

Kumabe, Kazuhiro; Itoh, Naoki; Matsumoto, Kohzoh; Hasegawa, Tatsuya

## Article

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

Energy Reports

## Provided in Cooperation with:

Elsevier

*Suggested Citation:* Kumabe, Kazuhiro; Itoh, Naoki; Matsumoto, Kohzoh; Hasegawa, Tatsuya (2017) : Hydrothermal gasification of glucose and starch in a batch and continuous reactor, Energy Reports, ISSN 2352-4847, Elsevier, Amsterdam, Vol. 3, pp. 70-75, <https://doi.org/10.1016/j.egyr.2017.04.001>

This Version is available at:

<https://hdl.handle.net/10419/187875>

### Standard-Nutzungsbedingungen:

Die Dokumente auf EconStor dürfen zu eigenen wissenschaftlichen Zwecken und zum Privatgebrauch gespeichert und kopiert werden.

Sie dürfen die Dokumente nicht für öffentliche oder kommerzielle Zwecke vervielfältigen, öffentlich ausstellen, öffentlich zugänglich machen, vertreiben oder anderweitig nutzen.

Sofern die Verfasser die Dokumente unter Open-Content-Lizenzen (insbesondere CC-Lizenzen) zur Verfügung gestellt haben sollten, gelten abweichend von diesen Nutzungsbedingungen die in der dort genannten Lizenz gewährten Nutzungsrechte.

### Terms of use:

*Documents in EconStor may be saved and copied for your personal and scholarly purposes.*

*You are not to copy documents for public or commercial purposes, to exhibit the documents publicly, to make them publicly available on the internet, or to distribute or otherwise use the documents in public.*

*If the documents have been made available under an Open Content Licence (especially Creative Commons Licences), you may exercise further usage rights as specified in the indicated licence.*



<https://creativecommons.org/licenses/by-nc-nd/4.0/>



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

Kazuhiro Kumabe<sup>a,\*</sup>, Naoki Itoh<sup>b</sup>, Kohzoh Matsumoto<sup>c</sup>, Tatsuya Hasegawa<sup>b,c</sup>

<sup>a</sup> Division of Environmental and Renewable Energy Systems (ERES), Graduate School of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan

<sup>b</sup> Department of Aerospace Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

<sup>c</sup> Institute of Materials and Systems for Sustainability, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan



## ARTICLE INFO

### Article history:

Received 2 November 2016

Received in revised form 21 March 2017

Accepted 3 April 2017

Available online 18 April 2017

### Keywords:

Hydrothermal gasification

Glucose

Starch

Batch reactor

Continuous reactor

## ABSTRACT

A batch reactor was used for the gasification of glucose and starch as carbohydrate model compounds. The effects of H<sub>2</sub>O 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)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>) 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)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> as catalysts in a molar ratio of 7:3 led to selective production of H<sub>2</sub> 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<sub>2</sub>, and 16 vol% CH<sub>4</sub>. 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.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

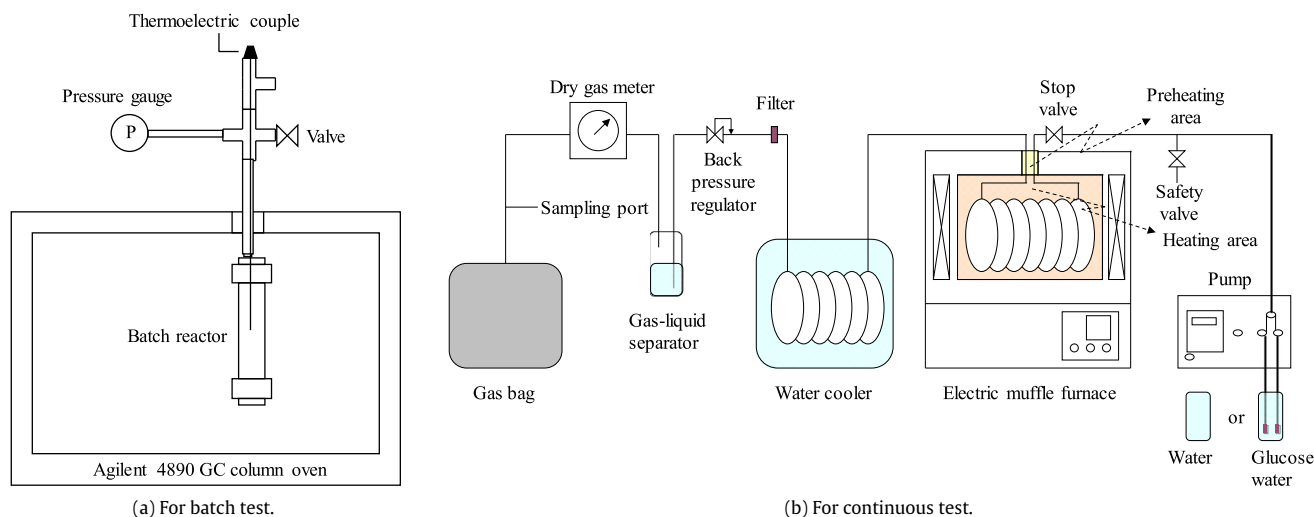
In 2010, 21 million tons of food waste was generated in Japan and 83% of it generated from restaurants, called kitchen waste, was not recycled; therefore, unused kitchen waste should be utilized more efficiently as an energy source using chemical reactions (Kojima and Ishikawa, 2013). A hydrothermal 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).

\* Corresponding author.

E-mail address: [k\\_kumabe@gifu-u.ac.jp](mailto:k_kumabe@gifu-u.ac.jp) (K. Kumabe).

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 (Giroto 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,



**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).

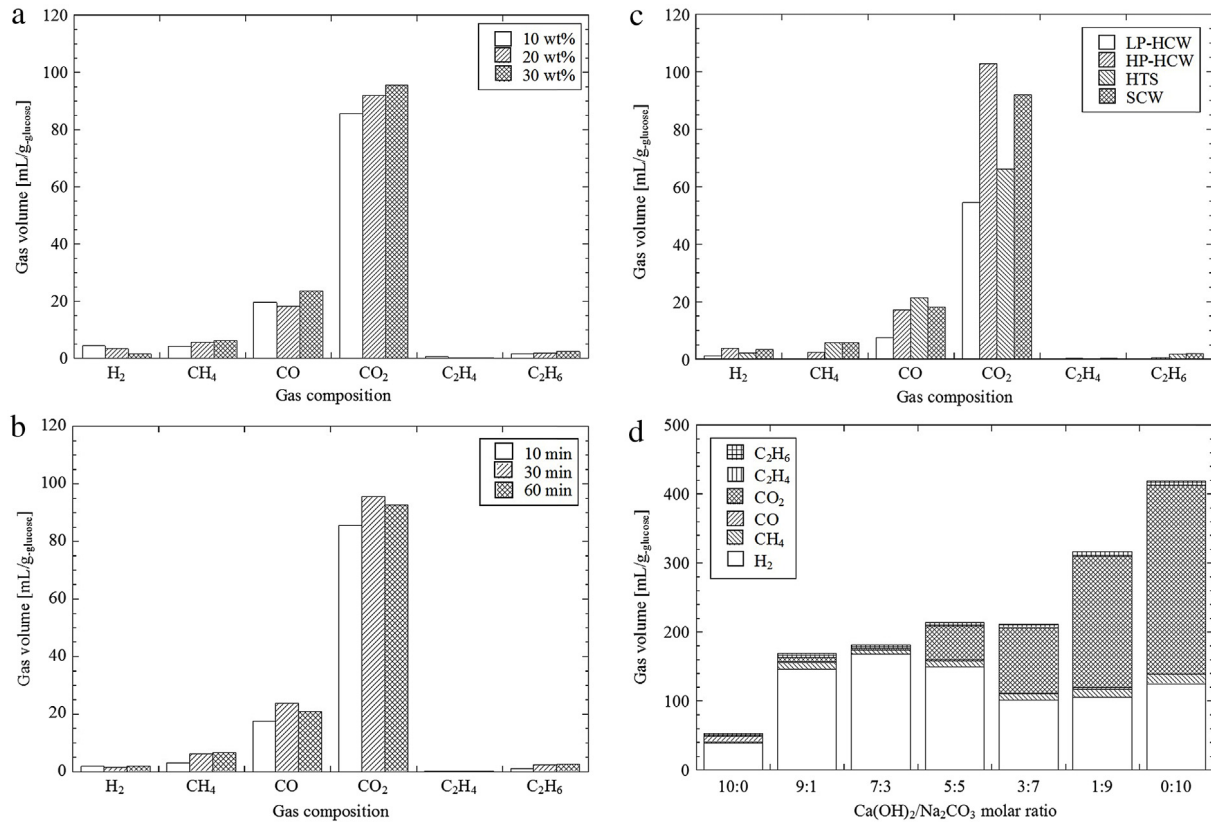
Under ambient conditions and a nitrogen atmosphere, the reactor was loaded with a mixture of reagent-grade glucose or starch (Kanto Chemical Co., Inc., Japan), distilled water, and 7.5 mmol reagent-grade  $Ca(OH)_2$  and/or  $Na_2CO_3$  (Wako Pure Chemical Industries, Ltd., Japan) prior to being sealed. 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



**Fig. 2.** Changes in the compositions of gas produced in (a) SCW gasification of glucose for 30 min with the glucose concentration, (b) SCW gasification of 30 wt% glucose with the reaction time, (c) gasification of 20 wt% glucose for 30 min with the H<sub>2</sub>O state, and (d) SCW gasification of 10 wt% glucose for 30 min with the molar ratio of Ca(OH)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub>.

were determined and analyzed offline with the dry gas meter and two GC-TCD systems mentioned in Section 2.1. The liquid collected in the gas–liquid separator was filtered to separate it from the solid (char), and then quantitated. The filtrate was extracted with toluene (Nacalai Tesque, Inc., Japan) to separate the organic (tar) and water (suspending solution) phases, and then quantitated. The tar and suspending solution were analyzed using GC with a flame ionization detector (Hewlett–Packard 5890A-GC) with a capillary column (Agilent J&W GC column DB-1 ms, 30 m × 0.25 mm inner diameter) coated with dimethylpolysiloxane (0.25 μm film thickness) with N<sub>2</sub> as the carrier gas and with a TOC analyzer (Shimadzu TOC-VCPH), respectively.

The conversions to gas ( $X_{\text{gas}}$ ), tar ( $X_{\text{tar}}$ ), water phase ( $X_{\text{WP}}$ ), and char ( $X_{\text{char}}$ ) on a carbon basis were defined as follows:

$$X_{\text{gas}} [\%] = \frac{\text{Molar number of carbon of CH}_4, \text{CO}, \text{CO}_2, \text{C}_2\text{H}_4, \text{ and C}_2\text{H}_6 \text{ [mol - C]}}{\text{Molar number of carbon of supplied glucose [mol - C]}} \times 100 [\%] \quad (1)$$

$$X_{\text{tar}} [\%] = \frac{\text{Average molar number of carbon in the organic phase [mol - C]}}{\text{Molar number of carbon of supplied glucose [mol - C]}} \times 100 [\%] \quad (2)$$

$$X_{\text{WP}} [\%] = \frac{\text{Molar number of total organic carbon in the water phase [mol - C]}}{\text{Molar number of carbon of supplied glucose [mol - C]}} \times 100 [\%] \quad (3)$$

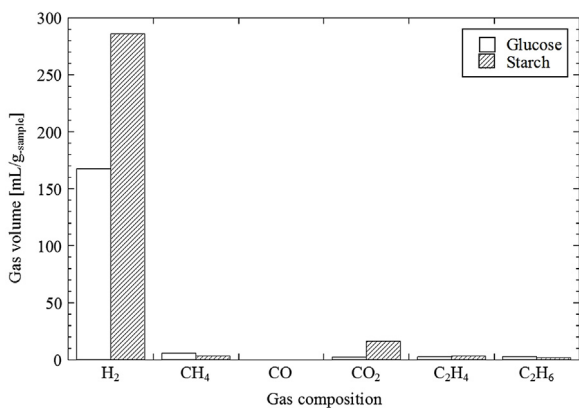
$$X_{\text{char}} [\%] = \frac{\text{Char weight [g]} \times 0.9 \div 12 \text{ g mol}^{-1}}{\text{Molar number of carbon of supplied glucose [mol - C]} \times 100 [\%]} \quad (4)$$

The suspending solution was extracted with chloroform to separate the organic (chloroform) and water phases, and then quantitated. The chloroform phase was analyzed with size exclusion chromatography (JASCO LC-2000Plus) and a 400 MHz (1H) nuclear magnetic resonance (NMR) spectrometer (Varian Unity INOVA 400 MHz).

### 3. Results

#### 3.1. Batch test

The SCW gasification of glucose was conducted for 30 min in the batch reactor in order to study the effect of sample concentration (10, 20, and 30 wt%) on gas production in the hydrothermal gasification reaction. The change in the produced gas composition with the glucose concentration is shown in Fig. 2(a). The produced gas compositions were independent of the glucose concentrations because the molar ratios of water to glucose for sample concentrations of 10, 20, and 30 wt% were 90, 40, and 23, respectively; thus, there was a large excess of water (Hao et al., 2003). The main product gases in the SCW gasification of 10, 20, and 30 wt% glucose for 30 min were 60, 68, and 71 vol% CO<sub>2</sub>, respectively. These values are different from the thermodynamic equilibrium composition of 49 vol% CO<sub>2</sub> and 48 vol% CH<sub>4</sub> in the SCW gasification of 10 wt% glucose, calculated using a commercially available software (Outotec Research Oy HSC Chemistry 6.1).



**Fig. 3.** Compositions of the gases produced in the SCW gasifications of 10 wt% glucose and starch for 30 min with the addition of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  in a molar ratio of 7:3.

SCW gasification of 30 wt% glucose was conducted in the batch reactor in order to study the effect of reaction time (10, 30, and 60 min) on gas production in the hydrothermal gasification reaction. The change in the produced gas composition with the reaction time is shown in Fig. 2(b). The main product gases in the SCW gasification of 30 wt% glucose for 10, 30, and 60 min were 73, 71, and 69 vol%  $\text{CO}_2$ , respectively.

The LP-HCW, HP-HCW, HTS, and SCW gasifications of 20 wt% glucose were conducted for 30 min in the batch reactor in order to study the effects of reaction temperature and pressure on gas production in the hydrothermal gasification reaction. The change in the produced gas composition with the  $\text{H}_2\text{O}$  state is shown in Fig. 2(c). The main product gases in the LP-HCW, HP-HCW, HTS, and SCW gasifications of 20 wt% glucose for 30 min were 77, 89, 57, and 68 vol%  $\text{CO}_2$ , respectively, and different from the thermodynamic equilibrium compositions of 50, 49, 48, and 48 vol%  $\text{CO}_2$  and 49, 48, 43, and 44 vol%  $\text{CH}_4$  in the gasifications of 20 wt% glucose, calculated using a commercially available software as stated previously in this section. The gasification was affected by the reaction temperature, but little effect of pressure was observed.

The SCW gasifications of 10 wt% glucose with mixtures of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  as a catalyst for 30 min were conducted in the batch reactor in order to study the effect of the molar ratio of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  on gas production in the hydrothermal gasification reaction. The change in the produced gas composition with the molar ratio of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  is shown in Fig. 2(d). The  $\text{CO}_2$  production increased from 1 to 65 vol% with the increase in the amount of  $\text{Na}_2\text{CO}_3$ , similar to a previous study (Muangrat et al., 2010b). With the addition of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  in a molar ratio of 7:3, 92 vol%  $\text{H}_2$  was produced selectively.

SCW gasifications of 10 wt% glucose and starch with the addition of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  in a molar ratio of 7:3 were conducted for 30 min in the batch reactor in order to study the effect of their chemical structures ( $\text{C}_6\text{H}_{12}\text{O}_6$  and  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$  ( $n = 300\text{--}600$ ), respectively) on gas production in the hydrothermal gasification reaction. The compositions of the gases produced under these conditions are shown in Fig. 3. The SCW gasification of starch produced much higher volumes of  $\text{H}_2$  and  $\text{CO}_2$  than that of glucose.

### 3.2. Continuous test

The hydrothermal gasification of glucose in a continuous reactor was examined in order to study the effect of  $\text{H}_2\text{O}$  in various states, namely LP-HCW, HP-HCW, HTS, and SCW, on the productions of gases and tar and the carbon mass balance. The change

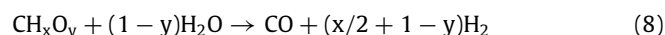
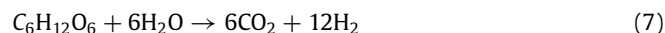
in the carbon mass balance with the state of  $\text{H}_2\text{O}$  is shown in Fig. 4(a). The carbon balance is almost 100%, which means that all of the product gas, tar, WP, and char were collected. Under HCW conditions, the conversion of glucose to gas was less than 0.4%. The conversion of glucose to gas was 26% under the SCW conditions. The change in the gaseous product composition with the state of  $\text{H}_2\text{O}$  is shown in Fig. 4(b). Under HCW conditions, the gaseous product was composed of more than 70 vol%  $\text{CO}$ . The composition of the gas product generated under the SCW conditions was 29 vol%  $\text{CO}$ , 23 vol%  $\text{H}_2$ , and 16 vol%  $\text{CH}_4$ .

The change in the tar product composition with the state of  $\text{H}_2\text{O}$  is shown in Fig. 4(c). The tar produced under HCW conditions was mainly composed of organic compounds with carbon numbers of 6 and 7. The amount of compounds with a carbon number of 7 in the tar product generated under the HTS and SCW conditions was lower than that in the tar product generated under HCW conditions.

## 4. Discussion

### 4.1. Batch test

The product gases in the SCW gasification of glucose were  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{H}_2$ . The reactions of glucose gasification are shown below (Hao et al., 2003; Fang et al., 2008):



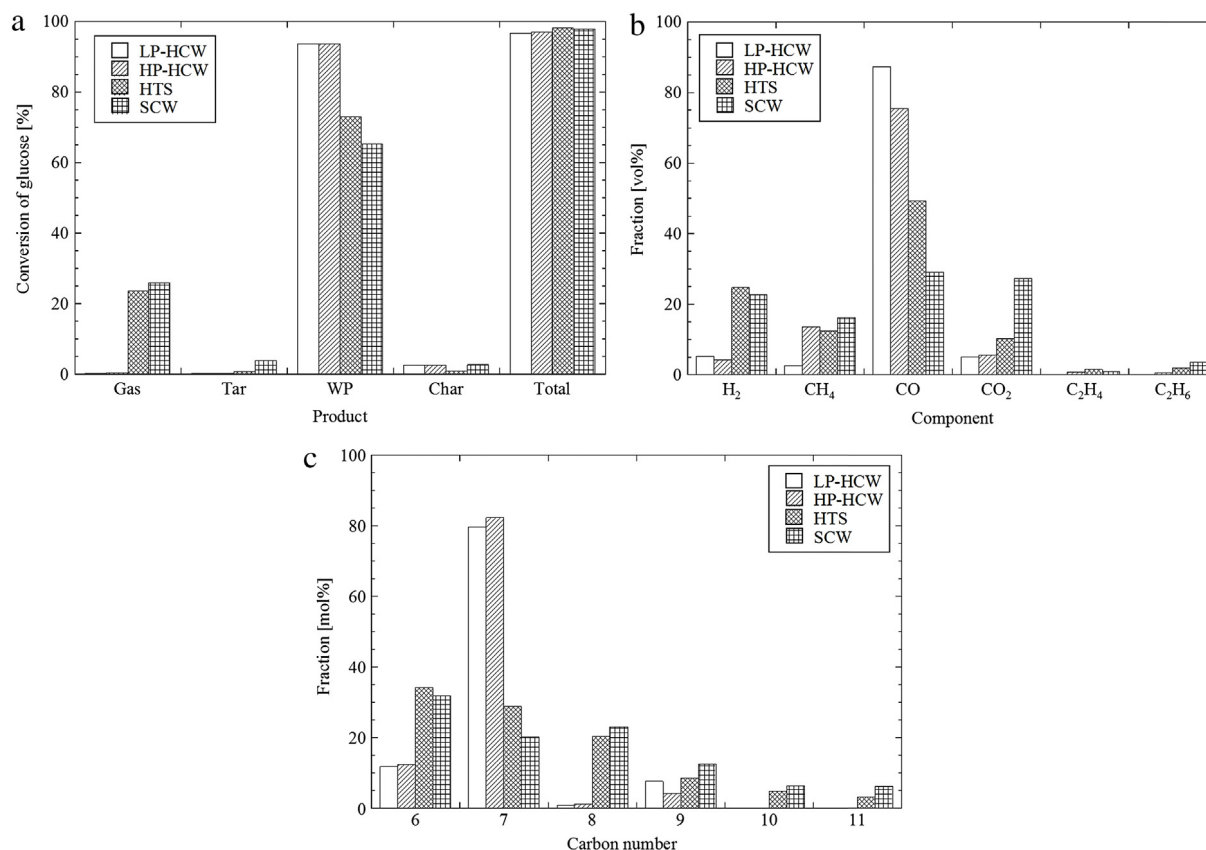
The procession of the reaction of Eq. (5) proceeds to the thermodynamic equilibrium state in the SCW gasification of glucose (the composition is 49 vol%  $\text{CO}_2$  and 48 vol%  $\text{CH}_4$ ). However, the reactions of Eq. (6)–(10) in the SCW gasification of glucose also proceed to produce mainly  $\text{CO}_2$ .

The molar conversions of carbon of 10, 20, and 30 wt% glucose into gases in the SCW gasification for 30 min were 14%, 15%, and 16%, respectively, whereas those into solid residue (char) were 47%, 71%, and 75%. The TOCs in the liquid residues after SCW gasification of 10–30 wt% glucose for 30 min were 4.4–4.5 g/L. In the study reported in Ref. (Qian et al., 2013), the molar conversion of carbon of a glucose solution (SCW gasification of 5 wt% glucose with 0.5 wt%  $\text{K}_2\text{CO}_3$  for 1 h) into  $\text{CO}_2$  and the TOC in the liquid residue were approximately 18% and 4.8 g/L, respectively. The molar conversions of carbon of 10, 20, and 30 wt% glucose into the liquid residue collected after the SCW gasification for 30 min were estimated to be 39%, 14%, and 9%, respectively, because it was difficult to quantitate the liquid residue owing to the batch reactor.

The characteristics of the gaseous products at reaction times longer than 10 min were scarcely different.

The molar conversions of carbon of 20 wt% glucose into gases in the LP-HCW, HP-HCW, HTS, and SCW gasifications for 30 min were 7.5%, 15%, 12%, and 15%, respectively. The gasification was affected by the reaction temperature, but little effect of pressure was observed.

Alkaline homogeneous catalysts/additives such as  $\text{Na}_2\text{CO}_3$  increase gasification efficiency and higher  $\text{H}_2$  yield by accelerating the water-gas shift reaction Eq. (10) via the formation of formate salts (Muangrat et al., 2010b). In addition,  $\text{Ca}(\text{OH})_2$  has the ability of reacting with  $\text{CO}_2$  to form metal carbonates and capture  $\text{CO}_2$



**Fig. 4.** Changes in (a) carbon mass balance, (b) gaseous product composition, and (c) tar product composition with the state of H<sub>2</sub>O in the hydrothermal gasification of glucose in a continuous reactor.

(Muangrat et al., 2010b). However, an optimum mixing ratio of Ca(OH)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> to obtain higher H<sub>2</sub> and lower CO<sub>2</sub> yields was not clear. This work investigated an optimum mixing ratio of Ca(OH)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> to result that with the addition of Ca(OH)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> in a molar ratio of 7:3, 92 vol% H<sub>2</sub> was produced selectively. It might be that CO<sub>2</sub> and H<sub>2</sub> were produced with Na<sub>2</sub>CO<sub>3</sub>, and then CO<sub>2</sub> reacted with Ca(OH)<sub>2</sub> to form CaCO<sub>3</sub>, which would have shifted the water-gas reaction Eq. (7) to the right (Muangrat et al., 2010b).

The SCW gasification of starch with the addition of Ca(OH)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> in a molar ratio of 7:3 produced higher volumes of H<sub>2</sub> and CO<sub>2</sub> than that of glucose. Williams and Onwudili (2006) studied the sub- and super-critical non-catalytic gasification of glucose and starch at temperature and pressure ranges of 330–380 °C and 9.3–22.5 MPa. They demonstrated that the production of H<sub>2</sub> gas for glucose was higher than that for starch. Thus, the gasification condition in this study is different in the use of a catalyst from that in their study. Therefore, the water-gas reaction might have progressed to a greater extent for starch ((C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub> + 7nH<sub>2</sub>O → 6nCO<sub>2</sub> + 12nH<sub>2</sub> (n = 300–600)) than for glucose Eq. (7) with the addition of Ca(OH)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> in a molar ratio of 7:3, since the solid residue was not observed after the SCW gasification of starch.

#### 4.2. Continuous test

The conversion of glucose to gas was 26% under the SCW conditions, whereas the cold gas efficiency was 30%. The conversion of glucose to gas and the cold gas efficiency under the HTS conditions were similar to those under the SCW conditions.

Higher temperatures and pressures decreased CO production and increased H<sub>2</sub> and CO<sub>2</sub> production, which suggested that the water-gas-shift reaction Eq. (10) occurred.

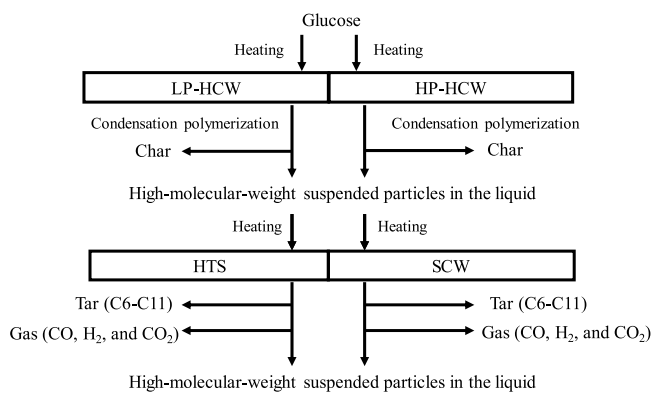
The liquid collected in the gas–liquid separator was brownish-red and this color faded as the reaction temperature increased. The results from size exclusion chromatography and 400 MHz (<sup>1</sup>H) NMR spectroscopy suggested that the suspending solution had a high molecular weight (approximately 2000 g/mol) and was mainly aliphatic (C<sub>n</sub>H<sub>2n+2</sub>), respectively.

Here, the reaction mechanism of the hydrothermal gasification of glucose is discussed. Fig. 5 shows the outline of the reaction mechanism for glucose under the present experimental conditions. Glucose is heated to HCW conditions to convert it to char and high-molecular-weight suspended particles in the liquid. The particles are then heated to the HTS or SCW conditions to convert them to tar, gas, and high-molecular-weight suspended particles. It will be an issue in the future to investigate the gasification of real biomass with the studies of the effects of H<sub>2</sub>O in various states, reactor type and scale, reaction time, sample concentration, and the catalyst on gas production in the hydrothermal gasification reaction.

## 5. Conclusions

A batch reactor was used for the gasification of glucose and starch in order to study the effects of H<sub>2</sub>O in various states, reaction time, sample concentration, and the catalyst on gas production in the hydrothermal gasification reaction. In addition, using a continuous reactor, the hydrothermal gasification of glucose was examined with H<sub>2</sub>O in various states in order to study the productions of gases and tar and the mass balance. The following conclusions were drawn:

- (1) The reaction temperature affected the gasification, but pressure had little effect.



**Fig. 5.** Outline of reaction mechanism for glucose under the present experimental conditions.

- (2) In the batch experiments, the characteristics of the produced gases were almost identical after a reaction time of 10 min, and H<sub>2</sub> was produced selectively with the addition of Ca(OH)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> as catalysts in a molar ratio of 7:3 in the SCW gasification of 10 wt% glucose for 30 min.
- (3) In the 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<sub>2</sub>, and 16 vol% CH<sub>4</sub>.
- (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.

### Acknowledgments

This study was carried out partly with financial support from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan under the “Asia Science and Technology Cooperation Promotion Strategy” program (No. 20061510) and in collaboration with Chubu Electric Power Co., Inc.

### References

- Azadi, P., Otomo, J., Hatano, H., Oshima, Y., Farnood, R., 2010. Hydrogen production by catalytic near-critical water gasification and steam reforming of glucose. *Int. J. Hydrog. Energy* 35, 3406–3414.
- Catallo, J.W., Shupe, F.T., Comeaux, L.J., Junk, T., 2010. Transformation of glucose to volatile and semi-volatile products in hydrothermal (HT) systems. *Biomass Bioenerg.* 34, 1–13.
- Fang, Z., Minowa, T., Fang, C., Smith, Jr., L.R., Inomata, H., Kozinski, A.J., 2008. Catalytic hydrothermal gasification of cellulose and glucose. *Int. J. Hydrog. Energy* 33, 981–990.
- Giroto, F., Alibardi, L., Cossu, R., 2015. Food waste generation and industrial uses: A review. *Waste Manage.* 45, 32–41.
- Hao, X.H., Guo, L.J., Mao, X., Zhang, X.M., Chen, X.J., 2003. Hydrogen production from glucose used as a model compound of biomass gasified in supercritical water. *Int. J. Hydrog. Energy* 28, 55–64.
- Ishida, Y., Kumabe, K., Hata, K., Tanifuji, K., Hasegawa, T., Kitagawa, K., Isu, N., Funahashi, Y., Asai, T., 2009. Selective hydrogen generation from real biomass through hydrothermal reaction at relatively low temperatures. *Biomass Bioenerg.* 33, 8–13.
- Kojima, R., Ishikawa, M., 2013. Resilient cities. In: *Prevention and Recycling of Food Wastes in Japan: Policies and Achievements*. Kobe University, Japan.
- Kuo, W., Cheng, K., 2007. Use of respirometer in evaluation of process and toxicity of thermophilic anaerobic digestion for treating kitchen waste. *Bioresour. Technol.* 98, 1805–1811.
- Muangrat, R., Onwudili, A.J., Williams, T.P., 2010a. Reaction products from the subcritical water gasification of food wastes and glucose with NaOH and H<sub>2</sub>O<sub>2</sub>. *Bioresour. Technol.* 101, 6812–6821.
- Muangrat, R., Onwudili, A.J., Williams, T.P., 2010b. Influence of alkali catalysts on the production of hydrogen-rich gas from the hydrothermal gasification of food processing waste. *Appl. Catal. B: Environ.* 100, 440–449.
- Muangrat, R., Onwudili, J.A., Williams, P.T., 2012. Reactions of different food classes during subcritical water gasification for hydrogen gas production. *Int. J. Hydrog. Energy* 37, 2248–2259.
- Müller, B.J., Vogel, F., 2012. Tar and coke formation during hydrothermal processing of glycerol and glucose. Influence of temperature, residence time and feed concentration. *J. Supercrit. Fluids* 70, 126–136.
- Qian, M.Y.-W., Elsa, W.-H., Radu, B., 2013. Hydrothermal conversion of glucose in multiscale batch processes. Analysis of the gas, liquid and solid residues. *J. Supercrit. Fluids* 79, 76–83.
- Sinag, A., Kruse, A., Rathert, J., 2004. Influence of the heating rate and the type of catalyst on the formation of key intermediates and on the generation of gases during hydrolysis of glucose in supercritical water in a batch reactor. *Ind. Eng. Chem. Res.* 43, 502–508.
- Tian, Y., Kumabe, K., Matsumoto, K., Takeuchi, H., Xie, Y., Hasegawa, T., 2012. Hydrolysis behavior of tofu waste in hot compressed water. *Biomass Bioenerg.* 39, 112–119.
- Williams, P.T., Onwudili, J., 2006. Subcritical and supercritical water gasification of cellulose, starch, glucose, and biomass waste. *Energy Fuels* 20, 1259–1265.
- Yu, D.H., Aihara, M., Antal, M.J., 1993. Hydrogen-production by steam reforming glucose in supercritical water. *Energy Fuels* 7, 574–577.