Open Access

Advances in Environmental and Engineering Research

LIDSEN Publishing Inc.

Original Research

Carbon–CO_2 Gasification to CO by Microwave Heating

June An, Young Nam Chun *

Department of Environmental Engineering, Chosun University, #309, Pilmun-daero, Dong-gu, Gwangju, 61452, Republic of Korea; E-Mails: soyobi@naver.com; ynchun@chosun.ac.kr

* **Correspondence:** Young Nam Chun; E-Mail: ynchun@chosun.ac.kr

Academic Editor: Zed Rengel

Adv Environ Eng Res
2021, volume 2, issue 4
doi:10.21926/aeer.2104031

Received: October 30, 2021
Accepted: November 23, 2021
Published: December 01, 2021

Abstract

Renewable energies such as solar or wind energy are highly unreliable, owing to uncertain energy intensity and discontinuity. This shortcoming could be overcome by converting renewable energies to a form such as chemical fuel storage. In the present study, we created an energy conversion system that uses microwave heating and a carbon receptor to transform CO_2, a greenhouse gas, into CO chemical fuel. The parametric investigation found that increasing the gasification temperature and feed gas temperature decreased the gas feed rate. In addition, the use of a carbon or charcoal receptor enhanced CO_2 conversion and heating values. Under ideal operating circumstances, CO_2 conversion was 83%, indicating that steady functioning was maintained consistently.

Keywords

Energy storage; microwave heating; carbon dioxide; greenhouse gas; renewable energy

1. Introduction

Renewable energy has been recognized as a means to address air and carbon pollution, the finite supply of fossil fuels, and related issues. To utilize renewable energy as an alternative energy source, we must first address the most serious challenge associated with renewable energy: intermittent energy output [1, 2]. Wind and solar power, two of the most common renewable energy sources, provide electricity in a discontinuous manner, depending on the time of the day and topographical conditions. Thus, manufacturing industries confront a major supply problem: supply does not always correspond with the peak demand periods. Therefore, renewable energy is currently employed as a backup energy source for fossil energy. Currently, interest in chemical energy conversion and storage technology as a solution to the aforementioned challenge is growing [3-7].

The gasification of carbon compounds has emerged as a promising solution to the above-mentioned chemical energy storage issues. This approach allows carbon-CO_2 gasification to utilize fixed carbon energy, allowing the recovery of energy lost during burning of the gas previously created by the gasification [8]. The carbon cycle for this advancement may be obtained by continually burning gasification products.

Because the Boudouard reaction—conversion of carbon and carbon dioxide (CO_2) to carbon monoxide (CO)—is highly efficient, a microwave heating approach for CO_2 gasification is more successful in creating CO than a traditional heating method under the same circumstances [9]. Unlike the traditional heating approach, which involves all parts of the reactor cavity to the requisite temperature for CO_2 gasification, the microwave heating method involves simply heating a carbon microwave receptor directly owing to its heating properties. Consequently, the microwave heating approach enhances the reaction, particularly in the local hot area within the carbon particle volume [10].

Carbonaceous materials are typically good microwave absorbers and can be utilized for microwave gasification [11]. Furthermore, microwave heating is a superior approach for catalytic heterogeneous processes. This is because, during heterogeneous processes of NO_x reduction [12], SO_2 reduction [13], and dry reforming of CH_4 [14-16], the conversion rate and selectivity can be enhanced. Microplasmas produced in the carbon absorber during microwave heating are attributable to the pseudo-catalytic effect [17].

As a carbonaceous material receptor, bio-charcoal has two good qualities [18]. First, bio-charcoal, a carbon receptor, has good polarization properties in the electromagnetic field, allowing rapid heating of the carbon receptor during microwave irradiation due to orientation and interfacial polarization. Second, the electromagnetic and thermal properties of bio-charcoal are nonlinear for temperature, resulting in the generation of a local hot spot known as microplasma, as well as small sparks and electric arcs. Although numerous studies have been performed on bio-charcoal, research on activated carbon as a microwave receptor for heating conversion is scarce [19-21].

Figure 1 depicts a carbon cycle with solar fuel production (CCSFP) that combines the carbon cycle with renewable energy storage to chemical energy for use as a solar fuel. The MW (or microwave) gas converter proposed in this work is the primary technology in this scenario, converting the carbons in the activated carbon and CO_2 to CO. The carbon material is heated by an MW gas converter powered by solar electricity.

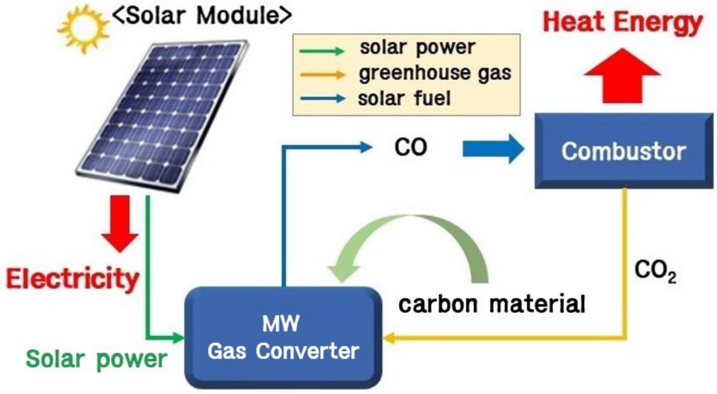

Figure 1 Carbon cycle with solar fuel production includes carbon-CO_2 gasification and CO combustion.

This study analyzes the progress of CO_2 gasification using microwave carbon receptors to study the conversion properties of CO_2 into chemical energy as a carbon capture utilization (CCU) technology. Furthermore, conversion characteristics of important influential parameters such as gasification temperature, feed gas temperature, gas feed rate, and carbon receptor were examined.

2. Methods and Apparatus for Experimentation

Figure 2 shows the experimental setup for carbon-CO_2 gasification by microwave heating, which included a microwave gas converter, a gas feed line, monitoring-control equipment, and a sampling/analysis line.

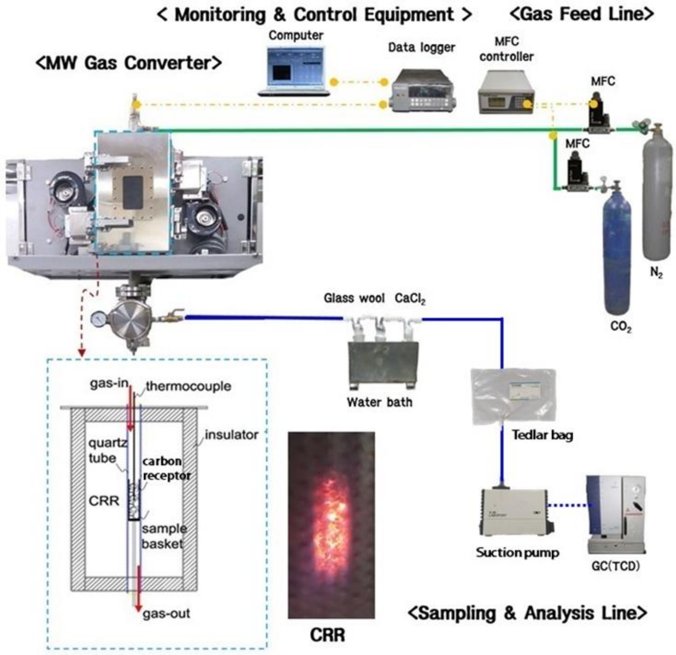

Figure 2 Experimental setup for microwave gasification.

A carbon receptor reactor (CRR) made of a quartz tube (23 mm in inner diameter, 410 mm in length) was vertically mounted on a multimode-microwave cavity oven. The carbon receptor's sample basket (22.5 mm in outer diameter and 90 mm in length; 57 perforations of ø1.85 mm on the bottom disc) could be moved up and down individually inside the CCR, allowing the receptor sample to be introduced and discharged into the reactor. The controller attached to a thermocouple (k-type, 2 mm in diameter) in the microwave carbon receptor efficiently adjusted the temperature of CRR, which can be set up to 1000 °C. Data recorded were used to continuously monitor the temperature inside the carbon receptor (Model Hydra data logger 2625A, Fluke, USA). The CCR was connected with a gas supply pipe.

Gasification gas CO_2 and carrier gas N_2 were delivered to the CCR via a cylinder and MFC or mass flow controller (Bronkhorst, F201AC-FAC-22-V, The Netherlands) that controlled the flow rate of each gas. For continuously monitoring and manipulating the gas supply rate and sample temperature, a LabVIEW (Model LabVIEW 8.6, National Instrument, USA) was used. The sampling-analysis line consisted of impingers with a glass wool filter and calcium chloride for removing soot and moisture, as well as a gas chromatography-thermal conductivity detector (GC-TCD; CP-4900, Varian, The Netherlands) for analyzing the product gas created from gasification.

The carbon receptor with a diameter of 2- to 3 mm, such as activated carbon (or charcoal), was used. The sample basket, which was located in the center of the CRR, was filled with an 8 g sample. The gasification gas was fed at a rate of 40 mL/min (volumetric hourly space velocity [VHSV] was 0.3 L/g·h). The gas flow rate was varied to examine the residence time in the CRR. After linearly increasing from room temperature, the microwave power supply was set at 1 kW to allow the sample temperature to retain the predetermined temperature. During the sample of the product gas, it was captured in Tedlar bags from the experiment at a fixed time interval to evaluate the components of the gas. GC-TCD was used to evaluate the collected product gases. To validate the physical properties before and after conversion by carbon-CO_2 gasification, Scanning Electron Microscope (SEM) (Model S-4800, Hitachi Co., Japan) investigation was performed.

The CO_2 conversion was computed using Equation (1).

$$\mathrm{CO_2 conversion}\ (\%) = \frac{(\mathrm{CO})_{\mathrm{out}}/2}{(\mathrm{CO_2})_{\mathrm{out}} + (\mathrm{CO})_{\mathrm{out}}/2} \times 100 \quad (1),$$

where $(CO_2)_{out}$, and $(CO)_{out}$ are carbon dioxide and carbon monoxide concentrations (%) evaluated at the outlet, respectively.

Activated carbon and charcoal constituted the carbon receptor for CO_2 gasification. To describe the carbon receptor, proximate analysis (Thermolyne Co., type 48000 furnace/Hansung Co., HS2140 Electronic Balance) and elemental analysis (Thermo Finnigan Co., EA2000/EA1112) were performed. Table 1 shows the chemical properties of carbon compounds for microwave receptors.

Table 1 Chemical properties of carbon compounds for microwave receptors.

	Proximate analysis (wt%)				**Ultimate analysis^{a,b} (wt%)**				
	M	A^a	VM^a	FC^a	C	H	N	S	O
Activated carbon	5.46	1.68	4.15	94.17	98.7	0.33	0	0	0.97
Charcoal	10.5	9.65	1.3	89.05	96.2	2.91	0.89	0	0

M: moisture, A: ash, VM: volatile matter, FC: fixed carbon. ^{a}Dry basis, ^{b}Ash-free basis.

An X-ray fluorescence (XRF) spectrometer (Shimadzu Co., ED-720) was used to detect K, Ca, and Fe to study the components involved in the catalytic activity of the carbide receptor during CO_2 gasification. Table 2 displays the results.

Table 2 Carbon compounds with an inorganic composition for microwave receptor (wt%).

Composition	K	Ca	Fe	Cu	S	Rb	Co
Activated carbon	73.4	20.3	4.22	0.96	0.68	0.44	0
Charcoal	65.4	20.6	9.85	2.08	1.15	0	0.92

3. Results and Discussion

3.1 Carbon-CO_2 Gasification Energy Storage

To characterize CO_2 gasification of carbon receptors under microwave heating, experiments were conducted at a CRR temperature of 900 °C and VHSV of 0.3 L/g·h.

With the initiation of CO_2 gasification, CO_2 conversion sharply increased to a maximum of 83% and was maintained for up to 4 h (Figure 3). The increase in the conversion rate at an early stage of gasification could be ascribed to the reaction of fixed carbon (C_{char}), a carbon receptor component, with CO_2 (gasification gas). This reaction leads to the formation of carbon monoxide (CO) during the Boudouard reaction (Equation (2)) by drastically increasing the temperature in the CRR as the microwave power started. This was further confirmed by a reduced concentration of CO_2 and increased concentration of CO during reforming. Although the rate of weight loss of carbide increased over time, the conversion rate was maintained at a constant level even 4 h later because of the sufficient fixed carbon (C_{char}) in the carbide that was used for carbon-CO_2 gasification reaction (Equation (2)).

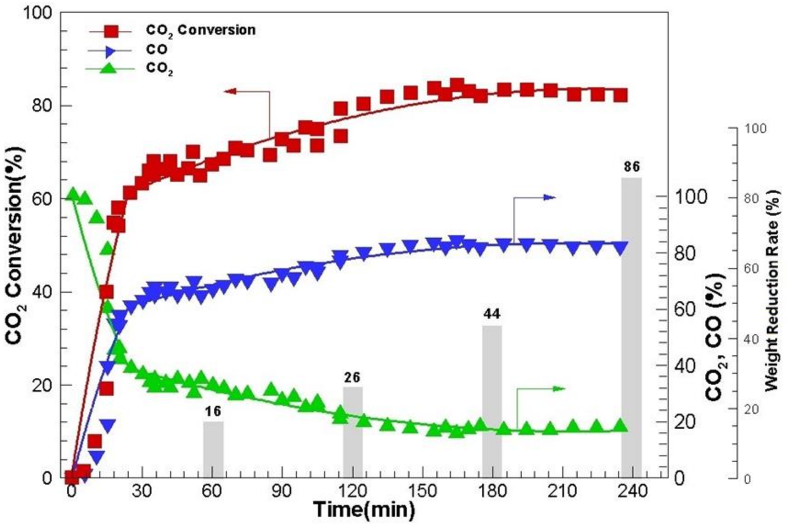

Figure 3 Carbon-CO_2 gasification results according to the passage of gasification time (bar graph indicates the rate of weight reduction of carbon receptor for each time interval).

$$\mathrm{Cchar} + \mathrm{CO_2} \leftrightarrow \mathrm{2CO} \qquad \triangle \mathrm{H_{298}} = +172\ \mathrm{kJ/mol} \tag{2}$$

During microwave heating, microwave energy is transferred to the inside of the receptor, followed by the conversion of kinetic energy, generated due to the object's vibration, into heat energy. Microwave heating is different from the conventional heating process, in which an object is heated by the heat transferred from the outside of the receptor. Microplasma, generated inside the carbon receptor, a dielectric solid, allows the maintenance of high temperatures at a specific value rather than at the temperature value of the bed of the heat receptor. Consequently, a gasification reaction is a heterogeneous reaction occurring in the hot spot. Figure 2 shows the microplasma phenomenon in the CRR.

The activated carbon, a carbon receptor, primarily consists of alkaline metal (K) and alkaline earth metal (Ca) as major catalyst components (Table 2). In addition, it is cheap with excellent catalytic activity and is less vulnerable to sulfur poisoning as compared with conventional catalysts. Moreover, the carbonaceous material promotes CO_2 gasification, resulting in an increased CO_2 conversion rate [20].

The CO_2 gasification reaction increased the rate of weight loss over time, suggesting that the oxidation of the fixed carbon in the carbon receptor increased the quantity of ash. Thus, the carbon receptor is present in a state of oxidizing flame (CaO and K_2O), continuously contributing to the catalytic reaction.

The activated carbon serves as a microwave carbon receptor before gasification (Figure 4a). Microwave-mediated irradiation and heating of this carbon receptor cause it to absorb the microwave energy. Further, it is subjected to volumetric heating to locally form microplasma, thereby generating local hot spots, causing surface deformation of the carbon receptor. The fixed carbon present on the surface of certain micropores are consumed during CO gasification, thus expanding the micropores and dissolving into ash (Figure 4(b)). This phenomenon continues over time, further expanding the micropores and dissolving into ashes on the surface of carbon receptors (Figure 4(c)).

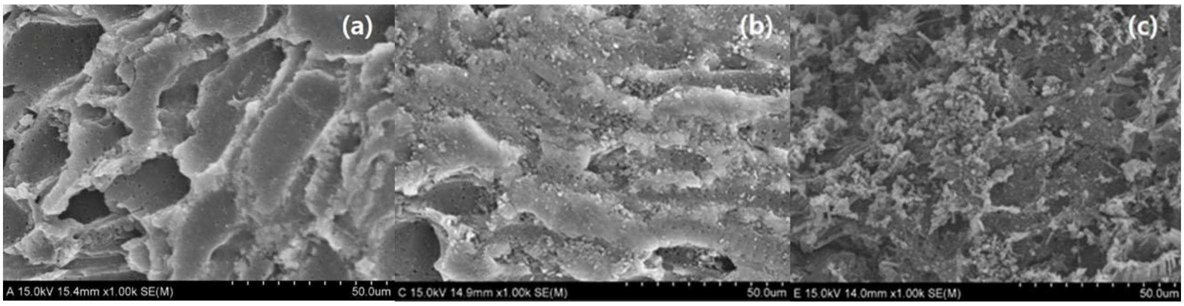

Figure 4 SEM images on activated carbon (a) before gasification, (b) 2 h after gasification, and (c) 4 h after gasification.

3.2 Studies on Major Influential Factors

The major factors influencing CO_2 gasification include gasification temperature, gas feed rate, feed gas temperature, CO_2 conversion, and product properties with respect to carbon receptor type and product characteristics. The results are shown below.

3.3 Effect of Gasification Temperature

During the experiment, the gas feed rate at room temperature (20 °C) was maintained at 40 mL/min (VHSV: 0.3 L/g·h) with charcoal as the carbon receptor (Figure 5). In addition, the gasification temperature was increased from 700 °C to 1000 °C—the temperature of the carbon receptor bed layer inside the CRR. The values shown on the bar graph are mean values of the measurements at constant time intervals across 60 min—the gasification time.

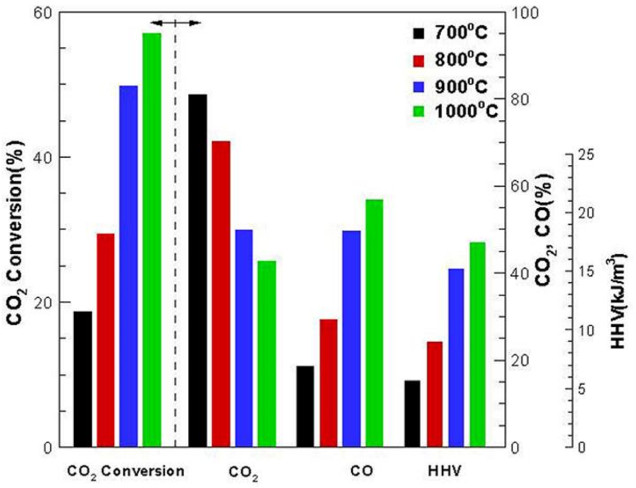

Figure 5 Carbon-CO_2 gasification results according to changes in the temperature.

The CO_2 conversion rate increased from 19% to 57% as the gasification temperature was increased from 700 °C to 1000 °C. This result suggests that the Boudouard reaction (Equation (2))—gasification reaction contributing to the conversion of CO_2—significantly affects the gasification temperature. The CO_2 conversion rate at 1000 °C was thrice higher than that at 700 °C. Boudouard reaction is an endothermic reaction that can be converted into a CO-producing reaction at high temperatures, resulting in a high CO_2 conversion rate. When a considerably larger entropic term ($T\Delta S$) is more dominant than an enthalpic component at high temperatures (typically > 700 °C), the Gibbs free energy ($\Delta G = \Delta$ H-$T\Delta S$) becomes negative. Thus, the Boudouard reaction predominantly becomes a forward reaction, resulting in the generation of CO. Therefore, the calorific value of the product gas increases from 5.75 kJ/m^3 (700 °C) to 17.49 kJ/m^3 (1000 °C).

During CO_2 gasification, the microwave heating method for Boudouard reaction under the same conditions results in the more efficient production of CO than by conventional heating methods [9]. Unlike the conventional hot-air method, in which all regions in the reactor cavity must be heated to and maintained at the required temperature for CO_2 gasification to proceed, microwave heating proceeds by directly heating the carbon receptor found in the CRR. Thus, the microwave heating method enhances the reaction in the volume of char particles, particularly at local hot spots.

3.4 Effect of Gas Feed Rate

During CO_2 gasification experiments, the raw gas feed rate was varied at room temperature, and the gasification temperature was maintained at 900 °C, with charcoal as the carbon receptor. The results are shown in Figure 6.

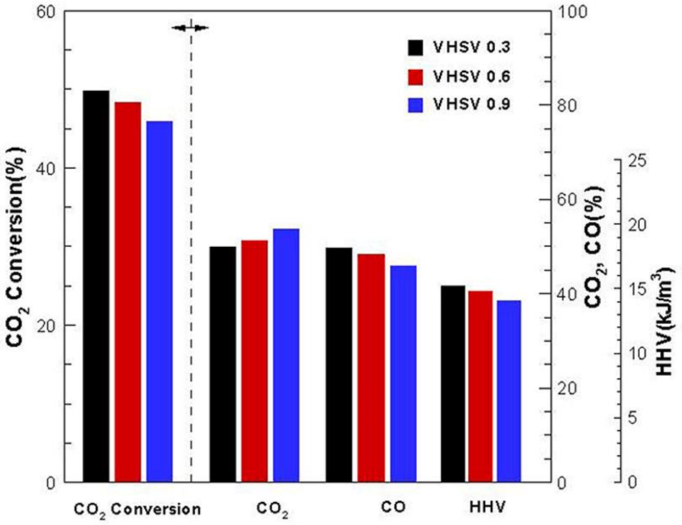

Figure 6 Carbon-CO_2 gasification results according to the change in gas feed rates.

The CO_2 conversion rate was 50% when the feed gas feed rate was 40 mL/min (VHSV = 0.3). The CO_2 conversion rate was reduced to 46% when the gas feed rate was increased to 120 mL/min (VHSV = 0.9). As the gas feed rate increased, the residence time for the raw gas was relatively reduced to remain in the carbon receptor bed, resulting in reduced Boudouard reaction. This can be further confirmed by the reduced amount of generated CO during the Boudouard reaction. In addition, the amount of CO_2 uninvolved in the reaction was relatively large. Thus, the calorific value of the product gas decreased as well.

Two distinguishable characteristics of microwave heating using biochar as a carbide receptor are as follows [16]. First, biochar, a carbon receptor, has good polarization property in an electromagnetic field, due to which the orientation and interfacial polarization during irradiation of microwaves allow rapid heating of the carbon receptor. Second, the nonlinearity of the electromagnetic and thermal properties of the biochar generate local hot spots called microplasmas. In addition, small sparks and electric arcs are nonlinearly observed.

A thermocouple measured a local temperature in the carbon receptor so that the value cannot represent the whole area in the CCR. Because the microplasma created in the carbon receptor had a relatively high temperature compared to the nearby areas, a temperature gradient was formed. Therefore, microwave heating on a carbon material such as activated carbon, which contains a catalyst, activates hot spots, thereby accelerating the reaction. This effect is also reported in a study on reforming carbon material using microwave heating [12].

In the case of VHSV 0.3 (gas feed rate: 40 mL/min), the residence time in the carbon receptor was increased compared with that under different conditions. Thus, the effect of microwave heating was enhanced, further promoting CO_2 gasification and resulting in a higher CO_2 conversion rate.

3.5 Effect of Gas Temperature

Figure 7 shows the results obtained by maintaining the raw gas temperature at 500 °C and the gasification temperature at 900 °C. The gas feed rate was maintained at 40 mL/min with charcoal as the carbon receptor.

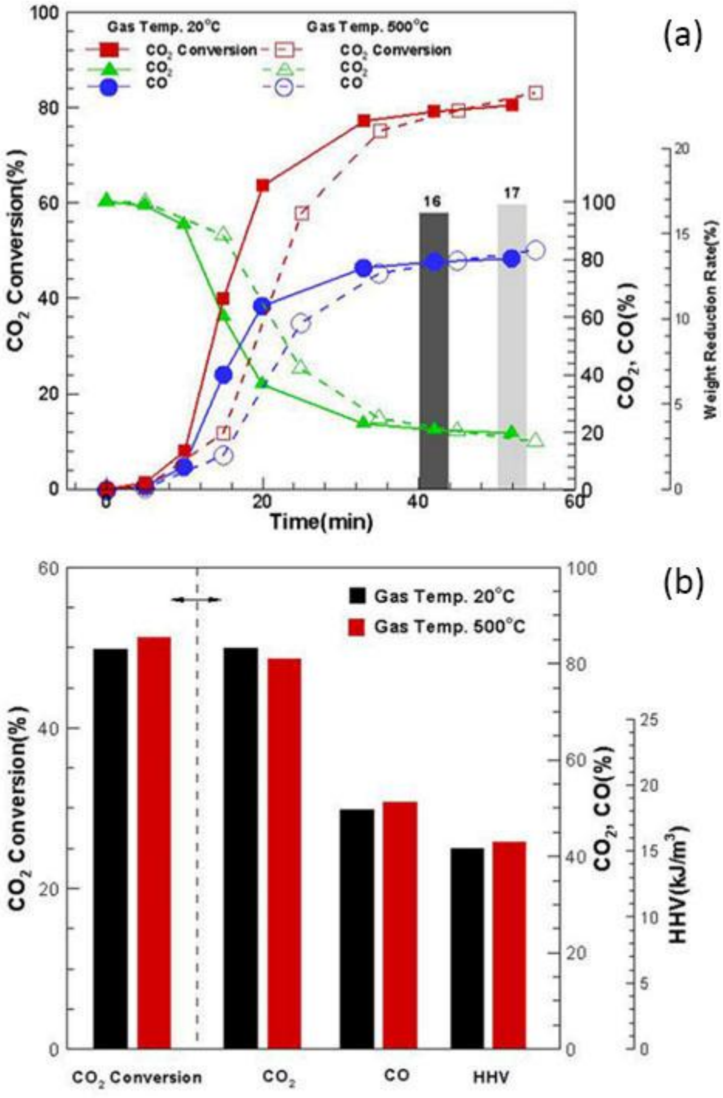

Figure 7 Carbon-CO_2 gasification results according to the change in the temperature of feed gas. (a) Conversion rate over time (at 500 °C). (b) Overall conversion rate and gas concentration.

The CO_2 conversion was slightly higher when the feed gas was supplied after being heated than when it was supplied at room temperature at the initial stage (Figure 7(a)). This could be confirmed by the concentrations of CO and CO_2 in the product gas. We attribute the low initial CO_2 conversion rate to the decrease in the gas density due to the expansion of gas volume because of an increase in the gas temperature, as well as reduced gasification reaction due to a decrease in the residence time in the carbon receptor. This increase in the conversion rate at its wake is ascribed to the activation of the gasification reaction under a slightly heated condition after the initial high-temperature gas heat was transferred to the carbon receptor. The bar graph shows a larger value at high temperatures, representing the rate of weight loss of the carbon receptor. Figure 7(b) shows the average value for each case. The supply of raw gas at high temperatures results in an increased CO_2 conversion rate with high amounts of generation of CO. Thus, the calorific value of the product gas was as high as 15.7 kJ/m^3, although its effect was insignificant.

3.6 Characteristics of Different Carbon Receptors

As shown in Figure 8, the gasification temperature was maintained at 900 °C and the gas feed rate at 40 mL/min, with the carbon receptor replaced with charcoal. Afterward, the results were compared with those obtained for the activated carbon.

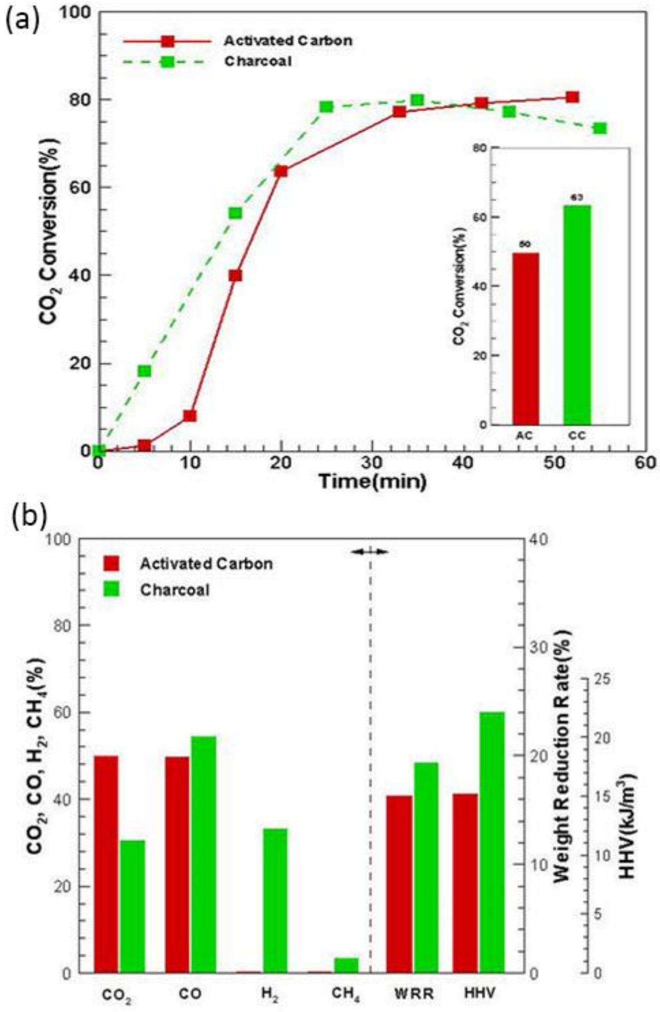

Figure 8 Carbon-CO_2 gasification results according to the change in carbon receptors (WRR: weight reduction rate, HHV: higher heating value). (a) CO_2 conversion rate and (b) concentration and calorific value of the product gas.

As shown in Figure 8(a), a relatively higher CO_2 conversion rate over time was observed with charcoal than with activated carbon, particularly in the initial stage due to the comparatively high microwave storage capacity of charcoal. In addition, it consisted of a relatively large amount of catalyst (Fe and Cu in particular), resulting in an efficient Boudouard reaction (Table 1). The bar graph shows the average values of the data over time, with a conversion rate of charcoal of 63%, which was higher than that of the activated carbon (50%).

Figure 8(b) shows the amount of converted product gas, calorific value, and the rate of weight loss. The presence of almost only carbon (C) in the activated carbon indicated that it was converted only into CO during CO_2 gasification. However, charcoal contained both carbon and some hydrogen atoms (H), resulting in hydrogen gas (H_2) and methane (CH_4) in addition to CO. Thus, the amount of the gas generated was higher with charcoal than with activated carbon, which was further confirmed by the weight loss rate. The result showed that the calorific value of charcoal was 22.2 kJ/m^3, which was higher than that of the activated carbon (15.3 kJ/m^3), suggesting that charcoal contains more valuable resources for fuel.

4. Conclusion

This study investigated the characteristics of carbon-CO_2 gasification by microwave heating as a core conversion technology for CCSFP. During CO_2 conversion, both gasification temperature and gas feed temperature were reduced. An increase in the gasification temperature significantly elevated CO_2 conversion. The carbons of activated carbon and CO_2 were increasingly converted to CO. However, CO_2 conversion slightly decreased as the gas feed rate increased due to a reduction in the conversion time in the CRR. Charcoal exhibited superior characteristics than the activated carbon in CO_2 conversion and product gas.

In conclusion, the gasification temperature should be maintained as high as possible, and the temperature of the supply gas should be maintained as the temperature of the combustion gas to achieve as a field scale for CCSFP (Figure 1). In addition, the CRR should have sufficient residence time for processing gas conversion. The microwave receptor should contain a large amount of fixed carbon, such as activated carbon.

Acknowledgments

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (2018R1D1A1B07040326).

Author Contributions

Young Nam Chun wrote and revised the manuscript. June An made the experiments.

Competing Interests

The authors have declared that no competing interests exist.

References

1. Lewis NS, Nocera DG. Powering the planet: Chemical challenger in solar energy utilization. PNAS. 2006; 103: 15729-15735.
2. Daud MZ, Mohamed A, Hannan MA. An improved control method of battery energy storage system for hourly dispatch of photovoltaic power sources. Energy Convers Manag. 2013; 73: 256-270.
3. Akhil AA, Huff G, Currier AB, Kaun BC, Rastler DM, Chen SB, et al. DOE/EPRI 2013 electricity storage handbook in collaboration with NRECA. Albuquerque: Sandia National Laboratories; 2013.
4. ECES Committee. Energy conservation through energy storage annual report 2011. Paris: International Energy Agency; 2011.

5. Verfondern K, Lensa WV. Past and present research in Europe on the production of nuclear hydrogen with HTGR. Nucl Eng Technol. 2005; 47: 472-483.
6. Tang S, Ji L, Lin L, Zeng HC, Tan KL, Li K. CO_2 reforming of methane to synthesis gas over sol-gel-made Ni/γ-Al_2O_3 catalysts from organometallic precursors. J Catal. 2000; 194: 424-430.
7. Jing QS, Fei JH, Lou H, Mo LY, Zheng XM. Effective reforming of methane with CO_2 and O_2 to low H_2/CO ratio syngas over Ni/MgO-SiO_2 using fluidized bed reactor. Energy Convers Manag. 2004; 45: 3127-3137.
8. Bermúdez JM, Ruisánchez E, Arenillas A, Moreno AH, Menéndez JA. New concept for energy storage: Microwave-induced carbon gasification with CO_2. Energy Convers Manag. 2014; 78: 559-564.
9. Chun YN, Jeong BR. Characteristics of the microwave pyrolysis and microwave CO_2-assisted gasification of dewatered sewage sludge. Environ Technol. 2018; 39: 2484-2494.
10. Song HG, Chun YN. Microwave Gasification and oxy-steam combustion for using the biomass char. J Mater Cycles Waste Manag. 2020; 22: 176-186.
11. Menéndez JA, Arenillas A, Fidalgo B, Fernández Y, Zubizarreta L, Calvo EG, et al. Microwave heating processes involving carbon materials. Fuel Process Technol. 2010; 91: 1-8.
12. Kong Y, Cha CY. Reduction of NO_x adsorbed on char with microwave energy. Carbon. 1996; 34: 1035-1040.
13. Cha CY, Kim DS. Microwave induced reactions of sulfur dioxide and nitrogen oxides in char and anthracite bed. Carbon. 2001; 39: 1159-1166.
14. Fidalgo B, Domínguez A, Pis JJ, Menéndez JA. Microwave-assisted dry reforming of methane. Int J Hydrog Energy. 2008; 33: 4337-4344.
15. Zhang F, Song Z, Zhu J, Liu L, Sun J, Zhao X, et al. Process of CH_4-CO_2 reforming over Fe/SiC catalyst under microwave irradiation. Sci Total Environ. 2018; 639: 1148-1155.
16. Zhang F, Song Z, Zhu J, Sun J, Zhao X, Mao Y, et al. Factors influencing CH_4-CO_2 reforming reaction over Fe catalyst supported on foam ceramics under microwave irradiation. Inr J Hydrog. Energy. 2018; 43: 9495-9502.
17. Menéndez JA, Juárez-Pérez EJ, Ruisánchez E, Bermúdez JM, Arenillas A. Ball lightning plasma and plasma arc formation during the microwave heating of carbons. Carbon. 2011; 49: 346-349.
18. Lahijani P, Mohammadi M, Zainal ZA, Mohamed AR. Improvement of biomass char-CO_2 gasification reactivity using microwave irradiation and natural catalyst. Thermochim Acta. 2015; 604: 61-66.
19. Anis S, Zainal ZA. Study on kinetic model of microwave thermocatalytic treatment of biomass tar model compound. Bioresour Technol. 2014; 151: 183-190.
20. Li L, Wang H, Jiang X, Song Z, Zhao X, Ma C. Microwave-enhanced methane combined reforming by CO_2 and H_2O into syngas production on biomass-derived char. Fuel. 2016; 185: 692-700.
21. Shen Y, Zhao P, Shao Q, Ma D, Takahashi F, Yoshikawa K. In-situ catalytic conversion of tar using rice husk char-supported nickel-iron catalysts for biomass pyrolysis/gasification. Appl Catal B. 2014; 152-153: 140-151.


AEER