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Transient behavior of devolatilization and char reaction during steam gasification of biomass

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HIGHLIGHTS

- We examine biomass steam gasification process in terms of temperature and *S*/*B* ratio.
- Transient characteristics of devolatilization and char reaction were investigated.
- Cumulative gas production and composition changes were monitored.
- Contribution of each reaction stage on the product gas yield was analyzed.

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ABSTRACT

Steam gasification of biomass is a promising method for producing high quality syngas for polygeneration. During the steam gasification, devolatilization and char reaction are key steps of syngas production and the contributions of the two reactions are highly related to gasification conditions. In this study, the transient characteristics of devolatilization and char reaction in biomass steam gasification were investigated by monitoring cumulative gas production and composition changes in terms of reaction temperature and *S*/*B* ratio. Contribution of each reaction stage on the product gas yield was studied in detail. The results provide important insight for understanding the complex nature of biomass gasification and will guide future improvements to the biomass gasification process.

1. Introduction

Biomass gasification is a promising technology for producing clean energy that allows flexibility for the end use, including the production of heat, electricity, Fischer–Tropsch (FT) fuels, dimethyl ether (DME), synthetic natural gas (SNG), methanol, etc. (He and Zhang, 2011; Moon et al., 2011a; Olofsson et al., 2005; Shie et al., 2011). Gasification is typically performed via partial oxidation or indirect heating with gasifying agents such as steam, air, or oxygen, principally producing hydrogen, carbon monoxide, carbon dioxide, methane, and higher hydrocarbons (Williams et al., 2007). The composition and yield of the gas produced varies widely depending on the desired end products, which can be controlled through reaction conditions including temperature, oxidant to biomass ratio, and residence time (Hannula, 2009). In general, a high H_2/CO ratio is required for successful biomass to liquid (BTL) or methanation processes as compared with the composition of conventionally-produced gas for heat or power generation.

In order to obtain hydrogen-rich gas, biomass steam gasification is essential (Gil et al., 1999), as the steam is crucial for heterogeneous char-steam gasification, the homogeneous water–gas shift reaction, and steam methane reforming. Devolatilization occurs in the earliest stages of biomass gasification, significantly influencing the subsequent homogeneous and heterogeneous reactions of released volatiles and char by altering initial conditions. Devolatilization is a complicated process including complex chemical pathways, multiphase reactions, and heat and mass transfer effects. Product gas and tar from devolatilization exhibit a range of characteristics in terms of the structure and composition of the biomass, which consists of lignin, cellulose, and hemicelluloses and decomposes differently depending on the reaction conditions (Lin et al., 2009).

Reaction temperature is one of the most critical of the parameters in gasification. Gas yield increases greatly with higher reaction temperature because the rates of the pyrolysis and steam-related

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reactions increase with temperature; the latter can enhance hydrocarbon reforming of the gas stream as well as char gasification. In addition, the kinds and amount of gasifying agents employed significantly affect the composition and yield of the gas produced. Higher steam to biomass (S/B) ratios generally increase the amount of hydrogen and carbon dioxide produced and decrease the amounts of carbon monoxide and methane through steam reforming and water–gas shift reactions. In addition, tar yield decreases with increasing steam, which contributes to cracking and reforming of tar (Li and Suzuki, 2009; Xiao et al., 2011).

Compared to coal, devolatilization of biomass is especially important because of the higher volatile content of the material (Bharadwaj et al., 2004; De Diego et al., 2002; Di Blasi, 2008; Gomez-Barea et al., 2010). Detailed mechanisms and accurate models of devolatilization are needed for both academic and industrial applications, so in-depth study is proceeding for biomass pyrolysis mechanism (Blondeau and Jeanmart, 2012; Ranzi et al., 2008). However, despite global research efforts, the mechanism of devolatilization is still not fully understood, in contrast to char gasification, and is still approached empirically with no reliable reaction models (Gomez-Barea and Leckner, 2010). In most reports in the literature, studies of devolatilization used very small biomass samples, making it challenging to accurately measure the resulting gas composition; in addition, there is a paucity of information on the transient behavior of the gasification process (Gomez-Barea et al., 2010; Lu et al., 2010; Yu et al., 2011). In the meantime, application and modeling have treated devolatilization and char reactions as separate processes for the sake of convenience even though, in principle, these reactions can occur simultaneously. Therefore, it is necessary to examine the complete biomass-steam gasification process all at once—drying, devolatilization, and the char reaction—independently as well as simultaneously.

Within this context, it is investigated that the transient behavior of devolatilization and the char reaction. The composition and yield of gas produced were monitored as a function of time, and the characteristics of each reaction stage were studied in terms of reactor conditions such as temperature, steam to biomass (S/B) ratio, and residence time. Changes in cumulative gas yield, synthetic gas (syngas) composition, gas generation rate, and H_2/CO ratios over time were analyzed in order to understand the complex nature of the biomass gasification process.

2. Methods

2.1. Materials

Korean pine wood chips with an average particle size of 5 mm were used as feedstock which has moisture 6.4%, volatile matter 75.9%, fixed carbon 17.4%, ash 0.3% and C: 49.5%, H: 6.2%, O: 44.1%, N: 0.1% on the basis of dry ash free, S: 215 mg/kg and lower heating value 19.7 MJ/kg. It was preferable to start with dry wood chips, as obtained higher heating values than when average biomass samples with higher moisture content were used.

2.2. Apparatus and procedures

Fig. 1 shows a schematic of the experimental biomass steam gasification system. Heat for a tube furnace (1050 mm long, 68 mm i.d.) was supplied by an electric heater with a maximum temperature of 1000 °C. Once the furnace reached isothermal conditions, steam at 400 °C was supplied from a steam generator while 10 g of biomass was introduced into the furnace using a sample boat. It is notable that using this amount of feedstock made it possible to measure the transient composition of the product gas as well as yield. Nitrogen was used to create an anoxic atmosphere and as a carrier gas with the flow rate of 1.7 L/min. The feedstock boat and steam were fed into the reactor simultaneously, and the amount of steam injected ranged from 0 to 0.24 g/min/g of biomass for each run. After a multistage tar trap, the produced gas was transferred into a continuous gas analyzer (ND-IR/TCD analyzer, ABB CO. Ltd., Model: AO2020) for composition analysis and a wet gas meter for measuring flow rate. The product gas composition and flow rate were monitored as a function of time to analyze the transient characteristics of each reaction stage. The reaction temperature ranged from 700 to 900 °C, and total reaction time was fixed at 20 min, a sufficient time period in which to see the devolatilization and char reaction characteristics.

3. Results and discussion

In general, the biomass steam gasification process can be divided into devolatilization and char reaction stages. In the first stage, volatiles are rapidly released from the biomass by thermochemical decomposition, which is governed mainly by the heat transfer rate, the convection and diffusion of released gases, and the chemical bond strength of the biomass. The thermal cracking process has been only rudimentarily modeled; similarly, a simple model for the pyrolysis reaction is available for use (1) (Yu et al., 2011) or a more comprehensive model for use kinetics (Ranzi et al., 2008). In the char reaction, homogeneous and heterogeneous reactions between major product gases, steam, and biomass char occur simultaneously, as shown below in reactions (2)–(7) (Bustamante et al., 2004; Lee et al., 2007; Thunman et al., 2001; Yan et al., 2010)

$$C_xH_yO_z \rightarrow aCO_2 + bH_2O + cCH_4 + dCO + eH_2 + fC_2 + \text{tar}(\text{Pyrolysis}) \tag{1}$$

$$C + H_2O \rightarrow CO + H_2 \ (\text{Char gasification}) \tag{2}$$

$$CO + H_2O \rightarrow H_2 + CO_2 \ (\text{Water-gas shift}) \tag{3}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \ (\text{Steam-methane reforming}) \tag{4}$$

$$C + CO_2 \rightarrow 2CO \ (\text{Boudouard}) \tag{5}$$

$$C + 2H_2 \rightarrow CH_4 \ (\text{Methanation}) \tag{6}$$

$$C_nH_m + 2nH_2O \rightarrow (2n + m/2)H_2 + nCO_2 \ (\text{Steam-tar reforming}) \tag{7}$$

In steam gasification process, it is hard to divide devolatilization and char gasification stages clearly since they occur almost simultaneously. However, characteristics of each stage are different and the two processes can be estimated in qualitative manner. The devolatilization occurs immediately after the feedstock is reached at a certain temperature and product gas is released rapidly even without any gasification agent. On the other hand, a gasification agent is needed for char gasification and relatively long residence time is required for char gasification comparing to devolatilization. The product gas from devolatilization stage can also participate to the char gasification but steam-char reaction is dominant in the steam gasification process.

Fig. 2 shows the transient syngas production in terms of reaction temperature and S/B ratio. The results show that the time required for devolatilization period decreased with increasing temperature. At 700 °C, it took about 5 min for most volatiles to be released, but at 900 °C it took only about 4 min. Fig. 2a shows the effect of temperature on the pyrolysis process in which devolatilization plays a dominant role. As the temperature increased, volatile gases escaped more rapidly and the amounts of CO, CH_4 and H_2 also increased, implying that more gaseous fuel was produced than liquid or solid material and thermal tar cracking contributed to gas composition during the devolatilization process. Primary tar such as acetic acid, phenol, xylene, furfural, etc. decrease as the temperature increases since H_2, CO and CH_4 generate