

Gasification of Isooctane into Hydrogen for Fuel Cells

Application Using Supercritical Water

Ratna Frida Susanti^{1,2}, Bambang Veriansyah¹, Jaehoon Kim^{1*}, [Jae-Duck Kim^{1,2*}](mailto:jaeduckkim@kist.re.kr) and Youn-Woo Lee³

¹Supercritical Fluid Research Laboratory, Energy and Environment Research Division,

Korea Institute of Science and Technology (KIST),

39-1 Hawolgok-dong Seoungbuk-gu, 136-791, Seoul, Korea

²Department of Green Process and System Engineering,

University of Science and Technology (UST)

³School of Chemical and Biological Engineering, Seoul National University,

Gwanangro 599, Gwanak-gu, Seoul 151-744, Korea

*Corresponding authors: Fax: +82-2-958-5879, E-mail: jaehoonkim@kist.re.kr (Jaehoon Kim);

Fax: +82-2-958-5205, E-mail: jdkim@kist.re.kr (Jae-Duck Kim)

ABSTRACT

The production of hydrogen by gasification of isooctane, a model compound of gasoline, was investigated in a continuous tubular reactor under supercritical water conditions without using catalysts. The influences of reactor temperature, residence time, oxidant concentration, and reactor geometrical configuration were examined at a fixed pressure of 25 MPa. The major components of the produced gas were hydrogen (H₂), methane (CH₄) and CO₂ and the minor components of the produced gas were CO and C₂H₆. The experimental results show that hydrogen yield increased by applying higher reaction temperature, longer residence time and small amount of oxidant concentration. It was found out that down-up reactor configuration that has inclination around 15° give better flow rate stability of gas and liquid and hydrogen yield at almost 4 times higher compare to downdraft type. On the basis of this study, gasoline or heavy oil can be gasified with satisfying hydrogen yields using a compact supercritical water gasification system

INTRODUCTION

Supercritical water gasification (SCWG) is a potential alternative to generate hydrogen in compact reformer system. The homogenous reaction and lower mass transfer resistance makes the reforming reaction to be conducted in very short residence time [1]. The homogenous reaction can be achieved due to the dielectric constant of supercritical water (SCW) is much lower than ambient

water/steam so that hydrocarbon is completely soluble in supercritical. Gases are also miscible in supercritical water [2] so that single phase reaction environment will occur instead of multiphase reaction under conventional condition [3, 4]. The density of supercritical water is higher than that of steam, resulting in higher thermal conductivity and specific heat that is beneficial to carry out endothermic reaction [1, 5]. Some efforts have been conducted to gasify hydrocarbons, model compounds of biomass, biomass, and model compound of fuel. Most of those efforts have been conducted in the presence of catalysts. Catalyst gave the better yield and gasification efficiency, meanwhile the phenomenon of catalyst deactivation due to sulfurous compound containing in fuel and tar/char as typical byproduct in reforming process become one of consideration to build compact onboard reforming system.

Herein we report the gasification of isooctane (2,2,4-trimethylpentane), a model compound of gasoline, in supercritical water using downdraft and down-up gasifiers type at low temperature (600-700 °C) and in the absence of catalyst. In downdraft type, the position of the reactor is vertical where the mixing tee located in the top and effluent flowed out from the bottom while in down-up type, the gasifiers was tilted at inclination of 15° with down-up introducing the water and the reactant in to the reactor system. The cooling zone was added to down-up type that is welded to the reaction zone. The primary goal of this study is to examine the performance of both reactor systems for the gasification of isooctane in supercritical water. The following section describes the new gasifier apparatus and process, the effect of reaction temperature, residence time and oxidant concentration on the hydrogen yield and effluent gas composition.

MATERIALS AND METHODS

Figure 1 shows the schematic diagram for downdraft type of gasifier. The apparatus consists of three feed tanks (FT1, FT2 and FT3), two high pressure pumps (HP), a tubular reactor (R), furnaces (PH and RH), a cooling unit (C), two metal filters (F), a back pressure regulator (PR), a gas-liquid separator (S), a wet gas meter (WG), a liquid container (L), isolation and safety valves (V1-V4), pressure gauges (P), thermocouples (T), and associated tubing. Figure 2 shows the schematic diagram for down-up type of gasifier. The apparatus consists of three feed tanks (T-01, T-02 and T-03), two high-pressure pumps (HP1 and HP2), a tubular reactor (R), furnaces (OP, WP, RH and IH). a tubular reactor (R), two cooling units (C and CZ), a filter (F), a back pressure regulator (BPR), a gas-liquid separator (S), a wet gas meter (WG), a liquid container (L), isolation and safety valves (V1, V2, V3 and V4), pressure gauges (P), thermocouples (T), and associated tubing. The reactor was tilted to 15° horizontal to the surface. The cooling tube (CZ) is welded with the reactor (R). The insulation zone with a length of 28 cm was added to keep the temperature of the reaction zone isothermal. The cooling zone (CZ) has 115 cm length with outside air used as cooling media. The reactor used at both of system was made of Hastelloy C-276, cylindrical in shape with an inside

diameter (I.D.) of 10 mm and an effective length of 380 mm, giving an internal volume of 29.86 cm³.

Prior to each gasification experiment, DDI water was introduced to the reactor system using the high-pressure pump and pressurized to an experimentally desired pressure of 25 MPa by adjusting the back pressure regulator. The temperature of the system was then increased to around 20 degree below the experimentally desired temperatures using the furnaces. The reactor was stabilized for at least 1 hour before isooctane was introduced into the reactor system. The gaseous effluent and liquid effluent flow rates were monitored during 90 – 120 minutes of the gasification. The gaseous effluent was collected in a sampling bag every 30 minutes and analyzed using two gas chromatographs (GC).

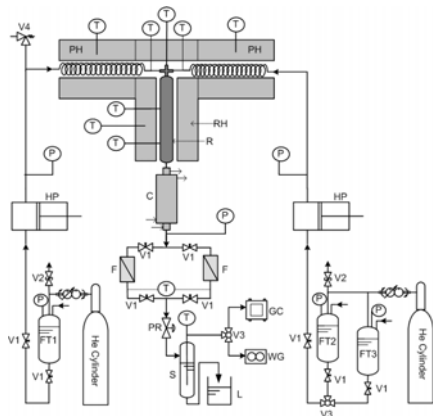


Figure 1. Schematic diagram of downdraft gasifier

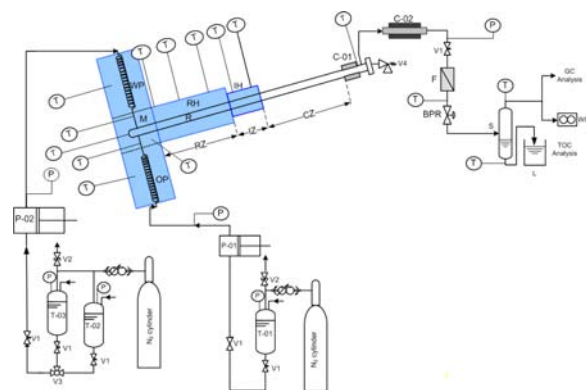


Figure 2. Schematic diagram of down-up gasifier

The gaseous samples were analyzed using two gas chromatographs (GC) in triplicates and their volumetric flow rates were measured using a wet gas meter (WG) (model 525722, Sinagawa Corp., Japan). The first GC was Hewlett-Packard model 5890 Series II GC with HP Plot Q column., a thermal conductivity detector (TCD) detector, and helium as the carrier gas. It was used to quantify carbon dioxide (CO₂), methane (CH₄) and ethane (C₂H₆), The second GC was Young Lin model ACME 6100 GC with a pulsed discharge helium ionization detector (PDHID, Vici Valco Instruments Co. Inc.), 50µm Rt-Msievetm 5A Plot column and helium as carrier gas. It was used to quantify hydrogen (H₂) and carbon monoxide (CO). Both of the GC was calibrated using pure gases.

RESULTS

The effect of reaction temperature on the gas yield of downdraft type reactor was studied at a fixed pressure of 25 MPa, residence time of 16 s and isooctane concentration of 21wt%. When the reactor temperature increased from 597 to 694 °C, the gas yields of H₂, CO₂ and CH₄ increased (from 0.29 to 0.75 mol/mol isooctane for H₂, from 0.1 to 0.56 mol/mol isooctane for CO₂, from 0.21

to 1.07 mol/mol isooctane for CH₄) while CO and C₂H₆ yield was slightly increased (from 0 to 0.06 mol/mol isooctane for CO, from 0 to 0.13 mol/mol isooctane for C₂H₆). The sequence of experiments to study the temperature effect at down-up gasifier has been conducted at a fixed pressure of 25 MPa, residence time of 6.9 s and isooctane concentration of 11.2 wt%. When the reactor temperature increased from 601 to 676 °C, the gas yields of H₂, CO₂ and CH₄ increased (from 0.93 to 2.31 mol/mol isooctane for H₂, from 0.42 to 0.78 mol/mol isooctane for CO₂, from 0.55 to 1.27 mol/mol isooctane for CH₄) while that of CO and C₂H₆ increased (from 0.01 to 0.08 mol/mol isooctane for CO, from 0.03 to 1.19 mol/mol isooctane for C₂H₆). This indicates that high temperature is favored for higher isooctane conversion. Hydrogen yield obtained by down-up type was three times higher than that of the down draft type even though conducted at lower temperature, shorter residence time and lower isooctane concentration .

The effects of residence time on the gas yield were investigated at a fixed pressure of 25 MPa, fixed temperature and isooctane concentration of (598 °C, 19.5 wt% for downdraft type and 632 °C, 15.2 wt% for down-up type). At downdraft type, as the residence time was increased from 14.4 to 16.1 s, the yield of H₂, CO₂ and CH₄ were increased (from 0.09 to 0.37 mol/mol isooctane for H₂, from 0.10 to 0.24 mol/mol isooctane for CH₄, from 0.03 to 0.14 mol/mol isooctane for CO₂ while CO and C₂H₆ were found in marginal amount. The observation on the down-up type with the wider ranges of residence times (6 s to 33 s) showed the same trend. As the residence time increased from 6 s to 33 s, the H₂, CO₂ and CH₄ increased (from 1.14 to 5.52 mol/mol isooctane for H₂, from 0.5 to 1.59 mol/mol isooctane for CH₄, from 0.29 to 1.7 mol/mol isooctane for CO₂). An increase in residence time would allow the reaction to achieve the complete conversion of isooctane.

The effects of oxidant (H₂O₂) concentration on the gas yield was investigated at downdraft type gasifier by varying the H₂O₂ concentration from 0 to 2265.1 mmol/L at a temperature of 663 °C, a residence time of 15 s, an isooctane concentration of 22 wt% and a fixed pressure of 25 MPa while the effect was examined at down-up type by varying the H₂O₂ concentration from 0 to 4507 mmol/L at a temperature of 637 °C, a residence time of 18 s, an isooctane concentration of 10 wt% and a fixed pressure of 25 MPa. The results are shown in Figure 3(a-b). Both of them show similar H₂ production yield trends. When the H₂O₂ concentration increased from 700 to 1600 mmol/L, H₂ yield increased from 0.63 to 1.68 mol/mol isooctane while when H₂O₂ concentration was further increased from 1600 to 2300 mmol/L, H₂ gas yield decreased from 1.68 to 1.04 mol/mol isooctane. At down-up type, when the H₂O₂ concentration increased from 0 to 2701 mmol/L, H₂ gas yield increased from 4 to 6.13 mol/mol isooctane and further decreased to 4.56 mol/mol isooctane when the H₂O₂ concentration was further increased to 4507 mmol/L. Within these experimental oxidant concentration ranges, H₂ is a reactive intermediate product because its molar yield increases to a maximum value and afterward decreases with higher oxidant concentration.

As discussed above, even though the experiments were conducted at slightly different

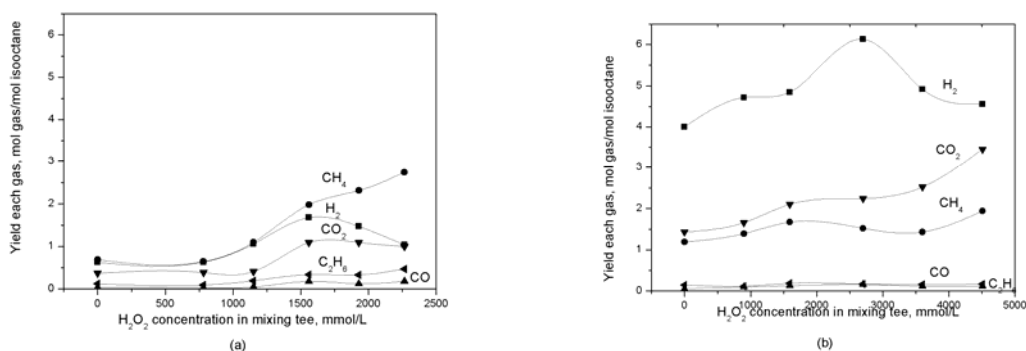


Figure 3. Oxidant Effect on gas yield (a) down-draft type (b) down-up type

reaction condition, the results clearly showed that the down-up configuration gave the better hydrogen yield compare to the down-draft type. The best result of hydrogen yield with down-draft type was 1.68 mol H₂/mol isooctane that was achieved at a temperature of 663 °C, a residence time of 15 s, an isooctane concentration of 22 wt% with additional of H₂O₂ as much as 1600 mmol/L. The best hydrogen yield obtained by down-up type was 6.13 mol H₂/mol isooctane (around four times higher) that was observed at temperature of 637 °C (26 degree lower), a residence time of 18 s (2 s longer) and isooctane concentration of 10 wt% (12 wt% smaller) and H₂O₂ concentration of 2701 mmol/L(1000 mmol/L higher). The down-draft reactor has some drawbacks. The reactor was vertically set up above the condenser in which the feed (isooctane and DDI water) was flowed from the top. The high pressure and temperature of the reactor effluent was quenched suddenly in the condenser so that gasses were separated from liquid in the condenser. Due to gasses always has tendency to goes up while liquid goes down, there can be a collision between gas and liquid flow that made virtual plugging around the condenser and the bottom part of reactor. As a result, there was instability of gas and liquid flow rate, so that the gasses did not separate completely in separator and flowed along with liquid to liquid tank resulting in gasses lose. At down-up configuration, the reactor was inclined with horizontal position around 15 °. With this modification, the liquid will be easy to go up and the liquid will not find difficulty to flow due to the declivous inclination applied. The presence of cooling zone that is welded with reaction zone also gives contribution to the increasing of hydrogen yield. This design allows for gradual temperature decrease due to the cooling media used is ambient air. As a result, the highly free radical intermediates that are produced at gasification in supercritical water may react further and finally improve the gas yield. This is supported by Akiya and Savage[6] who reported that the reactions in which water participates often involve the formation or destruction of highly reactive free radical intermediates. This intermediate product is more reactive and easy to gasify than real isooctane.

CONCLUSION

The supercritical water gasification has been proved to be an effective technique to produce hydrogen from isooctane even without addition of any catalyst. The results showed that higher hydrogen yield was achieved by applying higher temperature, longer residence time and small amount of oxidant for both of the downdraft and down-up gasifier types. The drawbacks owned by the downdraft configuration made the hydrogen yield obtained was much lower than down-up type. The down-up gasifier offers a promising chance to develop compact onboard reformer for processing heavy oil.

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