

Kenaf as a Bioresource for Production of Hydrogen-rich Gas

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Abstract

The two-step gasification of biomass via carbonization-step followed by steam gasification, which produces hydrogen-rich water gas without any byproducts, was achieved using a small laboratory system. Carbonization of kenaf from 600 to 1000°C produced suitable chars for further steam gasification, which generated clean hydrogen-rich gases without any byproducts. On the other hand, carbonization of kenaf at 400°C yielded an insufficient char that still contained raw chemical components, and generated hydrocarbons and tar-like materials during gasification. Importantly, the wood gas generated during carbonization had a sufficient Higher Heating Value (HHV) to serve as the heating source for the gasification. A lower gasification temperature induced the water-gas shift reaction, which led to a change in the hydrogen content in the water gas composition. Raising the gasification temperature increased the specific HHV and decreased the gas yield. In addition, at these gasification temperatures, the H₂ concentration in the water gases was greater than 58%, and the H₂/CO ratio ranged from 1.8 to 3.0. On the other hand, increasing the steam supply rate decreased the specific HHV and CO yield and increased the H₂ and CO₂ yields. Therefore, the water-gas shift reaction played an important role under these conditions. On the basis of all of the above results, it was concluded that the water-gas reaction, $C + H_2O \rightarrow CO + H_2$, leads to effective gasification of the kenaf char.

Keywords: Kenaf; Carbonization; Steam gasification; Hydrogen-rich gas

Introduction

Countries in eastern Asia and Japan, like many EU countries, have little or no reserves of good quality fossil fuels and thus must depend on imported energy. Therefore, it is in the national interest of these countries to develop alternative energy resources. The gasification of biomass (wood-based materials, agricultural residues, forestry waste, etc.) is a promising technology that provides a competitive means for producing chemicals and energy from renewable energy sources [1]. The gas mixture generated during the gasification process can be utilized in both conventional and advanced technologies for the production of electrical energy, thermal power, and as transportation fuels. Such fuels derived from biomass are environmentally favorable because they are considered to be carbon neutral [2,3]. Syngas which has direct application in hydro-treating operations, ammonia production, and the synthesis of methanol, dimethyl ether, and super-clean liquid fuels (such as Fischer-Tropsch oil) can also be produced from gasification products [3,4]. Furthermore, there is growing demand for hydrogen due to its increasing use as a fuel. Currently, hydrogen gas is largely produced via the catalytic reforming of natural gas, liquefied petroleum gas, and naphtha with steam. Such a process, however, results in a significant amount of carbon dioxide emissions and thereby contributes to global warming. For this reason, alternative methods for the production of hydrogen are being investigated, including direct gasification of biomass [5,6]. A critical review of the relevant literature reveals that steam is the most widely accepted gasification agent for the production of hydrogen gas, mainly due to the quality and high yield of the generated hydrogen [7].

Progress in the field of hydrogen production from biomass has largely been hampered by technical issues associated with tar formation, which reduces the efficiency of gas production and interferes with equipment operation [8]. Formation of tar compounds generally renders the product gas mixture unsuitable for commercial applications. Therefore, numerous studies have been conducted on the elimination/destruction of tar compounds formed during biomass gasification [9-12]. Practical possibilities for tarremoval/destruction other than in-bed and multi-step methods include high medium-temperature downstream methods that are typically based on catalytic tar cracking [13]. Processes such as hot electrostatic precipitation and adsorption by various solvents at temperatures below 400 °C are considered to be auxiliary methods [14].

Gasification generally consists of two primary steps: initial pyrolysis and subsequent char gasification. The latter is the rate-determining step that controls the overall conversion process [15]. Gasification of biomass chars has been investigated in order to gain a better understanding of char reactivity, and kinetic models have been reported using steam and carbon dioxide as gasification agents [16-20]. In addition, several studies have been reported on the gasification of biomass char from different types of biomass, e.g., grapefruit skins [21], Japanese cedar [22], sunflower shells [23], beech wood [24], slash pine [25], and bagasse [26]. Notably, Yan et al. [27] attempted to produce hydrogen-rich gas via the steam gasification of char formed as a byproduct in a fast pyrolysis liquefaction process. They concluded that both a high gasification temperature and introduction of the proper amount of steam led to a higher yield of dry gas and a higher carbon conversion efficiency. Umeki, et al. [2] also proposed that untreated char produced from high temperature steam gasification systems can be extracted from the gasifier and combusted to generate high temperature steam.

Kenaf (*Hibiscus cannabinus*) is a plant in the Malvaceae family that has a high potential biomass (22 t ha⁻¹), stem yield (18 t ha⁻¹), and a high growth rate (180–220 kg ha⁻¹ day⁻¹) throughout the growing season [28]. In addition, in some tropical regions, kenaf can be harvested two times a year. The cuticle of kenaf, which is located on the outer parts of the shoot and is composed of long fibers, is becoming an important resource for paper production. On the other hand, the inner parts of the kenaf shoot or the core, cannot be used because of the characteristics of these tissues, and thus they are considered waste material. This material could therefore be a potential biomass source. The gasification of kenaf was reported by Zhou et al. [29], and it was determined that the gas produced from kenaf could meet the requirements for gas engines used to generate electricity; however, the gasification efficiency was insufficient, with significant ash production.

On the basis of the above information, we have proposed a tar-free gasification system using kenaf chars as the gasification source. The system consists of two reactors: carbonization furnace for char production and gasification furnace. The wood gas and char produced in the first reactor are separated, and the wood gas, including any tar, is directed to the outside of the second reactor, while the char is fed to the second reactor. The wood gas can be used as the heat source for the gasification unit in commercial plants. To develop an effective and efficient process for the production of clean hydrogen gas from biomass char using steam, various chars were prepared from kenaf, and their effects on the steam gasification as well as gasification conditions, such as the gasification temperature and steam supply rate, were investigated.

Materials and Methods

Raw materials

The kenaf was grown at a plantation located in Jollabuk-do, Korea. The matured kenaf was harvested 152 days after planting and dried in the ambient temperature for more than three months. The air dried kenaf was then debarked to obtain the kenaf core, which was cut to a length of approximately 15 cm.

Carbonization

Two step gasification processes is illustrated in upper site of Figure 1. Preparation of the bio-char was performed by charging 400 g of kenaf core 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 for 180 min to a given temperature (400, 600, 800, and 1000°C), and then held at that temperature for 180 min. The char produced at each carbonization temperature is referred to as Char 400, Char 600, Char 800, and Char 1000, respectively. 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:

$$\text{Char yield (\%)} = 100 \times \text{dried char weight (g)} / \text{dried kenaf weight (g)}.$$

Wood vinegar or pyro-ligneous acid is a by-product from the charcoal production process [30]. It is a red-brown liquid generated from the gas and combustion of fresh wood burning under airless conditions. When the gas is cooled, it condenses into liquid, which contains acetic acid, methanol, acetone, wood oils and tars.

Uncondensed gas is called wood gas. These compounds are formed from decomposition of cellulose and lignin. In this study, the produced wood gases were forced through a cyclone and collected in a gas bag 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-Sciencelab 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 raw kenaf sample and kenaf chars were performed according to JIS M8812. Elemental analysis was conducted using an elemental analyzer (J-Sciencelab Micro-corder JM10). The structural characteristics of Char800 were observed using a scanning electron microscope (SEM, JEOL JSM-5310LV) without a conductive coating.

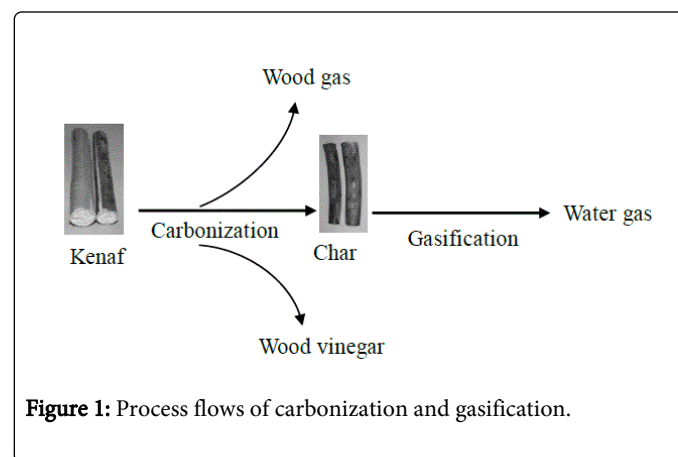


Figure 1: Process flows of carbonization and gasification.

Gasification

The prepared kenaf char was crushed and screened to obtain particle sizes from 5 to 10 mm. A fixed bed gasifier was placed inside the electric furnace, and the char (50 g) was placed into the gasifier. Prior to gasification, the air in the gasifier was forced through a cyclone and then replaced with nitrogen. The gasifier reached the desired temperature at 30 min after heating was initiated; steam was supplied to the gasifier using a water pump. Gasification of the kenaf char was performed at 800, 900, and 1,000°C using a steam supply rate ranging from 0.05 to 0.15 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.

Results and Discussion

Carbonization of kenaf

The results for the carbonization of kenaf at various temperatures are listed in Table 1, and the results for the proximate and ultimate analyses of the produced kenaf chars are shown in Table 2. The yield of kenaf char decreased as the carbonization temperature increased and then leveled off at 800°C as shown in Figure 2.

This tendency is similar to that reported for larch char production (indicated as the dotted line in Figure 2) [31]. The char yield and volatile matter obtained for Char400 were higher than those of the chars produced at higher temperatures due to insufficient carbonization. On the other hand, carbonization was sufficiently completed above 600°C. This conclusion is supported by the elemental analysis results for the kenaf chars, which indicated that the volatile material and carbon content for Char600, Char800, and Char1000 were decreased notably.

		C400	C600	C800	C1000
Temperature, °C		400	600	800	1000
Char yield, wt. %		63.29	37.08	31.37	29.73
Wood gas yield, Nm ³ /kg		0.138	0.308	0.369	0.412
HHV of wood gas, MJ/Nm ³		7.54	12.36	13.59	13.84
Gas composition%	H ₂	0.00	19.80	26.80	30.89
	CO	36.08	23.38	24.47	24.90
	CH ₄	2.79	13.41	13.61	12.81
	CO ₂	61.13	43.71	35.12	31.40

Table 1: Results of carbonization of kenaf at various temperatures; *Carbonization time was fixed at 360 min for all samples

Sample name	kenaf	C400	C600	C800	C1000
Carbonization Temp., °C	-	400	600	800	1000
Volatile matter, wt.%	80.36	32.48	15.36	10.58	8.6
Fixed carbon, wt.%	17.21	63.77	78.16	81.68	83.12
Ash, wt.%	2.43	3.75	6.48	7.74	8.28
C	42.49	61.71	86.97	92.86	94.31
H	5.92	4.91	2.86	1.97	1.83

Table 2: Proximate and ultimate analyses of kenaf chars

The gas from char production is referred to as wood gas and can be used as a fuel for following gasification process. Therefore, the gas yield and specific HHV of the wood gas are important factors. The yield and the specific HHV of the wood gas produced during kenaf carbonization increased with the carbonization temperature, while the gas yields were inversely proportional to the char yields. The yield and specific HHV of the wood gas obtained at each carbonization temperature are shown in Figure 3. Carbonization at 400°C resulted in a significantly low specific HHV due to the low CH₄ content in the wood gas as compared with that in the wood gases obtained at higher carbonization temperatures.

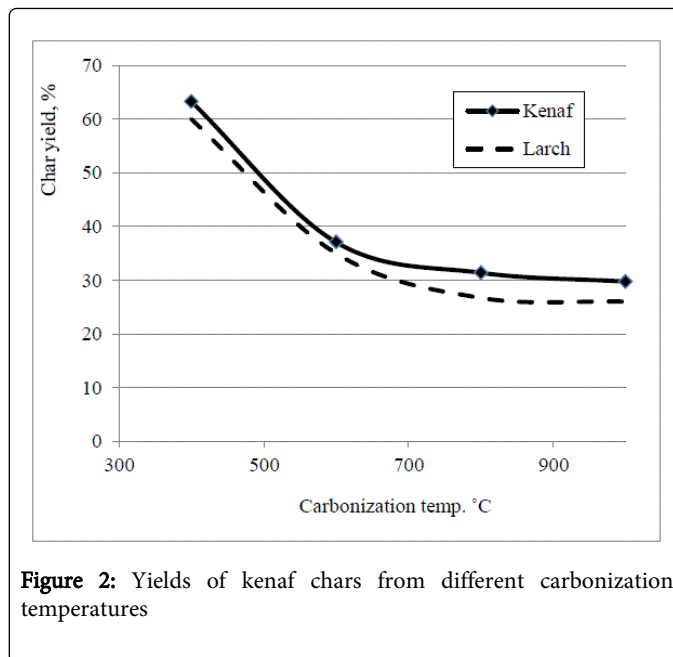


Figure 2: Yields of kenaf chars from different carbonization temperatures

The specific HHV depended on the wood gas composition; CH₄ has a higher caloric value than H₂ and CO. Generally, pyrolysis of biomass, such as via gasification and carbonization, initially generates tar as a byproduct that, under high temperature conditions, is then decomposed to hydrocarbons [13]. Thus, during the carbonization of kenaf at 400°C, it was concluded that decomposition of the tar did not occur, resulting in the low CH₄ content in the produced wood gas. It means that carbonization of kenaf at 400°C remained tar in the kenaf char, and did not provide the suitable char for gasification. Interestingly, raising the carbonization temperature led to an increase in the CO and H₂ content, as well as the CH₄ content, while CO₂ production leveled off above 600°C.

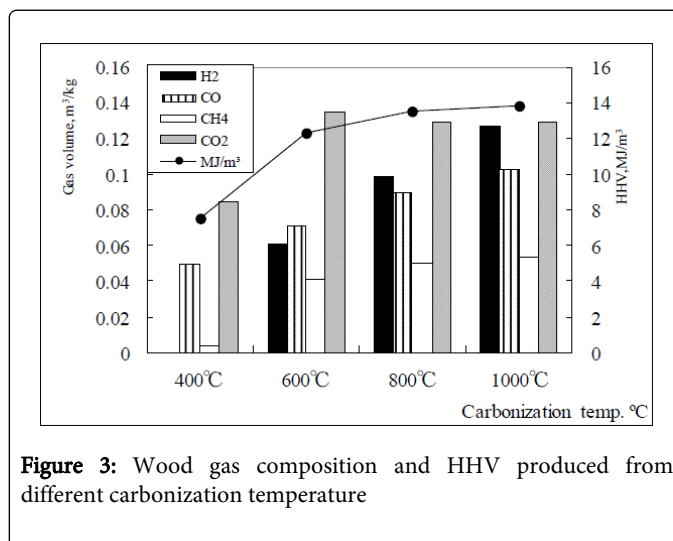


Figure 3: Wood gas composition and HHV produced from different carbonization temperature

The structural characteristics of the kenaf char are shown in Figure 4. A photograph of the kenaf before debarking can be seen (left) next to an image of the Char800 sample (right) in Figure 4a. This comparison confirms that the kenaf was indeed cracked during the carbonization process and carbonized completely. Figures 4b and

Figure 4c are low and high magnification transverse section SEM images of Char800, respectively. Interestingly, the tissue structure of Char800 remained the same as that in the original kenaf, and the parenchymatous pith (left) and woody tissues (right) can be observed (Figure 4b). In addition, vessel members with small pits can be seen (Figure 4c). A more detailed observation was previously reported by Voulgaridis, et al. [32].

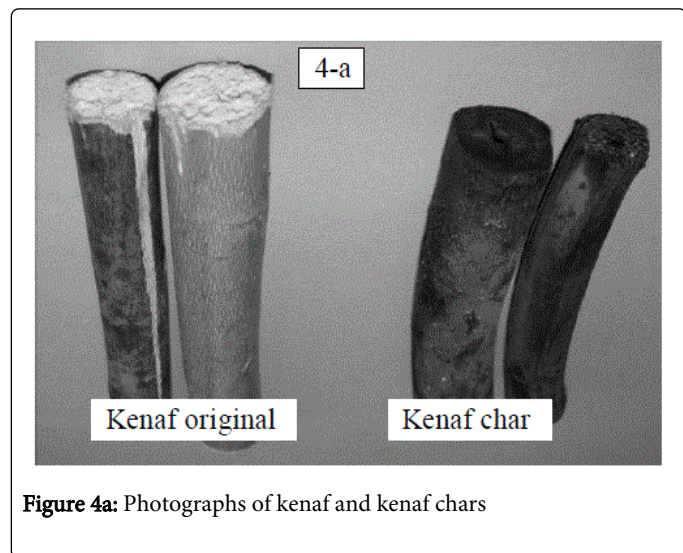


Figure 4a: Photographs of kenaf and kenaf chars

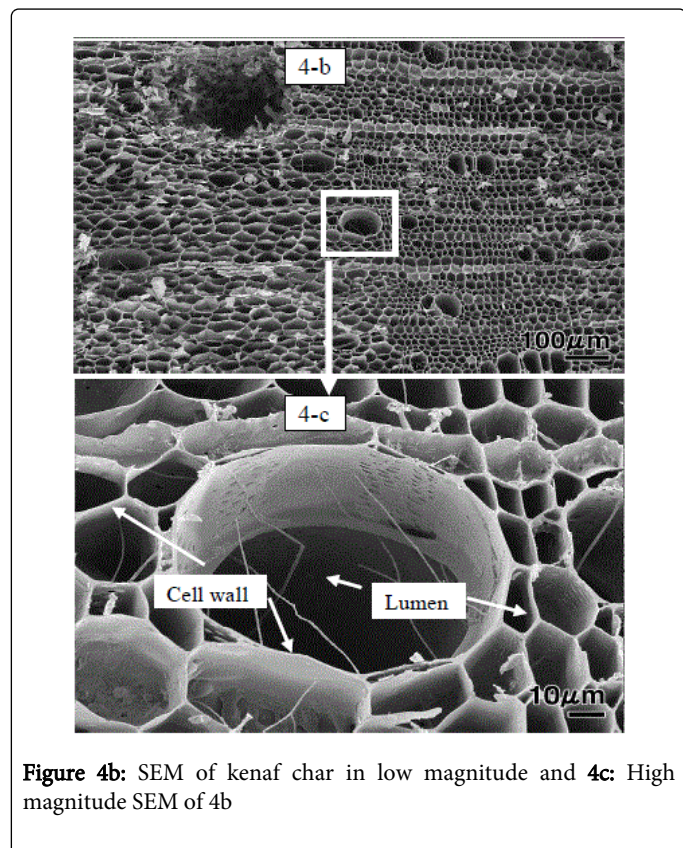


Figure 4b: SEM of kenaf char in low magnitude and 4c: High magnitude SEM of 4b

Gasification of the kenaf char

During gasification of the char with steam, clean fuel gases with high caloric value were produced. The final gas composition and HHV

is the result of the combination of a series of complex and competing reactions shown as follows:

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

The water-gas reaction is a solid-gas heterogeneous reaction; thus, the reaction mechanism should be more complex. We proposed formation mechanism of H and CO for char with steam via the water-gas reaction is $5C + 5H_2O \rightarrow 5CO + 5H_2$ (not including the initial release of 4 H radicals from the char), as illustrated in Figure 5. Char is a Hydrocarbons (PAHs), chemical structure showed in Figure 5 have been used as a structure model of char surface.

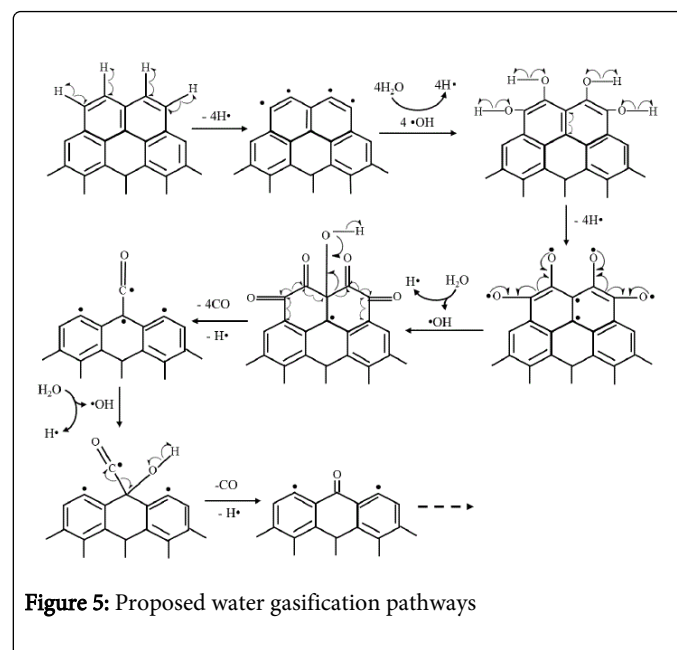


Figure 5: Proposed water gasification pathways

In the first step, H radicals are released from the char surface of the bio-char, and 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. Electron transfer then occurs at the adjacent C-C bonds, and CO gas is formed. The chain reaction then continues on the char surface in the presence of H_2O . In this steam gasification process, hypothetical transport route of steam and generated gas is proposed that the steam first diffuses into the lumen (intracellular space), and then gasification proceeds in the cell wall. The generated gases are then released to the lumen and spread to the exterior of the cell wall (Figure 4).

Effect of gasification temperature on the gas yield, HHV, and gas composition

The results of the steam gasification of the kenaf chars are listed in Table 3, and the effect of the gasification temperature and char preparation temperature on the specific HHV are shown in Figure 6. The gasification of Char400 produced water gas with a high specific HHV at all gasification temperatures due to the high CH_4 content of the water gas. However, the Char400 sample contained chemical

Sample name	C400			C600			C800			C1000		
Gasification temp. °C	800	900	1000	800	900	1000	800	900	1000	800	900	1000
HHV of water gas MJ/m ³	12.12	13.39	13.31	11.74	13.09	13.31	11.55	13.07	13.58	10.69	12.72	13.05
Total gas yield m ³ /kg of kenaf char	3.06	3.20	3.33	5.11	4.92	4.72	5.43	4.83	4.91	6.21	6.13	6.06
H ₂	1.81	1.80	1.92	3.23	2.83	2.79	3.37	2.75	2.80	3.90	3.22	2.92
CO	0.59	0.94	0.95	0.96	1.50	1.55	1.12	1.60	1.66	1.14	1.60	1.49
CH ₄	0.07	0.08	0.07	0.04	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO ₂	0.57	0.39	0.40	0.87	0.56	0.38	0.94	0.49	0.32	1.42	0.62	0.45

Table 3: Properties of water gas from kenaf chars; *Steam supply rate; 0.05 ml/min/g

components of the kenaf raw material in its char structure due to insufficient carbonization.

These intact chemical components, such as carbohydrates and lignin, produced the CH₄ along with tar during the gasification process. While the tar was not analyzed quantitatively, a small amount of tar-like substance was detected inside the pipe system and the cyclone after gasification of Char400. On the other hand, gasification of Char1000 yielded water gas with a low specific HHV due to the high content of CO₂. Water gas produced from steam gasification of Char600 and Char800 showed intermediate HHV values between those obtained for Char400 and Char1000. In addition, the gasification temperature had a significant effect on the specific HHV of the water gas produced from the kenaf chars; the results were noticeably different when the gasification temperature was increased from 800 to 900 °C. No significant effect on the specific HHV, however, was observed when the gasification temperature was raised from 900 to 1000 °C. In this temperature range, it seems that gasification reaction (1-3) was occurred in same degree.

The effects of the gasification temperature and char preparation temperature on the water gas yield are shown in Figure 7. Notably, the gasification temperature did not have a significant effect on the gas yield; the gas yield from Char400 only slightly increased, while the gas yield from Char600 and Char800 slightly decreased when the gasification temperature was increased. On the other hand, the char preparation temperatures had a significant effect on the water gas yield. The gas yield from Char400 was low despite its high volatile matter content. As mentioned above, this volatile material was converted to a tar-like substance during the gasification process, while the fixed carbon reacted with steam to form the water gas. The gas yield from Char1000 was approximately two times that from Char400, and was slightly higher than those from Char600 and Char800, which were 1.8 times that from Char400. Thus, the gas yield, as well as the specific HHV, depends on the char microstructure, such as the specific surface area and the pore volume of the char, which influences the reaction of the steam with the char.

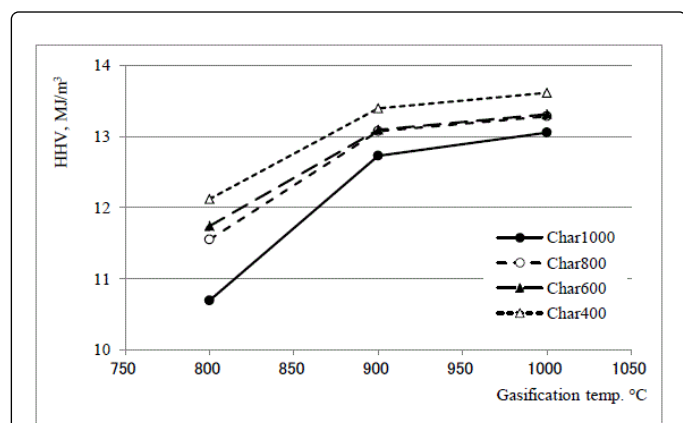


Figure 6: Effect of the char preparation temperature and the gasification temperature on gas production (steam supply rate 0.05 g/min/g)

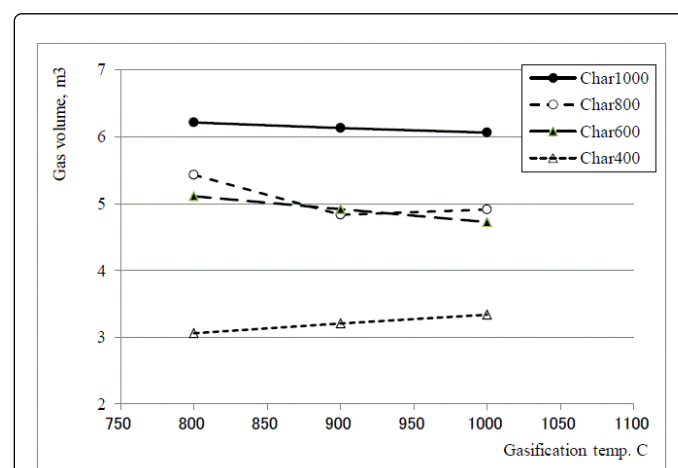


Figure 7: Effect of the char preparation temperature and the gasification temperature on gas production (steam supply rate 0.05 g/min/g)

The gasification of all of the kenaf chars proceeded in a similar manner, and the gas compositions produced from Char600, Char800, and Char1000 were also similar. Gasification of Char400 was complex because it involved both char gasification and biomass gasification. Therefore, the composition of the gas generated from gasification of Char400 contained hydrocarbons, such as methane, and tar-like substances that were not detectable by GC-TCD. The gas composition from the gasification of Char800 as a representative sample is shown in Figure 8. The gasification of Char800 at 800°C yielded higher amounts of H₂ and CO₂ and a lower CO content than that at 900 and 1000°C. This result suggests that gasification at 800°C accelerated the water-gas shift reaction because it is an exothermic reaction and dominant at the lower gasification temperatures used in this study. In the water-gas shift reaction, two moles of gas (H₂ and CO₂) are produced from one mole of gas (CO), and the relative specific HHV is reduced by the additional CO₂ production. During gasification of the kenaf char, the generated water gases were obtained without the formation of tar or other byproducts. This phenomenon is attributed to the absence of compounds including hydrogen and oxygen in the char structure.

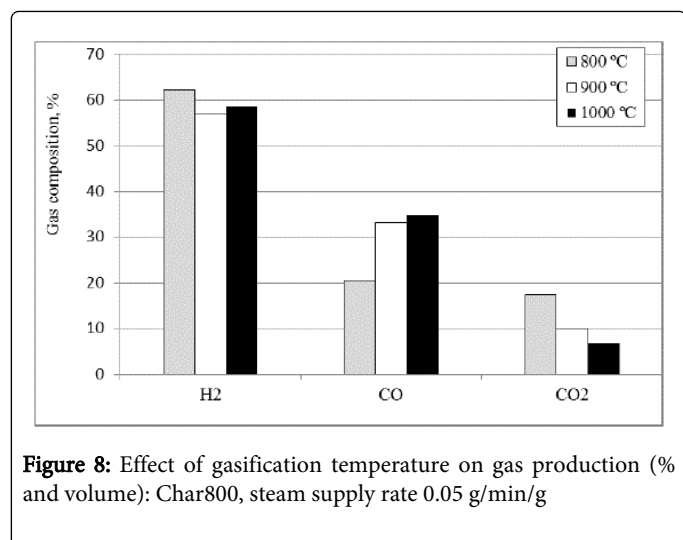


Figure 8: Effect of gasification temperature on gas production (% and volume): Char800, steam supply rate 0.05 g/min/g

The H₂/CO and CO/CO₂ ratios in the gas mixture produced from Char800 are shown in Figure 9. The highest H₂/CO ratio was obtained for the gasification at 800°C, while the gasification processes at 900°C and 1000°C yielded the same H₂/CO ratio. On the other hand, the lowest CO/CO₂ ratio was observed for the gasification at 800°C, and this ratio increased with the gasification temperature.

Effect of the steam supply on the gas yield, HHV, and gas composition

The results for the gasification of Char800 at 900°C at various steam supply rates (0.05 to 0.15 g/min/g char) are listed in Table 4. The specific HHV and gas yield decreased as the rate of the steam supply increased. The yields of H₂ and CO₂, however, increased with the steam supply rate, while the CO yield decreased, as shown in Figure 10. These results suggest that the increase in the steam concentration in the gasifier that occurs when the steam supply rate is increased leads to acceleration of the water-gas shift reaction. Furthermore, increasing the steam supply led to a reduction in the gasification temperature. Yan, et al. [27] reported that increasing the steam flow rate decreased

the CO yield and increased the H₂ and CO₂ yields in the gasification of char produced from fast pyrolysis liquefaction.

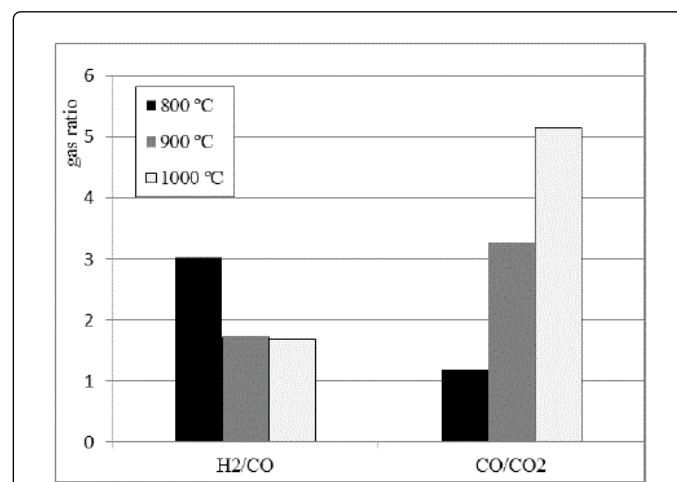


Figure 9: Effect of gasification temperature on water gas ratio: Char800, steam supply rate 0.05 g/min/g

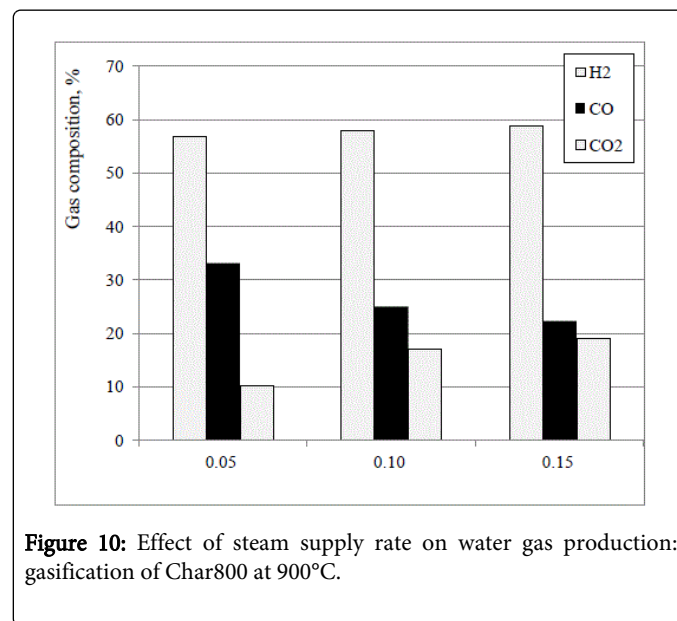


Figure 10: Effect of steam supply rate on water gas production: gasification of Char800 at 900°C.

Steam supply, ml/min/g of char	0.05	0.10	0.15
HHV of water gas, MJ/m ³	13.07	11.82	11.77
Gas yield, m ³ /kg	4.83	4.95	4.84
H ₂	2.75	2.87	2.82
CO	1.60	1.24	1.21
CH ₄	0.00	0.00	0.00
CO ₂	0.49	0.84	0.81

Table 4: Effect of steam supply on water gas properties

Thus, the specific lower heating value increased and the total gas yield decreased when the steam flow rate was increased. Li, et al. [33] also indicated that with municipal solid waste, the CO yield decreased and the H₂ and CO₂ yields increased with an increase in the mass ratio of the steam to the biomass. Therefore, it is possible that this effect of the steam supply rate may be observed for all types of biomass samples.

Conclusion

To evaluate kenaf as a second step gasification resource, carbonization of kenaf to produce char and gasification of the char were performed using a small laboratory system. Carbonization of the kenaf from 600 to 1000°C produced suitable chars as the source for steam gasification. The gasification of these kenaf chars produced clean hydrogen-rich gases without the formation of any byproducts. On the other hand, carbonization of kenaf at 400°C yielded insufficient char that contained raw chemical components and generated hydrocarbons and tar-like materials during the gasification process. Importantly, the wood gas from the carbonization step had a sufficient HHV for use as a fuel for heating the gasifier. In the gasification of the chars, notably, a lower gasification temperature induced the water-gas shift reaction, which led to a change in the water gas composition. Raising the gasification temperature increased the specific HHV and decreased the gas yield. The specific HHVs were 11, 12, and 13 MJ/m³ for gasification reactions run at 800, 900, and 1000°C, respectively. For all of these gasification temperatures, the H₂ concentration in the water gases was greater than 58%, and the H₂/CO ratios ranged from 1.8 to 3.0. Increasing the steam supply rate decreased the specific HHV and the CO yield, while the H₂ and CO₂ yields increased. In these cases, therefore, the water-gas shift reaction played an important role.

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