INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–13

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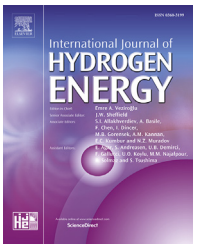

Dry reforming of model biomass pyrolysis products to syngas by dielectric barrier discharge plasma

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ARTICLE INFO

Article history:
Received 28 November 2017
Received in revised form
2 April 2018
Accepted 14 April 2018
Available online xxx

Keywords:
Biomass
Tar
Reforming
Dielectric barrier discharge (DBD) plasma
Hydrogen
Syngas

ABSTRACT

Biomass is frequently used to produce CO and H_2 together with undesirable by-products containing CO_2 and liquid tar by pyrolysis and gasification. This leads to decreased energy efficiency and increased maintenance costs. This study investigated the reforming of biogas and tar, respectively, using non-thermal plasma featuring dielectric barrier discharge (DBD). The gas surrogates studied were CH_4 and CO_2, and toluene was used as a substitute for tar. During reforming of biogas, CO or H_2 was added to the CH_4 and CO_2 to investigate their effects on CH_4 and CO_2 conversion. Both the discharge power and gas components influenced the conversion of CH_4 and CO_2. The conversion efficiency of CH_4 and CO_2 and the selectivity of H_2 and CO both increased with the discharge power while reforming the mixture of CH_4 and CO_2. The maximum conversion efficiency of CH_4 and CO_2 and selectivity of CO and H_2 were obtained with a CH_4:CO_2 ratio of 1:2. During reforming of toluene, the conversion efficiency of toluene reached a maximum value of 90% and the production yields of H_2, CO, and CO_2 reached respective maximums of 0.79, 2.24, and 1.51 mol/mol-toluene at a discharge power of 90 W and temperature of 300 °C. Higher temperatures of 400–500 °C did not favour toluene destruction due to the thermal breakdown of the quartz dielectric and the rapid decrease in the discharging intensity. In addition, reaction mechanism for reforming of both biogas and toluene was proposed to improve our understanding of the reforming process in DBD plasma.

Introduction

The utilization of biomass, a potential renewable energy species, is attracting increasing attention, with the growing consumption of fossil fuel energy and the environmental pollution problems that it causes [1]. Biomass can be used in thermal chemical, biological, or physical processes [2,3]. Biomass pyrolysis/gasification is the dominant mode for the conversion of biomass to energy and hydrogen production [4]. The main products of biomass pyrolysis are non-condensable gas products such as H_2, CO, CO_2, and CH_4, liquid tar, and solid char [5,6]. Of these, the most attractive product is high-quality syngas (mainly CO and H_2), which can be used to synthesise fuels, such as Fischer–Tropsch liquids, methanol, or mixed alcohols [7]. However, the production of undesirable products

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https://doi.org/10.1016/j.ijhydene.2018.04.112

containing CO_2 and liquid tar is a troublesome issue, which leads to decreased energy efficiency [8]. In addition, the condensation and aggregation of tar may plug downstream equipment and poison catalysts, leading to higher maintenance costs [9]. Therefore, the products of biomass pyrolysis have to be purified for most applications [10]. Efficient destruction of these undesirable products and improved syngas production are important for biomass pyrolysis.

Tar is a complex mixture of organic compounds, including single- and multiple-ring compounds, along with oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbons (PAHs) [11]. Therefore, tar removal studies usually consider the use of model compounds, such as phenol [12], naphthalene [13], and toluene [14]. Two approaches are used to reduce CO_2 and tar contents in the gas product: treatment inside the gasifier (primary methods) and hot gas cleaning after the gasifier (secondary methods) [15]. Secondary methods involve physical methods (wet scrubbing, filtration, and electrostatic precipitation), as well as thermal destruction and catalytic reforming [16].

The most common secondary techniques used for conversion of biomass pyrolysis products are thermal destruction, catalytic reforming, partial oxidation, plasma reforming, and miscellaneous reforming [17–20]. Direct thermal destruction can destroy hydrocarbons efficiently; however, it is generally conducted at temperatures above 1000 °C, leading to high energy consumption [21,22]. Catalytic reforming can efficiently reduce the temperature to ~600 °C, but the copious production of coke during reforming will deactivate catalysts and prevent the further conversion of CO_2 and tar into energy products [23]. Therefore, the application of non-thermal plasma to reforming of biogas and tar has attracted increasing attention because of its low temperature, high conversion efficiency, wide feasibility for a broad range of hydrocarbons, and the reduction in catalytic sensitivity and deterioration [24].

Tao et al. [25] demonstrated that plasma-enhanced catalytic steam reforming performed the best in terms of toluene decomposition, compared with direct thermal decomposition, plasma-assisted decomposition, or catalytic steam reforming. Zhu et al. [26] investigated toluene destruction using a rotating gliding arc discharge (GAD) reactor. The maximum destruction efficiency exceeded 95% at a toluene concentration of 10 g/Nm^3 and a flow rate of 0.24 Nm^3/h. This destruction efficiency was much higher than that obtained with direct thermal decomposition or catalytic reforming. Nunnally et al. [27] investigated the oxidative steam reforming of a simulated syngas containing vaporized naphthalene and toluene in a gliding arc discharge plasma reactor. The result indicated that conversion of naphthalene and toluene was higher than 90% and the energy efficiencies were 62.5 g/kWh for naphthalene and 215 g/kWh for toluene at a low tar concentration of 30 g/m^3 and a specific energy input (SEI) of 0.1 kWh/m^3. At high tar concentration of 75 g/m^3, conversion of naphthalene and toluene reached more than 70%, together with energy efficiencies of 93.6 g/kWh for naphthalene and 369 g/kWh for toluene at a SEI of 0.1 kWh/m^3. Wang et al. [28] used a dielectric barrier discharge (DBD) plasma-catalysis system to remove toluene, and achieved a maximum toluene conversion of 96% and a maximum CO_2 selectivity of 91% over Ce1Mn1 catalyst.

Removal of CO_2 has also attracted widespread attention due to its promotion effect on global warming as a greenhouse gas [29,30]. CO_2 could be reformed to produce syngas in the presence of CH_4. Zeng et al. [31] developed a DBD plasma reactor for CO_2 reforming of CH_4 and investigated the effect of CO_2/CH_4 molar ratio on the reforming performance. The results indicated that conversion of CH_4 increased with molar ratio of CO_2/CH_4 increasing from 1:9 to 9:1. However, the increase of CO_2/CH_4 molar ratio from 1:9 to 1:3 resulted in the obvious decrease of CO_2 conversion from 41.5% to 21.3%, which increased slightly with the further increase of CO_2/CH_4 molar ratio from 1:3 to 9:1. In contrast, Zhu et al. [32] demonstrated that conversion of CH_4 decreased from 75% to 59% with an increase of CO_2/CH_4 molar ratio from 0.17 to 1.00. Conversion of CO_2 increased initially from 16% to maximum 29% at the ratio of 0.17–0.67, followed by slowly reducing to 25% at the ratio of 1.00. Tu et al. [33] found that CH_4 conversion decreased from 16.2 to 8.2% with CH_4/CO_2 molar ratio increasing from 3:7 to 7:3, together with CO_2 conversion increasing from 10.5 to 16.1% and CO selectivity decreasing from 66.9 to 20% in dry reforming of methane by a GAD plasma. Zhu et al. [34] investigated reforming of biogas with a CH_4/CO_2 molar ratio of 3:7 using a rotating GAD plasma, and found that conversion of CH_4 conversion reached up to 52.6% at a total feed flow rate of 6 l/min.

Based on the above analysis, most studies have focused on the reforming of CH_4 and CO_2 in DBD plasma, few papers studied the reforming of biogas also containing H_2 and CO. Since H_2 and CO are also main components of biogas, it is important to investigate the effects of H_2 and CO on the direct reforming of biogas. Most previous studies focus on the reforming of biogas or reforming of tar. Few studies investigated reforming of both biogas and tar. In addition, the mechanism of reforming biogas and tar from biomass pyrolysis using DBD plasma was rarely reported.

In this study, a coaxial DBD non-thermal plasma system was applied for reforming of biogas and tar from biomass pyrolysis into syngas, respectively. The biogas surrogates were CH_4 and CO_2, and toluene was used as a substitute of tar. During reforming of biogas, the effect of discharge power and gas composition (CH_4:CO_2, CH_4:CO_2:H_2 and CH_4:CO_2:CO ratios) was studied. During reforming of tar, the effect of discharge power and heating temperature was investigated. In addition, the conversion mechanism of biogas and tar reforming were deduced by analysing the gaseous and liquid reforming products and their reaction pathways. These results will help to establish an overall view of the reforming of actual biomass pyrolysis products.

Materials and methods

At temperatures from 400 to 800 °C, the main products of biomass pyrolysis were CH_4, CO_2, H_2, CO, and liquid tar, as reported previously [6]. In the current study, the gas surrogates selected were CH_4 and CO_2. CO or H_2 was also added to the CH_4 and CO_2 to reflect realistic biogas reforming. In addition, toluene was selected as a tar model compound because (1) it is the main product of biomass pyrolysis [35], (2) it has a simple structure and high thermal stability, (3) it is less

Please cite this article in press as: Liu L, et al., Dry reforming of model biomass pyrolysis products to syngas by dielectric barrier discharge plasma, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.04.112