

Hydrogen-rich gas production by steam gasification of bio-char: Influence of char characters, reaction temperature and steam supply on gas composition and hydrogen gas yield

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Summary

We have proposed two stage thermal gasification, carbonization stage and steam gasification stage, as a new system, in which any by-products such as tar are not produced. In this new gasification system, effects of wood resources used to bio-char production, char particle size, gasification temperature, and steam supply rate on gasification rate and hydrogen gas yield were estimated with a small electrical simple furnace. On this gasification, hydrogen gas was produced in a yield close to the theoretical value, and by-products such as tar and oil were not formed in steam gasification process. Therefore, it is considered that the thermal gasification reaction of char with steam proceeded in a very simple mechanism. The difference of wood resources had a small effect on the bio-char steam gasification, and physical properties such as density had a slight effect on gasification rate. Increases in gasification temperature and steam supply rate changed the water gas and water-gas shift reaction rates. The produced gases contained hydrogen gas in higher content from 56 to 62vol. %, which contained carbon monoxide from 12 to 32vol. %. Specific higher heating values of the gases were around 12MJ/m³ and total calories of the gases were over 50MJ/kg of bio-char. Increase in char particle size caused higher gasification rate because of decrease in the bulk density.

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Key words : Bio-char, steam gasification, hydrogen production, reaction rate

Gasification of biomass (wood-based materials, agricultural residues, forestry waste etc.) is a promising technology that provides competitive means for producing chemicals and energy from renewable energy sources (Bridgwater, 2003). The gas mixture from the gasification process can be utilized in both conventional and advanced technologies for production of electrical energy, thermal power and automobile fuel giving a positive environmental contribution as biomass fuels are considered as a carbon neutral (Cetin *et al.*, 2005). The gas mixture resulting from the gasification process can also be used to produce syngas which has a direct application in all hydro-treating operations, ammonia production, and the synthesis of methanol, dimethyl ether and super-clean liquid fuels, such as Fisher-Tropsch oil (Kim *et al.*, 2013). The demand for hydrogen is on the rise due to increase utilization of hydrogen as a new fuel. Currently, hydrogen gas is mostly produced by process as the catalytic reforming of natural gas, liquefied petrol gas, and naphtha with steam. Such a process, however, results a significant amount of carbon dioxide emission and thereby contributed to the global warming. For this reason, alternative methods of producing hydrogen gas are being studied including direct gasification of biomass which is a renewable source (Wang *et al.*, 2008; Kawamoto *et.al.*, 2009). A critical review of the

relevant literatures reveals that steam is the most widely accepted as a gasification agent for production of hydrogen gas mainly due to quality of the product gas and high yield of hydrogen (Mermoud *et al.*, 2006). Xiao *et al.* (2007) evaluated the effect of gasification temperature on gas composition from bamboo using a lab-scale fluidized bed. Kinetic study on bamboo pyrolysis was studied to understand, model, and control the decomposition process (Edward *et al.*, 2008).

The progress in the field of hydrogen production from biomass has been largely hampered by technical issues associated with tar formation, which reduces the efficiency of gas production and interferes with the equipment operation (Sun *et al.*, 2011). Formation of tar compounds generally renders the product gas mixture unsuitable for commercial application. Numerous investigations have been conducted on the elimination/destruction of tar compounds formed during biomass gasification (Rath and Staudinger, 2001; Devil *et al.*, 2003; Li *et al.*, 2004; Han and Kim, 2008). Practical possibilities of tar removal/destruction methods involve (with exclusion of in-bed methods and multi stage methods) high medium temperature downstream methods, usually based on catalytic tar cracking (Sulk *et al.*, 2012). The other methods (like hot electrostatic precipitators and adsorption by various solvents at temperatures below 400 °C) can be considered rather as

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auxiliary methods (Zwalt, 2009).

Gasification process generally consists of two primary steps: initial pyrolysis and subsequent char gasification. The latter is a late-determining step that may control the overall conversion process (Zhang *et al.*, 2008). Gasification of biomass chars called bio-chars has been developed to gain a better understanding of the 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 been reported on the gasification of bio-char from different kinds of biomass, e.g. grapefruits skin (Montesions *et al.*, 2002), Japanese cedar (Matsumoto *et al.*, 2009), sunflower shell (Haykiri-Acma *et al.*, 2006), bamboo (Kato *et al.*, 2014), kenaf (Kojima *et al.*, 2014), beech wood (Wolfgang and Michael, 2005), slash pine (Fermoso *et al.*, 2009) and bagasse (Chaudhari *et al.*, 2003). Yan *et al.* (2010) tried to product hydrogen rich gas by steam gasification of bio-char as a by-product from fast pyrolysis liquefaction process. They concluded that both high gasification temperature and introduction of proper steam led to higher yield of dry gas and higher carbon conversion efficiency. Umeki *et al.* (2012) proposed that untreated char produced from high temperature steam gasification system can be extracted from the gasifier and combusted to generate high temperature steam.

We have been proposed a new gasification system without tar formation using chars as the gasification sources. The system design is consisted of two reactors separated as follows: the first reactor is a carbonization furnace for char production and the second reactor is gasification part. Wood gas and char produced in the first reactor are divided, wood gas including tars is led to outside of the second reactor, and char is led to inside of the second reactor. Wood gas can be used as the heat source of the second reactor for gasification in practical plants. The purpose of this study is how to produce the clean hydrogen gas from char with steam more effectively. Therefore, various bio-chars were prepared from four wood species and gasified with steam under various gasification conditions, such as gasification temperature, steam supply rate and char particle size.

2. Experimental

2.1 Materials

Four wood species of two softwoods, Japanese cedar (*Cryptomeria japonica*) and Japanese larch (*Larix leptolepis*), and two hardwoods, Japanese oak (*Quercus mongolica*) and white birch (*Betula platyphylla*), were provided from Forest Research Station, Hokkaido University. These samples were dried and cut with a laboratory small chipper to the size ranged from 30mm × 30mm × 3mm.

2.2 Carbonization

Preparations of the bio-chars were performed by charging 400 g of wood pieces into a stainless-steel reactor with a length of 500 mm and an internal diameter of 80 mm.

The reactor was heated using a cylindrical electric furnace, and the temperature was monitored using K-type thermocouples placed in the interior and on the exterior of the reactor. The reactor was heated in 180 min to 600 °C, and then held at that temperature for 180 min. In order to obtain more reliable data, each carbonization was repeated three times, and the average of the results was used. The char yields were calculated as follows:

Char yield (%) = 100 × dried char weight (g)/dried wood weight (g)

The wood gases were then forced through a cyclone and collected in a gasholder behind a gas flow meter with which the produced gas volumes were recorded. The major gases, including H₂, CO, CH₄, and CO₂, were analyzed on a gas chromatograph (J-Science lab GC-7000T) equipped with a packed column (2 m × 3.2 mm activated carbon) and a thermal conductivity detector (TCD) using argon as the carrier gas. The column oven temperature was 70 °C and the TCD current was 90 mA. The higher heating values (HHV) of the wood gases were calculated using the HHV of each gas (H₂: 12.75 MJ/Nm³; CO: 12.63 MJ/Nm³; CH₄: 39.72 MJ/Nm³). Proximate analyses of the prepared chars from four wood species were performed according to JIS M8812. Elemental analysis was conducted using an elemental analyzer (J-Science lab Micro-corder JM10).

2.3 Gasification

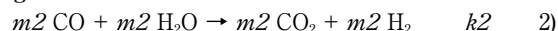
The prepared chars were crushed and screened to obtain particle sizes from 5 to 9 mm. To estimate of char size effect on the gas composition, cedar char was crushed and screened to four size fractions as follows: 1.7~2.0, 2~4.0, 4~9, 9~15mm. A fixed bed gasifier was placed inside the electric furnace, and 50 g of the char was placed into the gasifier. Prior to gasification, the air in the gasifier was forced through a cyclone and then replaced with nitrogen. The batch type gasifier reached the desired temperature in 30 min after heating was initiated; steam was supplied to the gasifier using a water pump. Gasification of the wood char was performed at 800, 900, and 1,000°C using a steam supply rate ranging from 0.025 to 0.10 g/min/g char. The generated gases were passed through a cyclone and a gasholder, and a gas meter was located behind the cyclone. The water gases were collected from the gasholder for measurement of the water gas composition, and the gas analysis was performed as described above for the carbonization step. Gasification rates were calculated initial gasification period from 0 to 90min in which the range of the gas production rate was linear.

The chemical reaction mechanism of char gasification with steam is considered to be very simple as described below.

Water gas reaction:



Water-gas shift reaction:



Boudouard reaction:

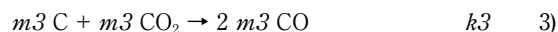


Table 1 Results of bio-char production from various wood sources

Carbonization results		Cedar	Larch	Oak	Birch
Reaction temperature, °C		600	600	600	600
Carbonization time*, min		360	360	360	360
Char yield, wt. %		32.1	33.2	31.6	30.2
Wood gas analysis					
Wood gas yield, Nm ³ /kg of char		0.23	0.22	0.26	0.27
Specific gas HHV, MJ/Nm ³		13.2	13.5	12.0	11.8
Gas composition, v.%	H ₂	12.8	11.3	11.1	8.2
	CO	33.1	30.3	28.3	35.5
	CH ₄	19.3	20.1	17.6	15.9
	CO ₂	35.0	36.7	43.1	40.8

Where,

$m1$ is reaction molar for water gas reaction.

$m2$ is reaction molar for water-gas shift reaction.

$m3$ is reaction molar for Boudouard reaction.

Then, weight of reacted carbon, and weight of produced H₂, CO and CO₂ gas were calculated as follows.

Weight of produced hydrogen (WH) = 2 ($m1 + m2$)

Weight of produced carbon monoxide (WCM) = 28 ($m1 - m2 + 2m3$)

Weight of produced carbon dioxide (WCD) = 44 ($m2 - m3$)

Values of WH, WCM and WCD were obtained from the experimental results from gas composition and each gas volumes. Approximations of each reacted moles, $m1$, $m2$ and $m3$ were derived from above equations. Reaction rate of $k1$, $k2$ and $k3$ were calculated from $m1$, $m2$, $m3$ and the gasification rate.

The structural characteristics of Char800 were observed using a scanning electron microscope (SEM, JEOL JSM-5310LV) without a conductive coating.

3. Result and discussion

3.1. Char preparation

Conditions of bio-char preparation from various wood species and their characters are shown in Table 1. Char yields from softwoods were slightly higher (33.21% in larch and 32.13% in cedar) compared to hardwoods (31.62% in oak and 30.16% in birch) because of their high lignin contents. Wood gases from carbonization of softwoods were consisted of lower CO₂ contents than those from that of hardwoods, and yielded lower wood gas volume. These results reflected to the higher specific HHVs of softwood gases than those of hardwood gases. As a result, HHVs of total wood gas were similar values in all wood species. These gases can be used as energy sources for the second stage gasification in a commercial plant system. The results of ultimate and proximate analysis of bio-chars are shown in Table 2. Volatile matter and fixed carbon of each bio-char were almost the same. Bio-char from cedar was low density caused by low density of raw wood and contained high ash content while other three chars were similar properties.

Table 2 Proximate and ultimate analysis of bio-chars from various wood sources

	Cedar	Larch	Oak	Birch
Volatile matter, wt. %	8.67	8.09	7.88	9.13
Fixed carbon, wt. %	87.62	88.931	89.56	88.31
Ash, wt. %	3.73	2.98	2.62	2.56
Apparent Density, kg/m ³	0.239	0.460	0.543	0.569
C content, %	87.32	89.12	90.14	89.67
H content, %	5.01	4.68	4.61	4.81

Table 3 Gasification results of bio-chars from various wood sources

	Cedar	Larch	Oak	Birch
Gas yield, Nm ³ /kg	4.99	5.08	4.89	4.83
Gasification rate, Ndm ³ /min/kg of bio-char	53.1	41.7	42.1	40.9
Specific gas HHV, MJ/m ³	11.9	12.2	12.5	12.8
Total gas HHV, MJ/kg of bio-char	59.5	62.2	61.0	61.6
Gas composition, vol. %				
H ₂	59.7	59.7	59.1	59.9
CO	21.2	22.4	23.6	23.5
CH ₄	1.9	1.1	1.7	2.2
CO ₂	17.2	16.8	15.5	14.4
Reaction rate of $k1$, m mole/min/kg of bio-char	860.2	670.6	696.2	681.1
Reaction rate of $k2$, m mole/min/kg of bio-char	399.0	322.6	301.5	299.5
Reaction rate of $k3$, m mole/min/kg of bio-char	26.6	13.7	21.5	24.7

* Gasification temperature: 800°C, steam supply rate: 0.025g/min/g of bio-char.

3.2. Gasification of biomass chars from various wood resources

Results of gasification of various bio-chars from wood species are shown in Table 3. Gas volumes produced from softwood chars were slightly higher than those from hardwood chars, and specific gas HHVs were lower. These results should be caused by char structure; particularly low density of cedar char accelerated the gasification rate. As a result, higher reaction rate of water gas reaction $k1$ of cedar char was observed. The values of $k2/k1$ were in the range of 0.43–0.48, and the values of $k3/k1$ were in the range of 0.02–0.04. This result indicates the water-gas shift reaction rate are lower than water gas reaction rate and Boudouard reaction rate was very low. Water gases compositions from each char samples were not differed and indicated the gasification mechanism of each samples was occurred in very similar manner. Figure 1 show the proposed gasification mechanism of bio-char with steam for water gas reaction of $5C + 5H_2O \rightarrow 5CO + 5H_2$ (first release of 4H radical are not counted) (Kojima *et al.*, 2014; Kato *et al.*, 2014). In first stage, bio-char released H radicals from the char surface and acted as OH radical acceptor at the surface carbon radicals. Then -C-O-H structure are induced at the char surface, H radicals are released from -C-O-H again and formed the carbonyl

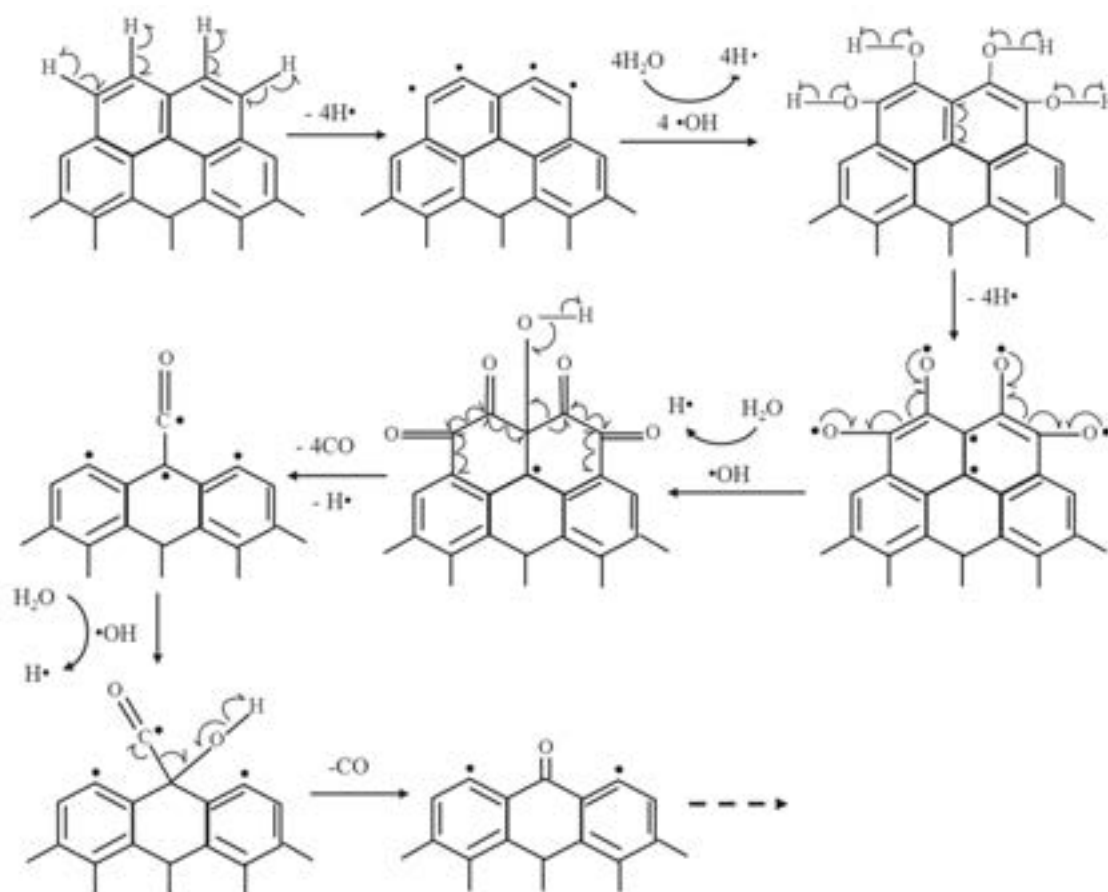


Fig 1. Proposed pathway of hydrogen production from bio-char with steam

structure. Electron transfers occur at the adjacent C-C bonds and form CO gas. This chain reaction is continued on the char surface in the presence of H₂O.

In this study, it was concluded that effect of biomass resources on the bio-char steam gasification are small and physical properties such as density have a slight effect on gasification rate. Boudouard reaction rate is very low and the effect on gas composition is little. Nilsson *et al.* (2012) showed that gasification rate with H₂O was faster than that with CO₂. In any bio-char from various woods, hydrogen rich water gases were obtained approximately 60% content in water gas produced.

3.3. Effect of gasification temperature on gasification rate and gas composition

Gasification temperature is a most impact factor on the gas composition and gasification rate. The effect of the gasification temperature with cedar char was shown in Table 4. Water gas yield was higher in 800°C gasification and decreased by gasification temperature. Gasification rate was very low in 800°C gasification and increased by increasing gasification temperature.

In the case of gasification at 800°C, gasification rate was

Table 4 Effect of gasification temperature on properties of water gas from cedar char

Temperature, °C	800	900	1000
Gas yield, Nm ³ /kg	4.66	4.22	4.15
Gasification rate, Ndm ³ /min/kg of bio-char	34.78	60.61	74.84
Specific gas HHV, MJ/m ³	10.23	12.04	12.66
Total gas HHV, MJ/kg of bio-char	47.61	50.73	52.31
Gas composition, vol. %			
H ₂	61.6	56.9	56.2
CO	11.9	25.7	29.8
CH ₄	0.8	0.7	0.5
CO ₂	26.0	16.9	13.8
Reaction rate of k ₁ , m mole/min/kg of bio-char	710.4	1197.2	1011.7
Reaction rate of k ₂ , m mole/min/kg of bio-char	393.7	487.4	238.5
Reaction rate of k ₃ , m mole/min/kg of bio-char	2.0	0.0	0.0

* Char size: free, Steam supply: 0.05g/min/g of bio-char.

Table 5 Effect of steam supply on properties of water gas from cedar char

Steam supply rate, g/min/g of bio-char	0.025	0.05	0.075	0.10
Gas yield, Nm ³ /kg	4.27	4.22	4.29	4.27
Gasification rate, Ndm ³ /min/kg of bio-char	54.27	60.61	75.03	72.15
Specific gas HHV, MJ/m ³	13.02	12.04	12.00	11.42
Total gas HHV, MJ/kg of bio-char	55.54	50.73	50.70	48.99
Gas composition, vol. %				
H ₂	56.68	56.90	57.31	59.52
CO	32.41	25.67	24.65	20.27
CH ₄	0.02	0.69	0.59	0.66
CO ₂	11.39	16.94	17.67	19.61
Reaction rate of <i>k</i> 1, m mole/min/kg of bio-char	1055.3	1197.2	1442.3	1391.7
Reaction rate of <i>k</i> 2, m mole/min/kg of bio-char	271.4	487.4	624.4	747.1
Reaction rate of <i>k</i> 3, m mole/min/kg of bio-char	0.0	0.0	4.0	3.8

* Char size: free, Gasification temperature: 900 °C ,

very low, which indicated that water gasification reaction was inhibited. On the other hand, higher gas yield, higher H₂ content and lower CO content in the produced gas indicated that water-gas shift reaction was promoted. These results were supported by reaction rates of *k*1, *k*2 and *k*3 and may be reasonable because water-gas shift reaction is exothermic reaction. Lower HHV of water gas from low temperature gasification was caused by low content of CO. As increasing gasification temperature, gas yield were decreased and gasification rate were increased because of increase of *k*1 and decrease of *k*2.

3.4. Effect of steam supply on gas yield, higher-heating value and gas composition

As well as temperature, steam supply is considered to be an important factor on gasification rate and gas composition of biomass using steam as gasification reagent. Fifty grams of bio-chars were used for gasification in this study and steam supply rate was from 0.025 to 0.10g/min/g of bio-char. The result was shown in Table 5. Increasing steam supply rate from 0.025 to 0.075g/min/g increased gasification rate, which hardly caused change of water gas yield. The steam supply rate decreased specific gas and total gas HHVs. Furthermore, in produced gas components, H₂ and CO₂ contents were increased and CO content was decreased. The decrease of CO content led to the decrease of specific gas and total gas HHVs. Steam as a gasification reagent can affect water gas and water-gas shift reactions. The increasing steam supply rate increased both reaction rates (*k*1, *k*2), which increased the value of *k*2/*k*1 from 0.26 to 0.43. These results indicate that increasing steam supply rate promote water-gas shift reaction rather than water gas reaction. Yan *et al.* (2010) reported that raising steam flow rate decreased CO gas yield and increased H₂ and CO₂ gas yield in the gasification of char produced by fast pyrolysis.

Table 6 Effect of char size on properties of water gas from cedar char

Char size, mm	1.7~2	2~4	4~9	9~15
Gas yield, Nm ³ /kg	4.40	4.27	4.29	4.35
Gasification rate, Ndm ³ /min/kg of bio-char	59.89	72.10	76.93	80.00
Specific gas HHV, MJ/m ³	11.09	11.44	11.62	11.62
Total gas HHV, MJ/kg of bio-char	48.65	48.98	49.78	51.18
Gas composition, vol. %				
H ₂	59.7	59.5	59.6	58.6
CO	17.9	20.3	21.3	22.7
CH ₄	0.6	0.6	0.5	0.7
CO ₂	21.8	19.7	18.6	18.2
Reaction rate of <i>k</i> 1, m mole/min/kg of bio-char	1110.4	1391.7	1462.9	1486.6
Reaction rate of <i>k</i> 2, m mole/min/kg of bio-char	631.3	747.1	767.7	722.5
Reaction rate of <i>k</i> 3, m mole/min/kg of bio-char	2.7	3.8	8.1	46.0

* Gasification temperature: 900°C, Steam supply: 0.05g/min/g of bio-char.

Increasing steam supply rate from 0.075 to 0.10g/min/g decreased gasification rate. Increasing steam supply led to decrease in the gasification temperature. Water gas reaction as endothermic reaction affects gasification temperature rather than water-gas shift reaction as exothermic reaction. The increasing steam supply rate decreased water gas reaction rate *k*1, while water-gas shift reaction rate *k*2 was increased. These results indicate that the decrease in the gasification rate results from suppression of water gas reaction caused by a drop in gasification temperature.

3.5. Effect of bio-char particle size on gas yield, higher-heating value and gas composition

Bio-char particle size is considered to be an important factor on gasification rate because decrease in the particle size increases specific surface area of feedstock. Cedar char particle sizes were divided into four groups and 50g of each the bio-chars was used for gasification in this study. The result was shown in Table 6. Increase in bio-char particle size increased gasification rate, while water gas yield and specific gas and total gas HHVs were similar. Furthermore, in produced gas components, CO content was increase. The variation of char particle size affects bulk density of feedstock into the reactor. Decrease in char particle size increases the bulk density because of decreasing pore space in feedstock. Therefore, decreasing the pore space would suppress contact between char and steam, decreasing the gas reaction rate. The fact also suggests that specific surface area of bio-char hardly affect steam gasification rate. The contact between char and steam affects water gas and water-gas shift reactions. By increasing the particle size, water gas reaction rate *k*1 was increased and the value of *k*2/*k*1 was decreased from 0.57 to 0.49.

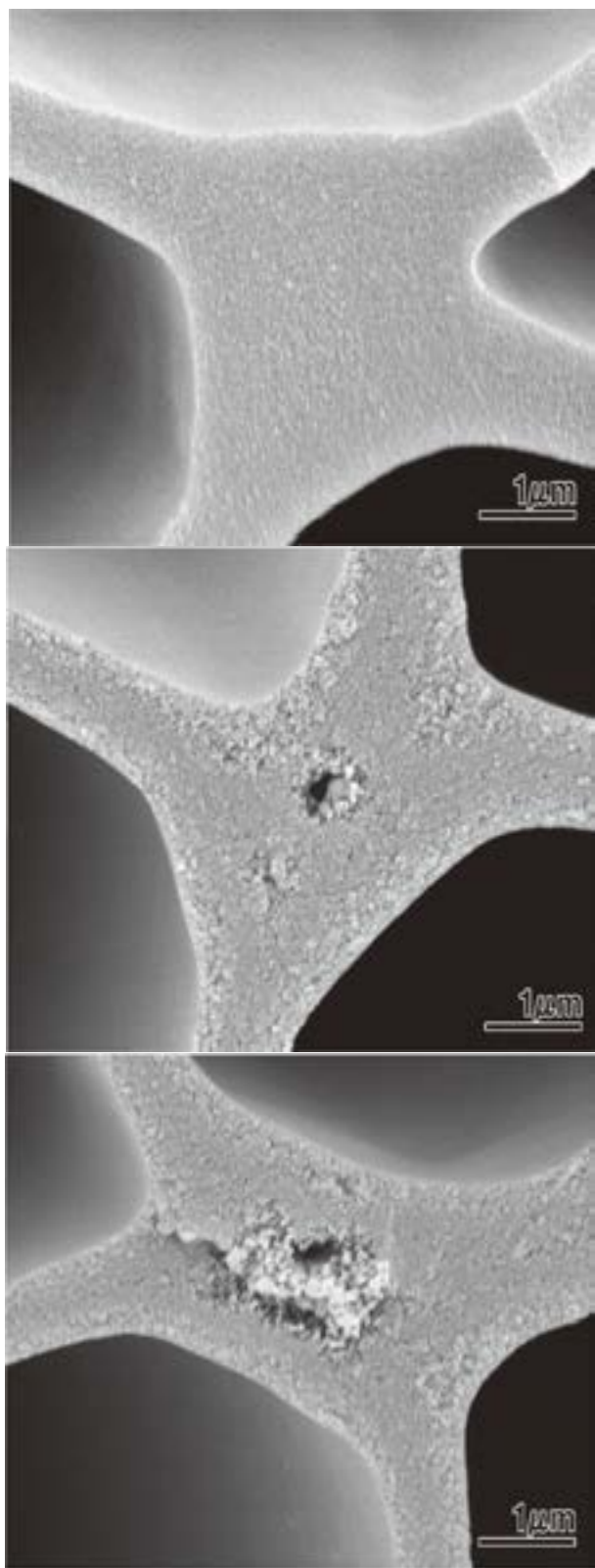


Fig 2. SEMs of char cross section before and after gasification. Top; char, middle; gasified for 30min, bottom; gasified for 60min.

3.6. Structural change of the wood tissue and the cell wall during steam gasification

Analytical Scanning electron micrographs (SEM) observation of the char structures from red oak before and after 30min gasification (28% weight loss), and 60min gasification (51% weight loss) were subjected. The feature of parenchyma cell walls and cell corners from char is observed clearly with no damage before gasification. Cell corners with high lignin content were collapsed during the gasification caused by thermal deformation of amorphous lignin structure as shown in Fig.2. The collapsed area is increased with proceed the gasification.

4. Conclusion

Gasification of bio-char using a laboratory small funnel yielded the production of higher hydrogen content gas without tar formation. Gas yield was over 4000m³ per ton of char (calculated) with over 2000kcal HHV. H₂/CO ratios in produced gas were ranged from 1.7 to 5.2 by changing the gasification temperature and steam/char ratio. For utilization of the gas as fuel in co-generation or as raw material for MeOH synthesis, gas cleanings and reform are not required, so clean gas can be obtained in variable H₂/CO ratio at outlet of gasifier.

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水蒸気ガス化によるバイオチャーからの高水素含有ガスの生産 - バイオチャーの特性および反応温度、水蒸気供給速度のガス組成と水素収量の与える影響

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要 約

バイオマスの二段階水蒸気ガス化は、バイオマスの炭化過程とその炭化物を用いた水蒸気によるガス化過程に分かれている。この二段階ガス化は、従来の直接ガス化で問題となっていたタールを発生しない方法である。本研究では、ガス化条件を最適化検討するために、炭化原料、ガス化温度、水蒸気供給速度、炭化物サイズに着目し、ベンチスケールの電気炉を用いて二段階水蒸気ガス化を行った。針葉樹としてスギ、カラマツ、広葉樹としてミズナラ、シラカンバの炭化物を用いてガス化した結果、生成ガスの樹種による影響は小さかった。また、生成ガス組成がメタンなどの炭化水素をほとんど含んでおらず、水素、一酸化炭素、二酸化炭素より構成されていることから、このガス化反応が水性ガス化反応、シフト反応、ブードア反応からなる単純なものであることが示された。そこで、スギ炭化物を用いてガス化温度、水蒸気供給速度、炭化物サイズのガス化への影響を検討した。ガス化温度および水蒸気供給速度に関しては、水性ガス化反応とシフト反応における反応速度に影響を与えることが明らかになった。また、炭化物サイズに関しては、嵩密度の変化によるガス化速度への影響が明らかになった。

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