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Abstract

Hydrogen can be produced from woody biomass by conventional gasification methods such as partial oxidation or steam gasification. Since these methods produce gas products with low content of hydrogen as well as high content of tar from gasification reactors, post-treatment processes including tar cracker and water-gas shift reaction process are usually necessary for obtaining clean hydrogen-rich gas from woody biomass. In this work, a two-step gasification method was experimentally studied as an alternative to the conventional methods. The first step of the gasification is the fast pyrolysis of biomass to obtain liquid-phase product (bio-oil) and the second step is to gasify the bio-oil to hydrogen-rich gas in supercritical water. The fast pyrolysis of woody biomass was carried out using a bench-scale fluidized-bed reactor. The gasification of bio-oil in supercritical water was performed using a continuous-flow reactor packed with catalyst. The effect of major reaction conditions such as temperature and catalyst on hydrogen yield will be discussed.

1 Introduction

In a conventional gasification, syngas is produced by partial oxidation of ligno-cellulosic biomass at high temperatures of about 800 ^{o}C. One of characteristics of the bio-syngas product is the low hydrogen content. It is required to employ hydrogen formation processes such as water-gas shift reaction system after the gasification reactor when the desired product is hydrogen. Two-step biomass gasification is an alternative technology to produce clean syngas rich in hydrogen, in which lingo-cellulosic biomass is first converted to liquid-phase bio-oil and then the bio-oil is subsequently gasified in water to clean combustible syngas. Two processes can be operated independently. Since bio-oil has much better storage and transportation characteristics than solid-phase biomass itself, it may be economical to convert biomass to bio-oil at the place where the biomass feedstock is collected, and then the bio-oil is transported to the syngas production facility.

In this work, woody biomass is first converted to bio-oil in a bubble fluidized-bed fast pyrolysis reactor at a bench-scale, and then the water-phase bio-oil is subsequently gasified in supercritical water to produce hydrogen-rich gas without contaminants such as tar or char. The SCWG technology is known to produce hydrogen-rich gas by complete gasification of aqueous organic wastes or wet biomass under appropriate reaction conditions. A wide range of whole biomass has been treated by the SCWG processes, including sewage sludge [1,2], agricultural wastes such as potato wastes [3], black liquor from pulp mill [4], and alcohol distillery wastewater [5]. More fundamental SCWG studies with model compounds as a reactant have also been carried out to understand the gasification chemistry [6-11].

2 Experimental Apparatus and Methods

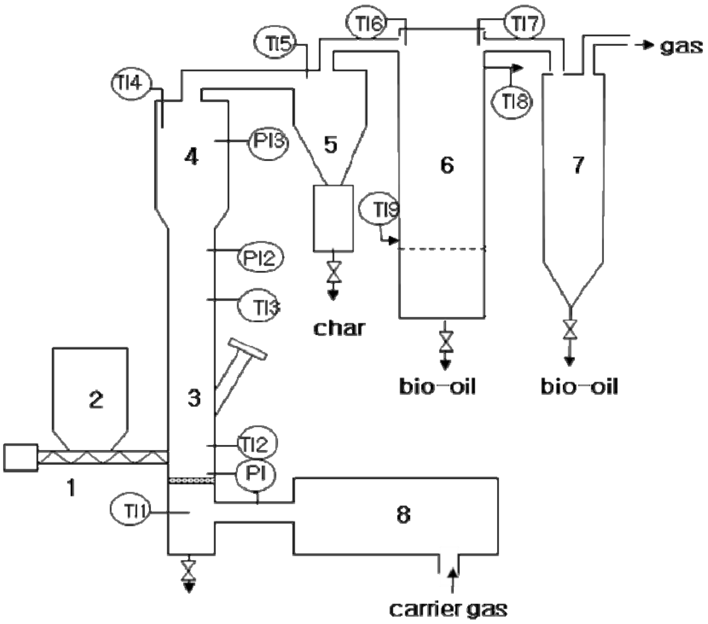


Figure 1: A schematic diagram of the fast pyrolysis reactor system for bio-oil production (1, screw feeder; 2, hopper; 3, reactor; 4, free-board; 5, cyclone; 6, condenser; 7, secondary separator; 8, carrier gas preheater).

The bio-oil production system consists of a sawdust feed hopper, a screw feeder, a bubbling fluidized-bed reactor, a cyclone, two heat exchangers, and a carrier gas preheater as shown in Figure 1. Sawdust from a saw mill was sieved to particle sizes less than 1.0 mm before used for the pyrolysis reaction. Sand with a particle size range of 0.4-0.8 mm was used as a fluidizing medium and nitrogen gas was used as a carrier gas. Pyrolysis reaction temperature was measured by a thermocouple (TI2 in Figure 1) employed inside the reactor. The capacity of the fast pyrolysis reactor was 4 kg/h of biomass on a design basis. Bio-oil product was obtained at the bottom of the quenching systems. The products were analyzed for their composition, heating value, and yield.

A schematic diagram of the apparatus used for bio-oil gasification is shown in Figure 2. The reactor was made of a Hastelloy C-276 tubing with 9.53 mm o.d., 6.22 mm i.d. and 293 mm total length. The reactor consisted of packed-bed of catalyst zone (5.6 cm^3) and reactant preheating zone (3.3 cm^3). The bio-oil feed was delivered into the reactor by a high pressure pump (Waters model 515). Reaction temperature was measured by a type K thermocouple installed inside the packed-bed of catalyst. A back-pressure regulator (Tescom model 26-1762-24) was used to reduce the pressure of product flow from 28 MPa to atmospheric pressure. The reactor effluent was disengaged into gas and liquid products in a gas-liquid separator. The flow rate of gas effluent was measured by a wet test meter (Sinagawa model W-NK-0.5A). Liquid product was collected at the bottom of the separator to measure its flow rate. For the catalytic experiments, purified sand was first packed in the cold zone of the downstream of the reactor and then catalyst was consecutively packed in the heating section (about 5.6 cm^3) of the reactor.

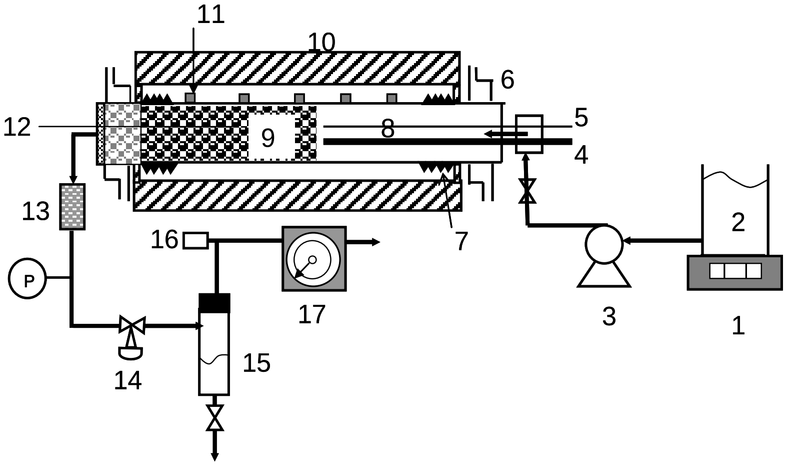


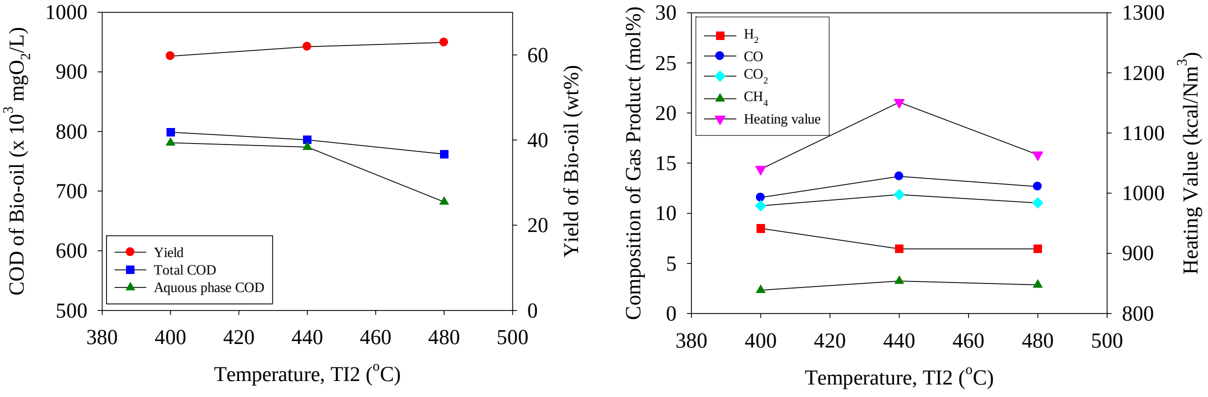
Figure 2: **A schematic diagram of the SCWG system for the gasification of bio-oil (1, digital balance; 2, feed reservoir; 3, high pressure pump; 4, rod heater; 5, annulus thermocouple; 6, heat exchanger; 7, coiled heater; 8, preheating zone of the reactor; 9, packed-bed of the reactor; 10, furnace; 11, thermocouple mounted on the reactor wall; 12, thermocouple inside the reactor; 13, filter; 14, back-pressure regulator; 15, gas-liquid separator; 16, gas sample outlet; 17, gas flow meter).**

The bio-oil obtained by the fast pyrolysis of sawdust consisted of two-phase; water-phase and tarry phase. The water-phase fraction of the bio-oil was separated and diluted with purified water to prepare for the feed solution for SCWG experiments. Activated charcoal (Sigma C3014) in 0.42-0.83 mm size was used as a catalyst or a support for nickel catalyst. The activated charcoal contains about 6 wt% ash and has a BET surface area of 920 m^2/g. A Ni-Y/AC catalyst was formulated by an incipient wetness method. The weight ratio between Ni and Y per 1g AC support was 0.25:0.0 for the Ni/AC and 0.25:0.10 for the Ni-Y/AC. Nickel(Ⅱ) nitrate hexahydrate (Aldrich No. 203874) and yttrium(Ⅲ) nitrate tetrahydrate (Aldrich No. 217239) were used as precursors. The catalyst was calcined in a nitrogen flow at 500 ^{o}C for 3 h, and reduced at 400 ^{o}C for more than 10 h under the flow of hydrogen gas.

3 Results and Discussion

Figure 3 (a) shows that the yield of total bio-oil slightly increased with pyrolysis temperature but the COD, as an indicator of organic content, decreased with pyrolysis temperature, which was more significant in water-phase fraction of the bio-oil product. The syngas product from the pyrolysis was about 20 wt% of the sawdust feed and its heating value was between 1,000-1,200 $kcal/Nm^3$. The seemingly low heating value of the syngas was due to the presence of high amounts of nitrogen gas which was used as a carrier gas. The hydrogen content of the syngas product was less than 8 vol% while the carbon monoxide content was over 12 vol%. A mass and energy balance analysis around the fast pyrolysis system indicated that the energy required by the pyrolysis reaction can be provided by the heat of combustion of the syngas product.

The water-phase fraction of the bio-oil product was separated and diluted to have COD values of about 100,000 mgO_2/L for the SCWG experiments. Table 1 displays the effect of temperature and catalyst on the gasification results. The COD destruction of the bio-oil feed was less than 80 wt% without catalyst at the high temperature of 720 °C, but increased to 99 wt% when the AC catalsyt was employed. The hydrogen content of the gaseous product was not changed in the presence of the AC catalyst. These results indicate that the AC catalyst catalyzes gasification of organic compounds in bio-oil, but does not influence hydrogen formation mechanisms such as water-gas shift reaction. When the SCWG temperature reduced from 720 to 660 °C, the hydrogen content significantly drop from 33 to 17 vol% in the presence of the AC catalyst. However, the hydrogen content was relatively high and did not reduce much with decreasing temperature in the presence of the Ni-Y/AC. It can be said that the Ni-Y/AC activates hydrogen production reactions in the SCWG of bio-oil.



(a) (b)

Figure 3: **Effect of pyrolysis temperature on the product characteristics in the fast pyrolysis of sawdust.**

Table 1: **SCWG results of the water-phase bio-oil at 28 MPa and 12^{-1} LHSV.**

Reaction conditions					
Catalyst	no	AC	AC	Ni-Y/AC	Ni-Y/AC
Temperature (°C)	720	720	660	720	660
Feed solution					
COD (mgO$_2$/L)	90,000	80,000	102,400	86,400	102,400
pH	2.2	2.4	2.0	2.5	2.1
Gaseous product					
HHV (kcal/Nm^3)	3,434	3,767	3,724	3,454	3,424
Composition (vol%)					
H$_2$	32.1	32.7	17.2	38.0	36.4
CO	12.2	3.3	7.3	1.9	1.1
CO$_2$	36.8	38.5	46.2	39.8	41.7
CH$_4$	15.2	22.0	21.7	16.6	17.4
Liquid effluent					
COD destruction (%)	79.1	99.2	92.0	97.8	96.9
pH	2.3	7.3	3.5	6.9	7.2

Acknowledgements

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