulose molar ratio, the molar numbers of hydrogen and carbon dioxide increased, whereas the molar number of carbon monoxide decreased. Less than 1.0 molar ratio of steam/cellulose was recommended for raw and torrefied celluloses. The methane steam reaction for severely torrefied cellulose at low steam/cellulose molar ratio was found. The molar number of the hydrogen increased from 1.992 to 2.016 mol with the increasing of torrefaction temperature from 250 to 300 °C. The influence of steam content on the water-gas reaction was more obvious than that of reaction temperature. This study will promote the development of steam gasification of biomass for the purpose of high efficiency utilization.

Keywords: Cellulose; Steam gasification; Torrefaction; Thermodynamic equilibrium model; High temperature;

1. Introduction

Gasification is a promising technique for thermochemical conversion of biomass into syngas, which can be conveniently used for fuels or chemical raw materials in many fields [1]. However, raw biomass is characterized by its high moisture content and oxygen content, lower higher heating value (HHV) and energy density levels,

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hygroscopic nature, and low bulk density [2]. These drawbacks will lead to low efficiency for its collection, grinding, storage and transportation [3], and result in poor quality syngas from biomass gasification [4]. Torrefaction occurs at a specific temperature range in the absence of oxygen, which can remove all the moisture and a part of oxygen-containing functional groups [3]. The torrefied biomass has lower oxygen content, higher heating value and energy density, which can improve the quality of syngas [5]. At present, torrefaction is considered to be a promising pretreatment technique of biomass before gasification. Lignocellulosic biomass is mainly consisted of cellulose, hemi-cellulose and lignin. Cellulose is the most abundant component among three components, which accounts for about 50 wt% of biomass [6]. Some thermally unstable functional groups in the cellulose molecule are largely decomposed during torrefaction. In addition, biomass gasification is a complicated chemical process, which is caused by interactions among three components. It is necessary to investigate individually the torrefaction of cellulose on its gasification behavior.

Gasification agent includes generally steam, air, oxygen, hydrogen and their mixtures. Steam gasification can generate high-quality syngas with higher heating value. This is because reduction reactions between steam and carbon, and reforming reactions between steam and the product gas (CH_4 and unsaturated hydrocarbons) both occur in the steam gasification [1]. In addition, the low-temperature gasification will lead to low heating value of the product gas, as well as the high content of tar [7]. Therefore, the high temperature steam gasification is selected as an good gasification technique.

Thermodynamic equilibrium analysis is suitable as a simulation tool for gasification processes, which can give a guide for the design, control, evaluation and improvement of processes. Thermodynamic equilibrium models possess general applicability for simulating different configurations as they are independent of the design and not limited to a specified range of operating conditions. At present, stoichiometric and non-stoichiometric equilibrium models are widely used for predicting the gaseous products at thermodynamic equilibrium state. Shabbar and Janajreh [8] conducted thermodynamics analysis of gasification process using the Gibbs energy minimization approach, considering three gasification agents including air, air-steam and solar steam, and found that the cold gasification efficiency of solar-steam gasification was the highest. Zainal et al. [9] applied equilibrium model to predict the gasification products of different biomass materials in a downdraft gasifier, and the calorific value and composition of the gaseous products could be predicted reasonably well. Li et al. [10] developed a non-stoichiometric equilibrium model based on the Gibbs free energy minimization to predict the product compositions of circulating fluidized bed coal gasifier. Jarungthammachote and Dutta [11] developed a modified thermodynamic equilibrium model of gasification in spouted bed and spout-fluid bed gasifiers, considering the carbon conversion in the constraint equations and the energy balance calculation, the modified model showed improvements. Ghassemiand Shahsavan-Markadeh [12] built a modified equilibrium model, considering carbon conversion and tar formation, for biomass gasification at air or mixture of air and oxygen. However, no investigation on the thermodynamic equilibrium analysis for the effect of torrefaction on high temperature steam of cellulose has been done.

In this study, a non-stoichiometric equilibrium model for cellulose steam gasification is established based on the Gibbs free energy minimization. The steam gasification behaviors of raw and torrefied celluloses are investigated, and the effect of torrefaction severity on the gaseous products of cellulose gasification is evaluated at several steam/cellulose molar ratios.

2. Materials and Methods

2.1. Material

The element components of raw and torrefied celluloses are shown in table 1, which are derived from the work of Wang et. al [13].

Table 1. H/C and O/C of torrefied cellulose.

Torrefaction temperature (°C)	O/C	H/C
raw	0.948	1.858
250	0.921	1.825