Hydrothermal gasification of glucose and starch in a batch and continuous reactor

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ABSTRACT

A batch reactor was used for the gasification of glucose and starch as carbohydrate model compounds. The effects of H_2O in various states (low-pressure hot compressed water (LP-HCW, 300 °C and 10 MPa), high-pressure hot compressed water (HP-HCW, 360 °C and 20 MPa), high-temperature steam (HTS, 400 °C and 10 MPa), and supercritical water (SCW, 400 °C and 25 MPa)), as well as reaction time (10, 30, and 60 min), sample concentration (10, 20, and 30 wt%), and catalyst (mixture of $Ca(OH)_2$ and Na_2CO_3) on gas production were investigated in the hydrothermal gasification. In addition, using a continuous reactor, the hydrothermal gasification of glucose was examined with LP-HCW (200 °C and 5 MPa), HP-HCW (200 °C and 25 MPa), HTS (600 °C, 5 MPa), and SCW (600 °C, 25 MPa) in order to study the productions of gases and tar, and the mass balance. The reaction temperature affected gasification considerably, but pressure had little effect. In the batch experiments, the characteristics of the produced gases were almost identical after a reaction time of 10 min, and addition of $Ca(OH)_2$ and Na_2CO_3 as catalysts in a molar ratio of 7:3 led to selective production of H_2 in the SCW gasification of 10 wt% glucose for 30 min. In a continuous experiment under the SCW conditions, the conversion efficiency of glucose to gas was 26% and the composition of the produced gas was 29 vol% CO, 23 vol% H_2, and 16 vol% CH_4. Under the hydrothermal conditions, glucose was mainly converted to char and suspended components of high-molecular-weight compounds such as fat, whereas starch was mainly converted to gas and liquid.

1. Introduction

In 2010, 21 million tons of food waste was generated in Japan and 83% of it generated from restaurants, called kitchen waste, was not recycled; therefore, unused kitchen waste should be utilized more efficiently as an energy source using chemical reactions (Kojima and Ishikawa, 2013). A hydrothermal reaction would be suitable for the utilization of kitchen waste owing to its high moisture content (Kuo and Cheng, 2007). Hot compressed water, including supercritical water, used in hydrothermal processes, is a special medium with a low energy requirement that is available at high temperatures and pressures. In the hot and compressed state, the properties of water, including density, ionic product, and relative dielectric constant, change evidently such that the decomposition of organics is more favorable. Compared to conventional gasification processes, the hydrothermal gasification process does not require the evaporation of water; thus, it is promising for the utilization of biomass with high water content, such as kitchen waste, with high energy efficiency (Tian et al., 2012).

Many hydrothermal gasifications of pre-treated kitchen waste as feedstock have been reported. On the other hand, only a few studies on the hydrothermal gasification of raw kitchen waste have been published because the performance of the hydrothermal gasification of kitchen waste is strongly dependent on its characteristics, such as elemental composition, heating value, ash, moisture, and volatile solid content (Girotto et al., 2015). For example, Muangrat et al. (2012) investigated the effect of carbohydrate, protein, and lipid proportions in several kitchen waste samples on hydrogen production by using subcritical water gasification and reported that carbohydrate-rich samples were preferred under the reaction conditions applied, as proteins and lipids promoted neutralization and saponification side reactions, respectively. Thus, kitchen waste consists of carbohydrate, protein, and lipid (Muangrat et al., 2012).

Therefore, in the past decades, much work on hydrothermal gasification has been conducted with carbohydrate model compounds such as glucose (Yu et al., 1993; Hao et al., 2003; Sinag et al., 2004; Williams and Onwudili, 2006; Fang et al., 2008; Catallo et al., 2010; Muangrat et al., 2010a, b; Azadi et al., 2010; Müller and Vogel, 2012; Qian et al., 2013), starch (Williams and Onwudili,

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(a) For batch test.

(b) For continuous test.
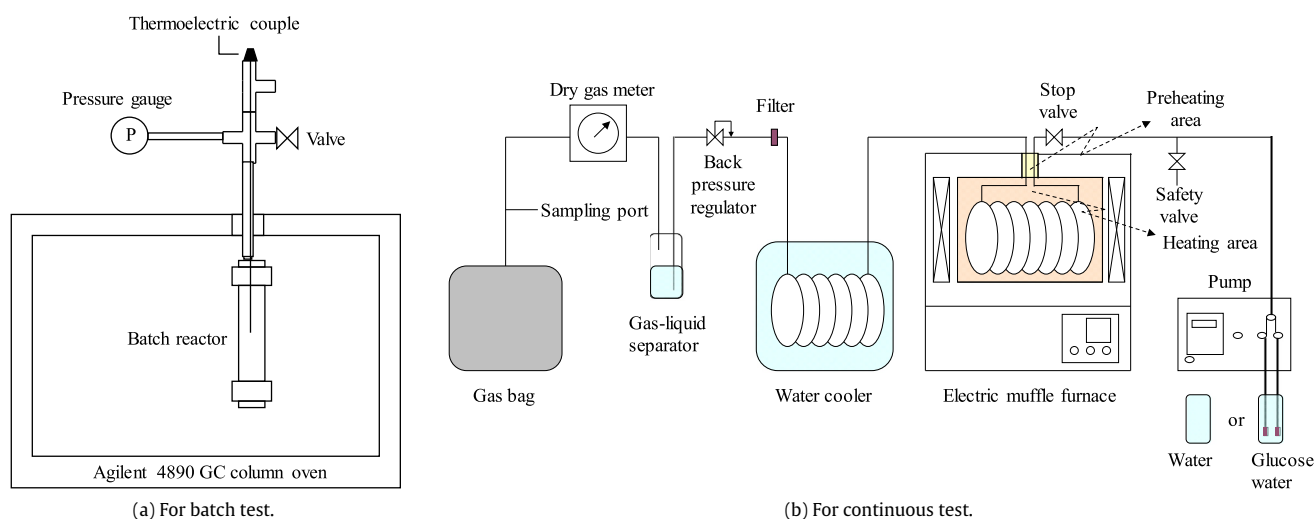
Fig. 1. Schematic diagrams of (a) batch and (b) continuous test apparatuses used in the present study.

2006), and cellulose (Ishida et al., 2009). However, most of the work was performed with supercritical and/or subcritical water, so the hydrothermal gasification behaviors of glucose and starch with water in other states, such as low-pressure hot compressed water (LP-HCW), high-pressure hot compressed water (HP-HCW), and high-temperature steam (HTS), are not clear thus far.

In this work, the gasification of glucose and starch as carbohydrate model compounds in a batch reactor was conducted in order to study the effects of H_2O in various states, namely, LP-HCW (300 °C and 10 MPa), HP-HCW (360 °C and 20 MPa), HTS (400 °C and 10 MPa), and supercritical water (SCW) (400 °C and 25 MPa), reaction time (10, 30, and 60 min), sample concentration (10, 20, and 30 wt%), and the catalyst (mixture of $Ca(OH)_2$ and Na_2CO_3) on gas production in the hydrothermal gasification reaction. In addition, the hydrothermal gasification of glucose in a continuous reactor was examined with LP-HCW (200 °C and 5 MPa), HP-HCW (200 °C and 25 MPa), HTS (600 °C and 5 MPa), and SCW (600 °C and 25 MPa) in order to study the productions of gases and tar and the mass balance, whereas the hydrothermal gasification of starch could not be examined because starch is not soluble in water.

2. Experimental

2.1. Batch test

The batch reactors used in the present study were composed of a seamless tube (6 or 12 cm long with an inner diameter of 1 cm and a volume of 5 or 10 cm^3, respectively) made of stainless steel (SUS-316) connected to a valve, pressure gauge, and thermoelectric couple, and sealed at the bottom with an SUS-316 cap, as shown in Fig. 1(a).

Under ambient conditions and a nitrogen atmosphere, the reactor was loaded with a mixture of reagent-grade glucose or starch (Kanto Chemical Co., Inc., Japan), distilled water, and 7.5 mmol reagent-grade $Ca(OH)_2$ and/or Na_2CO_3 (Wako Pure Chemical Industries, Ltd., Japan) prior to being sealed. The concentrations of water solutions of glucose or starch were 10, 20, and 30 wt%. The reactor was heated externally with a gas chromatography (GC) column oven (Agilent 4890 GC) to target temperatures of 300, 360, or 400 °C, as shown in Fig. 1(a). The pressures in the reactor was risen not by compressing nitrogen but by heating water because the compression of nitrogen diluted the product gas to increase the experimental error. The corresponding pressures in the reactor were 10, 20, and 25 MPa. After being held at the target reaction

temperature for 10, 30, or 60 min, the reactor was cooled to room temperature with a fan in order to quench the reaction. The valve was opened after the volume of produced gas was determined from the difference between the reactor pressures before and after the reaction, and then the produced gas was introduced into a gas bag. The gas composition was analyzed offline using gas chromatography with a thermal conductivity detector (GC-TCD) with two apparatuses (Shimadzu GC-14B and Yanaco G-1880) with identical column lengths of 2 m and identical inner diameters of 3 mm; the two columns were packed with 30/60 mesh Molecular Sieve 5A and 80/100 mesh Porapak Q with helium and argon carrier gases, respectively. After the produced gas was collected, the liquid and solid residues were collected, and then the solid residue was quantitated after being dried overnight in an oven at 90 °C. The total organic carbon (TOC) and amount of carbon in the liquid and solid residues were measured with a TOC analyzer (Shimadzu TOC-VCPH) and CHN analyzer (Yanaco CHN CORDER MT-5), respectively.

2.2. Continuous test

As shown in Fig. 1(b), the continuous reactor used in the present study was composed of a coiled SUS-316 tube, 2.0 m long with an inner diameter of 1.8 mm and a volume of 5.1 cm^3, and was set up in an electric muffle furnace (Yamato FO610).

Distilled water was pumped to the system at prescribed pressures (5 and 25 MPa) using a back pressure regulator (Swagelok Company, U.S.A.) during the preheating period. After the reactor was heated to the desired reaction temperatures (200 and 600 °C), 10 wt% aqueous glucose as a sample was supplied to the system at 1.0 mL/min for 60 min. The residence times of the sample in the continuous reactor were 4.2 min, 4.3 min, 4 s, and 21 s for LP-HCW, HP-HCW, HTS, and SCW, respectively. The hydrothermal gasification of glucose in a continuous reactor could not be investigated at 300−500 °C and 10–20 MPa because the reactor was blocked. Thus, the hydrothermal gasification of glucose in a continuous reactor was examined with LP-HCW, HP-HCW, HTS, and SCW. After the products released from the continuous reactor passed through a water cooler (Taiyo CoolPipe 75 L) and the back pressure regulator, the produced gas and liquid were separated in a gas–liquid separator. The separated gas passed through a dry gas meter (Shinagawa DC-1), and then was introduced into a gas bag. After the sample had been supplied to the system for 60 min, the volume and composition of the gas collected in the gas bag