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High-yield hydrogen production by supercritical water gasification of various feedstocks: Alcohols, glucose, glycerol and long-chain alkanes

Ratna F. Susanti^{a,b}, Laras W. Dianningrum^{a,c}, Taewoo Yum^a, Yunje Kim^a, Youn-Woo Lee^d, Jaehoon Kim^{e,f,*}

^a Clean Energy Research Center, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea

^b Chemical Engineering Department, Industrial Technology Faculty, Parahyangan Catholic University, Ciumbuleuit 94 Bandung, West Java 40141, Indonesia

^c Department of Clean Energy and Chemical Engineering, University of Science and Technology, 113 Gwahangno, Yuseong-gu, Daejeon 305-333, Republic of Korea

^d School of Chemical and Biological Engineering, Seoul National University, Gwanangro 599, Gwanak-gu, Seoul 151-744, Republic of Korea

^e School of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, GyeongGi-Do 440-746, Republic of Korea

^f Sungkyun Advanced Institute of Nano Technology (SAINT), 2066, Seobu-Ro, Jangan-Gu, Suwon, GyeongGi-Do 440-746, Republic of Korea

ABSTRACT

Continuous supercritical water gasification (SCWG) of various feedstocks of C1–C16 was conducted to produce hydrogen-rich gas. These feedstocks represent model compounds of biomass such as methanol/ethanol (alcohol-type), glucose and glycerol (byproducts of biodiesel synthesis), and model compounds of petroleum fuels such as iso-octane/n-octane (gasoline), n-decane/n-dodecane (jet fuels) and n-hexadecane (diesel). Almost complete gasification of all the feedstocks was achieved at 25 MPa, 740 °C and 10 wt% with low total organic carbon values of their liquid effluents. The hydrogen gas yields of each feedstock were very similar to the theoretical equilibrium yields estimated by Gibbs free energy minimization. SCWG at different gasification temperatures (650 and 740 °C) and concentrations (10 and 20 wt%) revealed that methanol and ethanol (alcohols), the simple oxygenated hydrocarbons, were easier to be gasified, producing negligible amounts of liquid products, when compared with long-chain hydrocarbons (iso-octane and n-decane) under the identical conditions. When the feedstock concentration was increased from 10 to 20 wt%, the equilibrium hydrogen ratio from iso-octane gasification decreased from 1.02 to 0.79 while that of n-decane increased from 1.12 to 1.50, implying that a branched hydrocarbon may be more resistant to gasification in supercritical water.

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Keywords: Supercritical water gasification; Hydrogen; Equilibrium yield; Hydrocarbon

1. Introduction

Hydrogen has been considered one of the most promising clean energy alternatives to fossil fuels due to the depletion

of fossil resources and the global warming. Hydrogen production by supercritical water gasification (SCWG), high-pressure gasification conducted above the critical point of water (374 °C and 22.1 MPa), has many advantages over conventional

* Corresponding author at: School of Mechanical Engineering, Sungkyunkwan University, 2066, Seobu-Ro, Jangan-Gu, Suwon, GyeongGi-Do 440-746, Republic of Korea. Tel.: +82 31 299 4843; fax: +82 31 290 5889.

E-mail addresses: jaehoonkim@skku.edu, kjh0508@gmail.com (J. Kim).

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gasification techniques owing to the unique physical properties of supercritical water (scH₂O). scH₂O has extremely low viscosity, high diffusivity, and high solubility of organic reaction intermediates, which promote fast reactions and reduce coke formation. The high energy efficiency (Calzavara et al., 2005; Matsumura, 2002), environmental friendliness, compact gasification equipment (Taylor et al., 2003), high hydrogen gas yield (Susanti et al., 2011), and in situ CO₂ separability owing to the high solubility of CO₂ in high-pressure water (Guo et al., 2010a) are some of the advantages of SCWG. Furthermore, SCWG can be conducted in the absence of external catalysts, avoiding challenges associated with catalytic gasification reactions such as catalyst deactivation due to the presence of heteroatoms (sulfur, nitrogen, phosphorus, etc.) in some feedstocks, carbon deposition, and reactor plugging issues.

Various types of feedstocks can be used to produce hydrogen by SCWG. They include oxygenated hydrocarbons (methanol, ethanol, glycerol, etc.), petroleum-based feedstocks (gasoline, diesel, jet-fuel, etc.), and biomass-based feedstocks (lignocellulosic biomass, sewage sludge, microalgae, etc.). SCWG of these feedstocks has been investigated at various conditions (different operation parameters, catalysts, oxidants, etc.) for different reactor systems (batch, plug-flow, fluidized bed, etc.) (Guo et al., 2010b; Peterson et al., 2008). In order to maximize hydrogen gas yield, operation conditions and reactor geometries need to be optimized. Although high feedstock concentration is preferable for high energy efficiency (Nakamura et al., 2008), both equilibrium calculations and experimental results have shown that an increase in feedstock concentration decreases the hydrogen gas yield while increasing the methane yield (Susanti et al., 2011). The SCWG of feedstocks of higher heating values (HHV) (e.g., long-chain hydrocarbons) can also provide high energy efficiency. However, based on the gasification reaction, long-chain hydrocarbons require more severe gasification conditions, e.g., high temperatures, because they are more reform-resistant than their short-chain counterparts.

In this study, SCWG of various feedstocks was investigated under similar operating conditions. These feedstocks represent the model compounds of biomass (methanol, ethanol and glucose), byproducts of biodiesel synthesis (glycerol), gasoline (iso-octane and *n*-octane), jet fuels (*n*-decane and *n*-dodecane) and diesel (*n*-hexadecane). Due to the considerable differences between the physical and chemical properties of the feedstocks, it is important to determine how these differences affect the gasification efficiency and individual gas yield. SCWG of methanol, iso-octane, and *n*-decane at different temperatures and concentrations was also carried out to examine the effect of both parameters to the gasification behavior of these typical feedstocks. We also demonstrate that each feedstock can be gasified in scH₂O with a hydrogen yield similar to its maximum theoretical hydrogen gas yield without added catalysts by using our recently developed reactor system.

2. Experimental methods

2.1. Materials

Methanol (>99.8%, JT Baker, USA), ethanol (>99.8%, Carlo Erba, France), glycerol (>99%, Junsei Chemical, Japan), D-Glucose (≥99.5%, Sigma Aldrich, USA), iso-octane (>99%, Daejung Chemical, Korea), *n*-octane (>97%, Yakuri Pure

Chemicals, Japan), *n*-decane (>99.5%, Daejung Chemical, Korea), *n*-dodecane (>98%, Kanto Chemical, Japan) and *n*-hexadecane (>99%, Alfa Aesar, UK) were used as received. The distilled and deionized (DDI) water was prepared using a Milli-Q Ultrapure water purification system. After each experiment, 2 M H₂O₂ (>99.5%, Junsei Chemical, Japan) was flowed through the gasification system under the scH₂O condition for 2 h to remove any solid carbon residue that may have remained inside the reactor.

2.2. Apparatus, procedure and characterization

The SCWG experiments were carried out using a custom-built, continuous-flow tubular reactor with an updraft configuration. Interested reader may obtain more information on the modification history, apparatus details, reactor temperature control and temperature measurements in previous papers (Susanti et al., 2010, 2011; Laras et al., 2014). A schematic of the apparatus is shown in Fig. S1. The reactor was made of Haynes® 230® alloy with an inside diameter of 20 mm and an effective length of 540 mm, giving an internal volume of 170 cm³. Prior to each gasification experiment, DDI water was introduced to the reactor system using a high-pressure pump and the system was pressurized to 25 MPa by adjusting the back-pressure regulator. The temperature of the system was then increased to experimentally desired temperatures using heat furnaces. The reactor was stabilized for at least 1 h before feedstock was introduced into the reactor system. The gaseous and liquid effluents were collected three times during the 2 h reaction and analyzed. Average values of the three times sampling were reported in this study.

The gaseous product was analyzed using a gas chromatograph (GC), which can quantify all the gaseous products, including H₂, CO₂, CO, CH₄, C₂H₆, C₂H₄, and C₃-C₅ compounds. The GC was the Clarus 600 GC-Model Arnel 1115PPC Refinery Gas Analyzer (RGA) (Perkin Elmer, USA) with two different detectors, the thermal conductivity detector (TCD) and the flame ionization detector (FID). The carbon content in the liquid product was analyzed using a total organic compounds analyzer (TOC-VCSH 200V, Shimadzu, Japan). Detailed descriptions of GC and TOC are given in our previous papers (Susanti et al., 2010, 2012). Organic species in the liquid product were analyzed using gas chromatograph/time-of-flight mass spectroscopy (GC/TOF-MS, Pegasus III, Leco Co., USA) equipped with a model 6890 N GC (Agilent Technologies Inc., USA), and a Hewlett Packard-5 ms column (29 m length × 0.25 mm I.D. × 0.25 μm thickness). The oven temperature was programmed increase from 50 to 90 °C at 20 °C/min, held for 2 min at 90 °C, and increased to a final temperature of 240 °C at 15 °C/min. Prior to an analysis, 2 mL of ethyl acetate was added to 1 mL of each liquid product, followed by shaking, centrifuging, and freezing. Details on liquid effluent analysis after glucose gasification are provided in the previous paper (Susanti et al., 2012).

In this work, the individual gas yield of every gas produced was defined as the moles of each produced gas per moles of feedstock fed to the reactor. The moles of each produced gas were estimated by real-time volumetric flow rate measurements and the gas compositions were analyzed by the GC. Carbon gasification efficiency (CE) was defined as the total moles of carbon in the produced gases per total moles of carbon in the feed. The CE values of over 100% for several feedstocks were observed, which is possibly due to an error in the estimation of amount of produced gas collected

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