



Gasification of bio-oil: Effects of equivalence ratio and gasifying agents on product distribution and gasification efficiency



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HIGHLIGHTS

- High quality gas can be obtained through gasification of bio-oil.
- H₂ and CO level of product gas was higher than that of solid biomass gasification.
- Cold gas efficiency was considerably higher than that of solid biomass gasification.
- Tar content in the product gas was lower than that of solid biomass gasification.
- Bio-oil gasification may be economical for syngas production.

ARTICLE INFO

Article history:

Received 19 February 2016

Received in revised form 15 March 2016

Accepted 16 March 2016

Available online 18 March 2016

Keywords:

Bio-oil

Gasification

Equivalence ratio

Gasifying agents

ABSTRACT

Bio-oil derived from fast pyrolysis of rice husk was gasified for producing gas. The effectiveness of equivalence ratio and gasifying agents on the gas composition, ratio of H₂/CO, tar amount, low heating value, degree of oxidation and cold gas efficiency of the gas were comprehensively investigated. Under different equivalence ratios and gasifying agents, the gases can be used as synthesis gas for Fischer–Tropsch synthesis, fuel gas for gas turbines in a power plant and reducing gas for ore reduction, respectively. The H₂ concentration, CO level and cold gas efficiency of the resulted gas derived from gasification of bio-oil were significantly higher, while tar content was remarkably lower than those derived from gasification of solid biomass using the same equivalent ratio value and gasifying agent. In short, bio-oil gasification is economically feasible for large scale production of fuels and chemicals.

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1. Introduction

Decreasing reserves of fossil-based fuel sources and rising demand for transportation fuels, together with increasing concerns on CO₂ emission-driven climate change have resulted in an imperative need for new and renewable energy sources. As a renewable source, biomass is an attractive substitute for fossil feedstock because it is widely available and the utilization of biomass contributes to a reduction of carbon dioxide emission into atmosphere.

Bio-oil can be produced from biomass by a simple atmospheric pre-treatment process called “fast pyrolysis” (Chen et al., 2015; Kumagai et al., 2015; Venderbosch and Prins, 2010). A key advantage of bio-oil is that the production of bio-oil can be uncoupled in time, place and scale from the final bio-oil application. Because of the presence of a remarkable amount of water and oxygen, the

heating value of bio-oil is far lower than that of fossil fuel. However, the combustion experiments have showed that bio-oil could substitute for fossil oils in diesel engines, gas turbines, boilers, and furnaces for heat and power production or the production of combined heat and power (CHP) (Li et al., 2015; Zheng and Kong, 2010). To replace natural gas, heavy oil or diesel, bio-oil combustion in a standard 250 kW hot water generation device has been actively performed by BTG since 2006. A successful co-firing experimental with 15 × 10³ kg of bio-oil was performed in a 350 MWe natural-gas fired thermal power plant in Dutch in 2002. Nevertheless, it should be noted that combustion of bio-oil in boilers still needs special start-up and shuts down combustion procedures (Zheng and Kong, 2010), and wear, erosion and buildup of carbon deposits can be a serious problem with bio-oil combustion in diesel engines (Chiaramonti et al., 2007). In addition, bio-oil generated via fast pyrolysis could not be directly used as transport fuels. To use bio-oil in motor vehicles, it should be significantly upgraded to reduce viscosity, improve thermal stability and increase volatility. These changes can be accomplished by catalytic

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hydroprocessing or catalytic cracking. In the case of hydroprocessing, the oxygen in bio-oil is removed by reaction with H_2 in the presence of suitable catalysts (Wang et al., 2007). The reaction is called hydrodeoxygenation reaction, and water is one of the major byproducts of this reaction. A hydrocarbon type of product with oxygen content less than 1% was obtained. A 1 tpd (1 ton per day) demonstration unit has been developed, aiming at producing of barrels per day of jet fuel, diesel and gasoline from bio-oil based on UOP (Universal Oil Products Company) hydroprocessing technology (Butler et al., 2011). A limiting factor of bio-oil hydroprocessing is the limited availability and high cost of hydrogen because the process is a high hydrogen consumption reaction. Moreover, the process conditions, such as temperature and pressure, are rather severe (350–450 °C and 50–150 bar hydrogen), resulting in the formation of a great deal of gases and char (Liang et al., 2008). Therefore, the energy efficiency is relatively low. In parallel with research on hydroprocessing, catalytic cracking of bio-oil derives in the main from the technology presently utilized for crude oil. Although oxygen is removed from bio-oil as carbon dioxide, finite yields of hydrocarbon products of about 18–25 wt % (or 40% energetically) is reached and coke yields usually vary greatly from 30 to 50 wt% in the process (Takanabe et al., 2006). Catalyst deactivation and coke formation usually are the two major obstacles to commercial developments of catalytic cracking of bio-oil. By contrast, bio-oil catalytic cracking could be performed in a circulating fluidized bed. Coke is periodically burned off to regenerate catalysts and simultaneously supply adequate heat for the process. However, a good mathematical models of heat balance has not yet been established for catalytic cracking of bio-oil. Other approaches were used to obtain transport fuels, including bio-oil alcoholysis (Efika et al., 2012) which aims to reduce acidity and water content in the bio-oil, and bio-oil fermentation (Waheed et al., 2015), further converting anhydrosugars in bio-oil into ethanol or butanol. Therefore, extensive experiments and modeling studies should be conducted to determine and optimize alcoholysis process conditions, and more investigations are needed so as to improve the fermentability of bio-oil.

Generally, bio-oil can be used as a feedstock for gasification to produce gas, such as CO and H_2 , for further processing (e.g. methanol, Fischer–Tropsch). As an end-of-pipe technique, gasification can use low-cost feedstocks that could not be processed elsewhere in bio-refineries. Bio-oil may play an important role as a feedstock for gasification because the high density of bio-oil will result in lower shipment charges and storage costs as compared to chopped or baled biomass (Rogers and Brammer, 2009; Wright et al., 2008). Bio-oil gasification for obtaining CO and H_2 has been previously reported by other researchers (Wright et al., 2008). Entrained flow gasification of bio-oil for synthesis gas was performed and the optimal operating conditions for thermal bio-oil gasification, such as temperature and pressure, were comprehensively examined (Venderbosch et al., 2002). Effect of original source of bio-oil on its conversion and gas yield has been investigated in a novel designed Jiggle Bed Reactor (Latifi et al., 2015). In addition, steam gasification of bio-oil has been also performed (Chhiti, 2011). Unfortunately, gasification of solid biomass have been usually performed rather than gasification of bio-oil (Pereira et al., 2012). Equivalence ratio (ER), a significant parameter for gasification processes, is defined as the ratio of fed oxygen or air to the required oxygen or air for complete combustion of the fuel. It is also an important factor for a specific gasifier design and is usually utilized to maintain acceptable product gas quality levels. Moreover, gasifying agent also has a profound effect on the product yield and gas composition during biomass gasification. Many studies on the effects of equivalent ratio (ER) and all kinds of gasifying agents on gas composition from gasification of solid biomass have been undertaken (Seggiani et al., 2012; Son et al., 2011). Regrettably,

no detailed studies focus on the effect of equivalence ratio and the gasifying agent on the product distribution and composition.

In the present study, gasification of bio-oil was performed in a entrained flow gasifier and the effects of ER ranging from 0.1 to 0.5 and gasifying agents (air, oxygen-enriched air and pure oxygen) on the product distribution and gasification efficiency were comprehensively investigated. Moreover, the comparison between gasification and steam reforming of bio-oil as well as that between bio-oil gasification and pyrolysis/reforming of biomass was assessed. This study could give insight and understanding of the technical and economic potential of entrained flow bio-oil gasification for gas or syngas production and indicate its potential engineering application.

2. Material and methods

2.1. Materials

Bio-oil was obtained by fast pyrolysis of rice husk in a fluidized bed reactor. The effects of operating parameters on the fast pyrolysis process, the specification of the fluidized bed reactor and main characteristics of the bio-oil have been previously reported (Zheng, 2007). A filter (Haimin, TYL-1400) was used to remove the impurities, such as ash and other solid components with particle size larger than 100 μm , avoiding the formation of char blockage. Pure oxygen, air, and oxygen-enriched air were used as gasifying agents. The used pure oxygen was of analytical grade. The oxygen concentration in the oxygen-enriched air was 50 vol.%.

2.2. Apparatus

A lab scale entrained flow gasifier, which was made by stainless steel, was used for bio-oil gasification. The schematic diagram of the gasifier is shown in Fig. 1a. It consists of a feed section of gasifying agent and bio-oil, a nozzle and a high temperature section for bio-oil gasification. In the feed section of gasifying agent and bio-oil, an air compressor (Haoyuan, Model DW-2/15) was used to absorb, compress, and force gasifying agent into the nozzle. Bio-oil was also pumped into the nozzle by a gear pump (Sheage, Model H1F), and a heater (Huachi, CYS90) was employed to pre-heat bio-oil to 80 °C to markedly reduce its viscosity. The flow rate of the gasifying agent was regulated by a return piping valve and measured by a rotary flowmeter (Zhongneng, ZNLZ-15), and that of bio-oil was controlled by adjusting the rotative speed of the gear pump.

The nozzle was a key component in the gasifier because it is necessary to atomize bio-oil prior to gasification to guarantee its couplets gasification. With a view to the characteristics of bio-oil, an internal mixed airblast atomizer nozzle was chosen and designed for the experiments of bio-oil gasification. A schematic diagram of the airblast atomizer nozzle is given in Fig. 1b. The nozzle provided a spray angle with 30° and produced a fine spray with a mean droplet size below 40 μm . The high temperature section for bio-oil gasification was composed of a gasifying chamber and a electric heating-jacket (Huachi, HCH0019). The gasifying chamber was a hollow cylinder which was 1000 mm in length and 60 mm in inside diameter. The temperature of the electric heating-jacket can be adjusted up to 1200 °C. To monitor the temperature in the gasifying chamber, six thermocouples (Yida, WRR2-130) were inserted on 6 locations equally divided along its length. The gasification reaction temperature was remained at 1000 °C.

The gas from the gasifier was firstly conveyed through a special sampling system to detect the tar amount. This tar sampling system consisted of six impinger flasks (200 cm^3). The first four flasks were placed in an ice and water bath (0 °C) and the last two ones in

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