

Pyrolytic bio-hydrogen production from chars prepared from unhulled rice, brown rice, rice husk, and rice straw

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Summary

A two-step biomass gasification process of carbonization and steam gasification has been investigated in our laboratory. This new production process of hydrogen-rich water gas without any byproduct can be carried out using a small simple electrical furnace. To evaluate the possibility of using unhulled rice, brown rice, and rice husk as resources for pyrolysis gasification, bio-chars were prepared using these materials as gasifying sources. The char yields of each of the rice tissues varied in response to their corresponding content of silica compounds. As expected, a high yield of water gas was produced from these rice tissues with no by-products such as tar, oil, and inorganic compounds in RH; moreover, rice straw accelerated the gasification. It was observed that the gasification process is significantly influenced by the gasification temperature. Boudouard's reaction ($C + CO_2 \rightarrow 2CO$) was accelerated and the water-shift gasification reaction ($CO + H_2O \rightarrow CO_2 + H_2$) was suppressed with increasing gasification temperature. Higher heating values (HHVs) and volume of the produced gas was increased by increasing the gasification temperature. An increase in the steam supply rates increased the produced gas volume and specific HHVs; nevertheless, an excessive supply rate cooled the reactor and decreased the gasification reaction rate. In this study, the hydrogen contents in the produced gases were higher than the predicted theoretical values. This result demonstrates that hydrogen gas can be produced without using gasifying sources and presumed that some hydrogen gas is produced by reaction with the metal on the inner surface of the reactor.

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Key words : Bio-char, steam gasification, hydrogen production, rice husk

Gasification of biomass, such as wood-based materials, agricultural residues, and forestry waste, is a promising technology that provides a competitive means for producing chemicals and energy from renewable energy sources (Bridgwater, 2003). The gaseous mixture from the gasification process can be utilized in both conventional and advanced technologies for the production of electrical and thermal power as well as automobile fuel. Because biomass fuels are considered to be carbon neutral, they provide a positive environmental contribution (Cetin *et al.*, 2005; Umeki *et al.*, 2012). Moreover, the gaseous mixture resulting from the gasification process can be used to produce syngas that has a direct application in all hydro-treatment operations, ammonia production, and in the synthesis of methanol, dimethyl ether, and super-clean liquid fuels such as Fischer-Tropsch oil (Cetin *et al.* 2005; Kim *et al.* 2013).

The demand for hydrogen is increasing because of the increasing demand for new sources of fuel. The catalytic reformation of natural gas, liquefied petrol gas, and naphtha with steam is currently the most widely used process for producing hydrogen gas. However, this process results in significant carbon dioxide emissions that contribute to global warming. Therefore, alternative methods ways to produce hydrogen gas are being studied, including the direct gasification of biomass, which is a renewable source (Wang *et*

al. 2008; Kawamoto *et al.* 2009). A critical review of the relevant literature reveals that steam is the most widely accepted gasification agent for the production of hydrogen gas, primarily because of the quality of the produced gas and high hydrogen yield (Mermoud *et al.* 2006). However, progress in the field of hydrogen production from biomass has been largely hindered by technical issues associated with tar formation, which reduces the efficiency of gas production and interferes with equipment operation (Sun *et al.* 2011).

Gasification of biomass generally consists of two primary steps: the initial pyrolysis and subsequent char gasification. Byproducts, such as tar, are formed during pyrolysis and char gasification is a rate-determining step that may control the overall conversion process (Zhang *et al.* 2008). Formation of tar compounds generally renders the produced gas mixture unsuitable for commercial applications and numerous investigations have been conducted to eliminate tar compounds (Rath *et al.* 2001; Devi *et al.* 2003; Li *et al.* 2004; Han *et al.* 2008). Practical methods of tar removal (with the exclusion of in-bed methods and multi-stage methods) involve high medium temperature downstream methods, which are usually based on catalytic tar cracking (Sulc *et al.* 2012). Other methods such as hot electrostatic precipitation and adsorption by various solvents at temperatures below 400°C are generally considered to be auxiliary methods (Zwart *et al.*

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2009).

Gasification of biomass chars, also referred to as biochars, have been developed to obtain a better understanding of char reactivity and kinetic modeling using steam and carbon dioxide as gasification agents (Cetin *et al.*, 2004; Klose and Wolki, 2005; Roberts and Harris, 2007; Nilsson *et al.*, 2012). Several studies have reported the gasification of bio-char from different biomass sources such as grapefruit skins (Montesions *et al.*, 2002), Japanese cedar (Matsumoto *et al.*, 2009), sunflower seed pods (Haykiri-Acma *et al.*, 2006), bamboo (Kato *et al.*, 2014), kenaf (Kojima *et al.*, 2014), beech wood (Wolfgang and Michael, 2005), larch and cedar (Kato *et al.*, 2014), slash pine (Fermoso *et al.*, 2009), spent mushroom beds (Kojima *et al.*, 2015), and bagasse (Chaudhari *et al.*, 2003). Yan *et al.* (2010) attempted to produce hydrogen rich gas by steam gasification of bio-char as a by-product from the fast pyrolysis liquefaction process. They concluded that a high gasification temperature and the introduction of steam led to a higher yield of dry gas and a higher carbon conversion efficiency. Umeki *et al.* (2012) proposed that untreated char produced from a high temperature steam gasification system could be extracted from the gasifier and combusted to generate high temperature steam.

The system design consisted of two separate processes. The first process is carbonization for char production and the second process is gasification with steam.

Rice husk (RH) and rice straw (RS) are potential agricultural waste biomass that have no other field uses. Moreover, in Japan, tainted rice (contaminated with heavy metals or corrupted in the mold) remains un-utilized and incinerated. The purpose of this study is to evaluate unhulled rice (UR), RH, brown rice (BR), and RS as potential gasification resources.

MATERIALS AND METHODS

The rice plants (cultivar; akitacomachi) were provided by a farmer in Akita, Japan, which were dried and separated into RS and UR. Then, the UR was hulled to separate BR and RH.

Carbonization was performed at 600°C with a cylindrical electric furnace (length, 500 mm; diameter, 80 mm).

Gasification of the chars was performed with steam as the gasification agent. The steam supply rate was 0.05 g/min/g and the gasification temperatures were 800°C, 900°C, and 1,000°C. For UR gasification of bio-char, the steam supply varied from 0.05 g/min to 0.15 g/min/g. A fixed bed gasifier was placed within the electrical furnace and 30 g of char was placed into the gasifier (Fig. 1). Prior to gasification, the air in the gasifier and cyclone were replaced with nitrogen. After 30 min of heating, the gasifier reached the maximum temperature and steam was supplied into the gasifier by controlling a water pump. The gases produced were passed through a cyclone and a gasholder. A gas meter was set up in front of the gasholder. The produced gases were then collected from the gasholder and the gas composition was

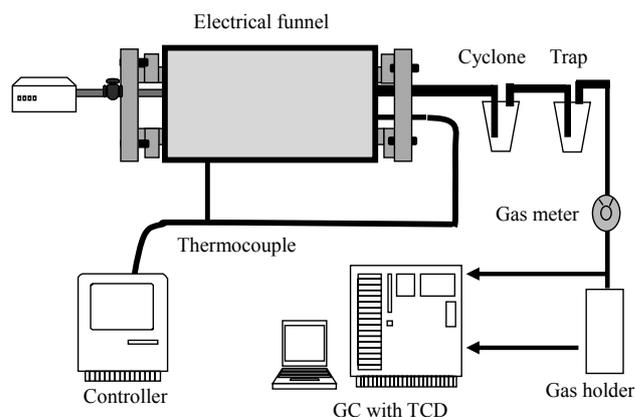


Fig 1. A gasification system

examined.

The composition of the gases was analyzed by gas chromatography with a thermal conductivity detector using activated carbon. Specific heating values of the produced gases were calculated using the gas composition, whereas the higher heating values (HHVs) and total heating values were calculated from the specific heating value and total gas volume. Subsequently, the energy conversion, gas composition, HHV, and gas yield were determined.

RESULTS AND DISCUSSION

1. Carbonization of rice tissues

Images of the char from UR carbonization are shown in Fig. 2. The UR char was formed by expansion of the UR along the inner space of the cylindrical reactor during carbonization while retaining the rice shape. Char yields produced from various rice tissues are shown in Fig. 3. The highest yield was obtained from RH carbonization and the lowest yield was from BR. The difference between the rice tissue yields is dependent on the amount of silica compounds they contain, ranging from 1%–22% in RH, 7%–10% in RS, and 3%–5% in UR, to 0%–1% in BR. Consequently, 27% of char and 18% of silica compounds were contained in the RH char.

2. Gasification of biomass chars from various rice tissues

Gas production curves for each of the rice tissue chars are illustrated as 15 min split values in Fig. 4. For RS and

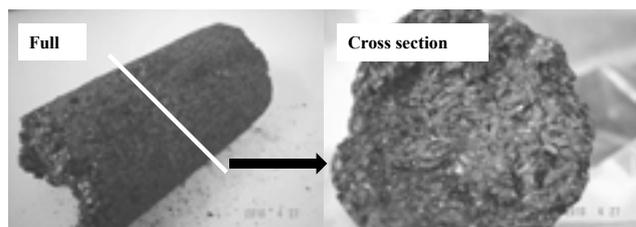


Fig 2. Photographs of char from unhulled rice

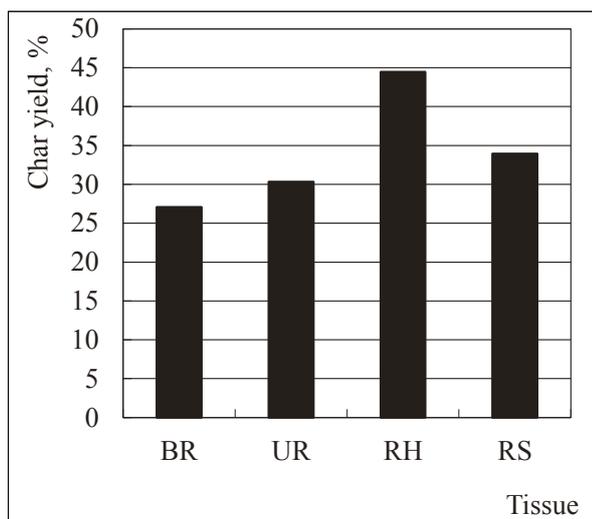


Fig 3. Char yield from various rice tissues

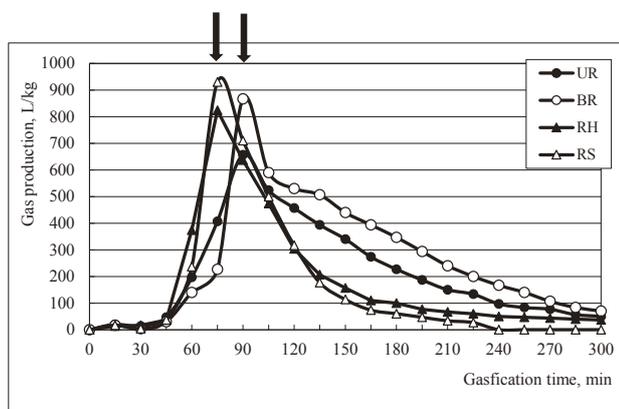


Fig 4. Split curves of gas production from various chars (900 °C, 0.05ml/min/g)

RH, the highest split gas productions were observed at 75 min after which gas production rates rapidly decreased. For UR and BR, the highest split gas production rates were observed at 90 min after which gas production rates slowly decreased. This result indicated the possibility that the silica compounds contained in the RS and RH chars acted as catalysts for gasification.

As mentioned above, chars from RH and RS contained considerably more silica compound and less carbon in their char. Therefore, the total gas production from RH and RS chars were lower than that produced from UR and BR (Fig. 5).

During gasification of the char with steam, clean fuel gases with high caloric values were produced (Kojima *et al.*, 2014). The final gas composition and HHV is the result of a combination of the following series of complex and competing reactions:

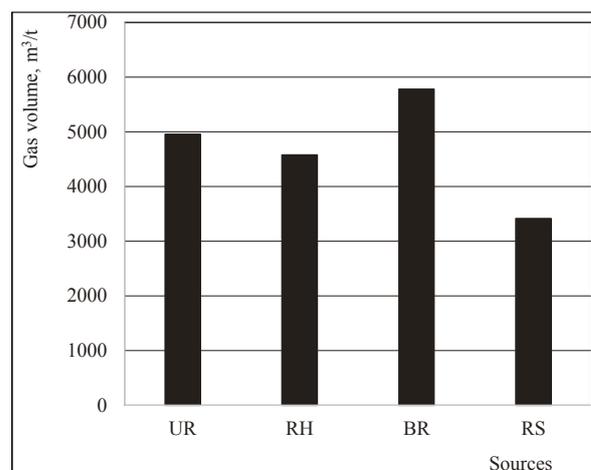
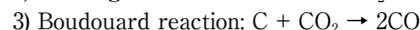
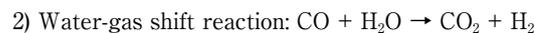


Fig 5. Gas volume production/t from various chars (900 °C, 0.05ml/min/g)



The water-gas reaction is a solid-gas heterogeneous reaction; thus, the reaction mechanism should be more complex. We propose a formation mechanism of H and CO for char with steam via the water-gas reaction as $5C + 5H_2O \rightarrow 5CO + 5H_2$ (not including the initial release of 4 H radicals from the char), as shown in Fig. 6. Char is composed of polycyclic aromatic hydrocarbons, the chemical structure of which has been used as a structure model of the char surface (Fig. 6). In the first step, H radicals are released from the char surface of the bio-char. The remaining surface carbon radicals act as OH radical acceptors, resulting in the formation of $-C-O-H$ structures at the char surface. A second release of H radicals from the $-C-O-H$ groups leads to the generation of carbonyl compounds. An electron transfer then occurs at the adjacent C-C bonds and CO gas is formed. The chain reaction continues on the char surface in the presence

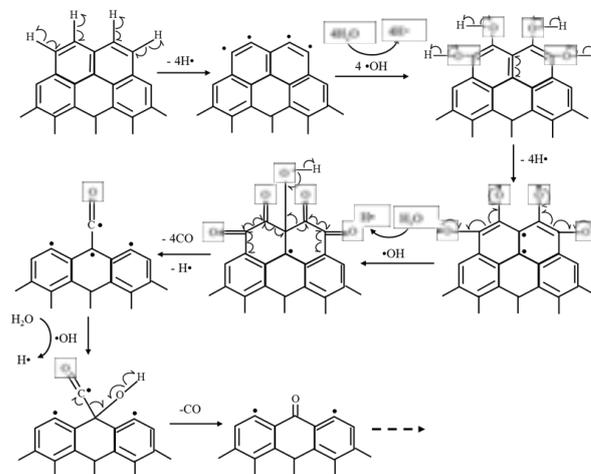


Fig 6. Proposed gasification mechanism of char with steam

of H₂O (Kojima *et al.*, 2015). In this steam gasification process, the generated gases are then released out of the rice tissues.

The gas proportions from each sample are illustrated in Fig. 7. The results from RS char gasification are different from the other three tissues where a lower rate of H₂/CO and higher rate of CO/CO₂ were observed. These results indicate that approximately half of the generated CO₂ from the water-gas shift reaction was consumed by the Boudouard reaction for RS char gasification compared with approximately 30% consumption for the other rice tissues. This is possibly due to different chemical and morphological properties of RS.

The HHVs of total gas (GJ/t of char) are shown in Fig. 8. Water gas from BR char had a higher HHV than other rice tissue chars and was dependent on the gas production volume.

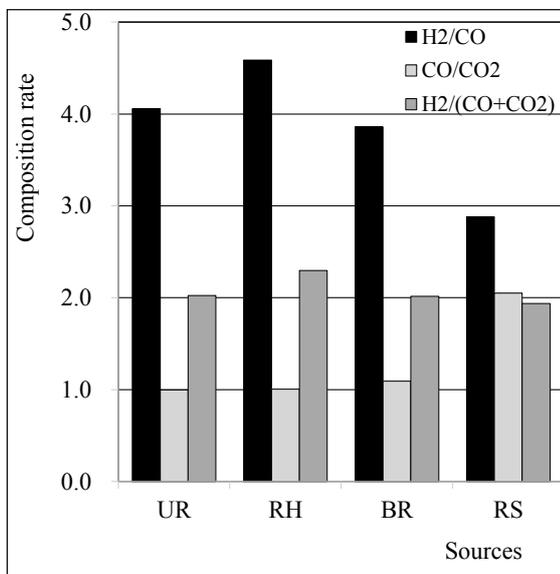


Fig 7. Composition rate of water gas from various chars (900 °C , 0.05ml/min/g)

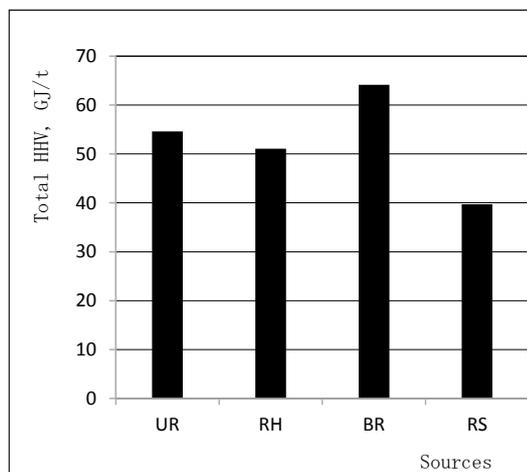


Fig 8. Total HHV of water gas from various chars (900°C , 0.05ml/min/g)

3. Effect of gasification temperature on steam gasification

Gasification temperature has the highest influence on gas composition and the gasification rate. The effect of the gasification temperature with UR chars is shown in Fig. 9. Steam gasification of UR at 1000 °C produced the water gas over 5000 m³/t, which decreased along with gasification temperature. For the gas composition, the CO₂ concentration decreased with increase in temperature and the CO concentration increased with increase in temperature (Fig. 10). This result suggests that the Boudouard reaction ($C + CO_2 \rightarrow 2CO$) was accelerated and the water-shift gasification reaction ($CO + H_2O \rightarrow CO_2 + H_2$) was suppressed by an increase in gasification temperature. In fact, the water-shift gasification reaction is known as an exothermic reaction, where the reaction rate decreases with increase in temperature. The HHVs of produced gas were increased by raising the gasification temperature, as reflected by the gas production volume (Fig. 11).

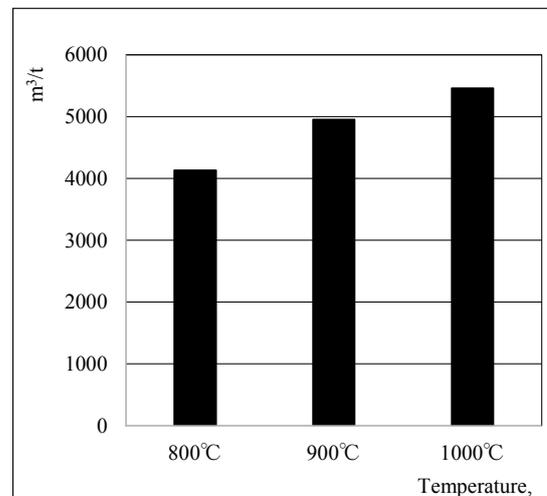


Fig 9. Gas volume production from UR at various temperature (0.05ml/min/g)

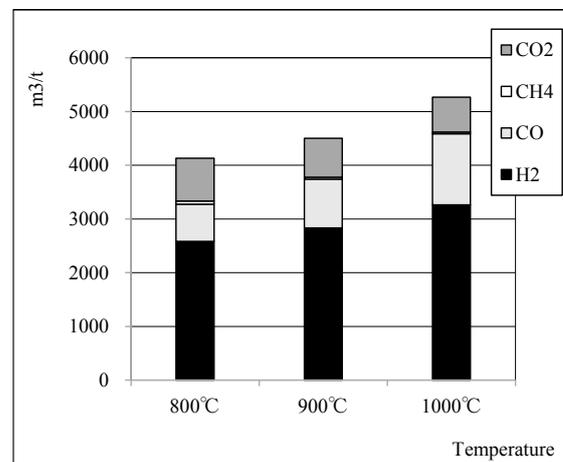


Fig 10. Gas composition produced from UR at various temperature (0.05ml/min/g)

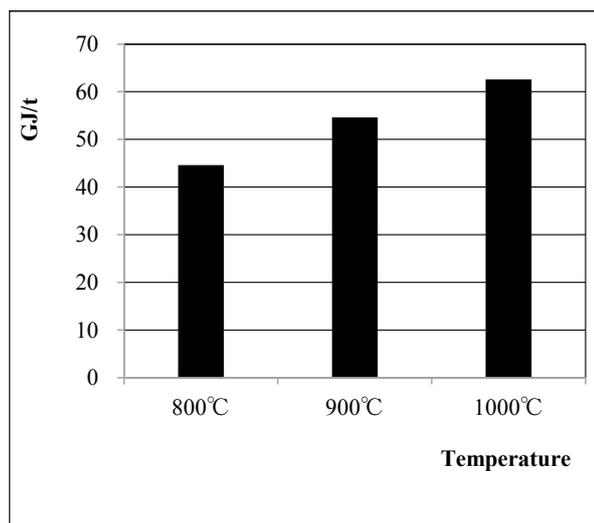


Fig 11. Total HHV of water gas from UR at various temperatures (0.05 ml/min/g)

4. Effect of steam supply on steam gasification

Similar to temperature, steam supply significantly affects the gasification rate and biomass gas composition. To investigate the effect of steam supply rate on gasification, 0.05–0.015 ml/min/g steam supply rates were applied for UR char gasification at 900 °C (Fig. 12). The gas production was significantly increased by increasing the steam supply rate from 0.10 to 0.15 ml/min/g. Increasing the steam supply rate accelerated the water gasification reaction within this range while raising it from 0.1 to 0.15 ml/min/g resulted in a slight decrease in gas production. It was assumed that excessive steam introduction to the reactor resulted in the cooling of the reactor temperature. The gas composition rates from gasification at various steam supply rates are shown in Fig. 13. Results from a 0.10 ml/min/g steam supply rate gasification differed from the other two conditions with a slightly higher H content and lower CO/CO₂ ratio because of

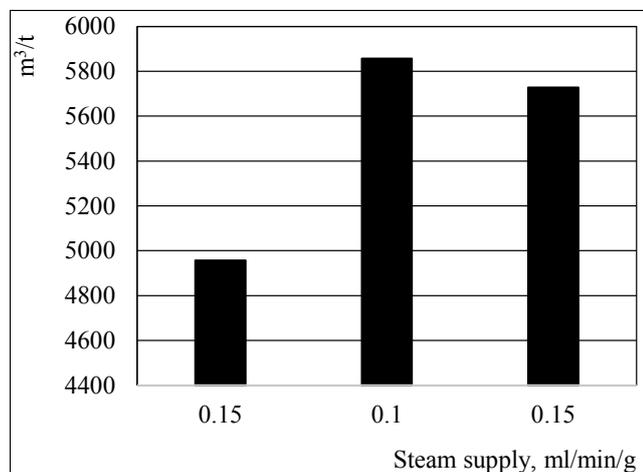


Fig 12. Gas volume produced from UR at various steam supply rate (900°C)

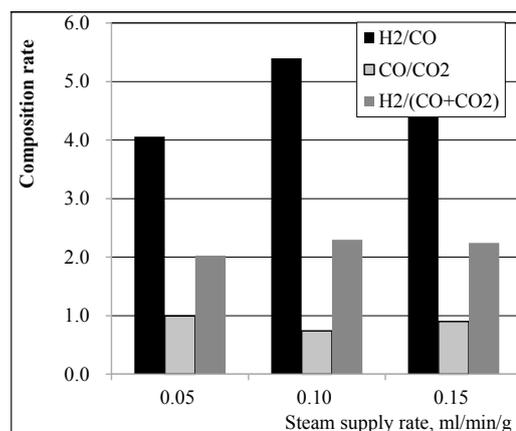


Fig 13. Composition rate of water gases from UR at various steam supply rate (900°C)

the acceleration of the water-gas shift and Boudouard reactions. HHVs of the total gas produced using various steam supply rates had a similar tendency as gas production as shown in Fig.14. Gas compositions produced using various steam supply rates were similar, and the effect on the HHVs of produced gas was minimal.

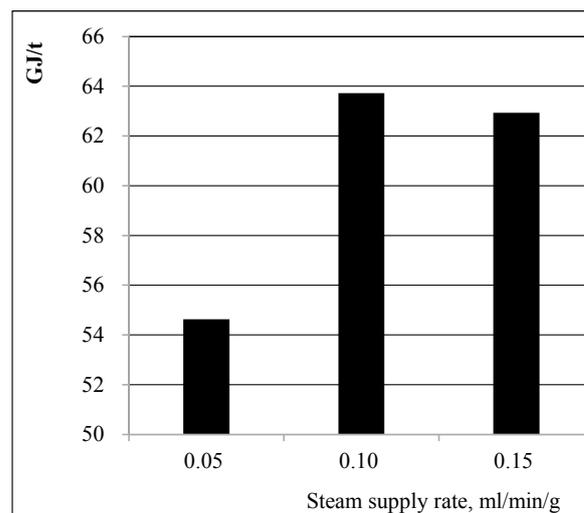


Fig 14. Total HHV of water gas from UR at various steam supply rate (900°C)

5. Discussion of theoretical and experimental gas composition

The theoretical relationship between gas composition and H₂/CO ratios were calculated and the theoretical curves of H₂, CO, and CO₂ concentrations to H₂/CO ratios are shown in Fig. 15. The gasification reaction calculations are as follows:

- 1) Water-gas reaction: $C + H_2O \rightarrow CO + H_2$
- 2) Water-gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$
- 3) Boudouard reaction: $C + CO_2 \rightarrow 2CO$

The calculations and experimental data are illustrated in Fig. 16. Point A indicates where the gasification reaction is

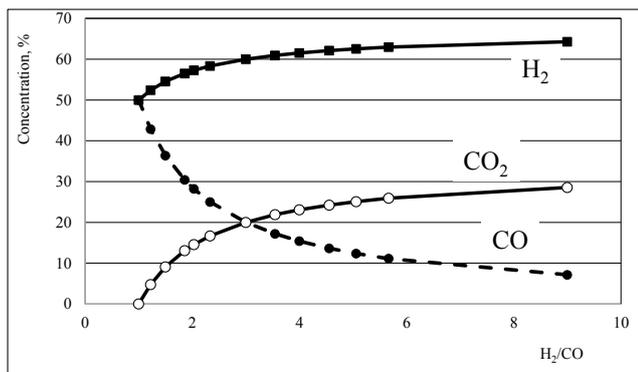


Fig 15. Theoretical gas composition diagram

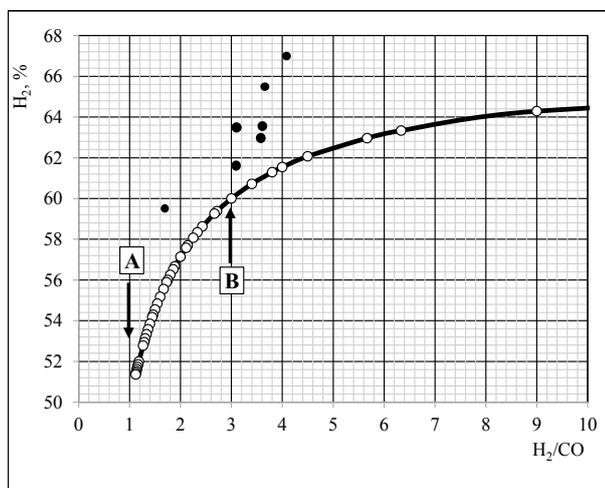
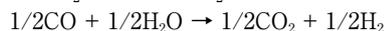
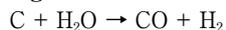


Fig 16. Theoretical gas composition curve and experimental values

preceded only in the water-gas reaction, whereas point B indicates where the gasification reaction is preceded in the water-gas and water-gas shift reactions. Half of the CO produced from the water-gas reaction is consumed in the water-gas shift reaction as follows:



$$H_2 = 1.5, CO = 0.5, CO_2 = 0.5$$

All of the experimental values had a higher hydrogen concentration than the theoretical values. A small amount of hydrogen was produced by the reaction of water with heavy metals, which was observed using an empty reactor and steam. Note that excess hydrogen production is caused by reaction with metals in a reactor.

CONCLUSIONS

We investigated a two-step gasification of rice samples via a carbonization step followed by steam gasification. A

high yield of clean water gas was produced with no by-products such as tar and oil; moreover, the effect of inorganic compounds in RH and RS on acceleration of the gasification process was indicated. Water gases were produced at a high yield of 4,700 m³/t of RH char, 3,400 m³/t of RS char, 5,000 m³/t of UR char, and 5,800 m³/t of BR char. Gas composition rates were approximately 4 for H₂/CO and 1 for CO/CO₂. HHVs of total produced gas were over 60 GJ/t of chars under a high gasification temperature. The Boudouard reaction was accelerated and the water-shift gasification reaction was suppressed by increasing the gasification temperature. HHVs of produced gas increased concurrently with an increase in gasification temperature, which is reflected in the gas production volume. However, an increased steam supply to appropriate rates increased the volume of produced gas and specific HHVs. Nevertheless, an excessive supply rate cooled the reactor and resulted in a decreased gasification reaction rate. In this study, the values of hydrogen contents were higher than those of the theoretical values. This result indicates that hydrogen gas is produced without gasifying sources. Various rice tissues were subjected to two-step gasification and were promising for water gas production energy source.

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粃、玄米、粃殻、稲藁から調製した炭からの熱分解による水素生産

小島康夫、加藤喜明

(平成27年10月14日受付)

要 約

炭化と水蒸気ガス化によるバイオマス2段階ガス化プロセスが検討されてきた。副生成物を発生せずに高濃度で水素を含有するこの新規な水性ガス生産プロセスは簡易な小型電気炉によって遂行することができる。粃、玄米、粃殻、稲わらが熱分解ガス化の資源としての可能性を評価するために、それらの試料はガス化原料として炭化された。炭化収率は、試料中のケイ酸化合物含有量に対応していた。期待したとおり、タールや油状物質など副生成物を発生することなく稲試料から高収量で水性ガスが生産され、粃殻や稲わらに含まれる無機成分はガス化を促進させた。ガス化プロセスはガス化温度によって著しく影響を受け、ガス化温度が上昇することにより Boudouard 反応 ($C + CO_2 \rightarrow 2CO$) は促進され、water-shift gasification 反応 ($CO + H_2O \rightarrow CO_2 + H_2$) は抑制されることが明らかになった。高位発熱量 (HHV) と生成ガス量はガス化温度が高いほど増加した。水蒸気投入速度の上昇は、ガス生成量と単位あたりの HHV は向上したが、過剰な投入速度の上昇は反応容器を冷却しガス化速度を低下させてしまった。この研究で、生成ガス中の水素濃度は理論値よりも高い値を示した。このことは水素がガス化剤を利用しなくても生成されることを示しており、1 部の水素が反応容器の内部表面に存在している金属と反応したものと推定される。

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