



Chemical Looping Gasification of Charcoal with Iron-Based Oxygen Carriers in an Annular Dual-Tube Moving Bed Reactor

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ABSTRACT

Charcoal used as solid fuel for chemical looping gasification (CLG) with $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ oxygen carriers was investigated in an annular dual-tube moving bed reactor (ADMBR). Pure CO_2 and steam/ CO_2 mixture were used to gasify the charcoal in a fixed bed reactor. More combustible gases, CO and H_2 , were observed in the outlet gas streams for charcoal gasification conducted with steam/ CO_2 mixture than those with only CO_2 . The yields of fuel gases were determined to modify the equation of oxygen carrier-to-fuel ratio (ϕ) for moving bed operation. More CO and H_2 were generated for charcoal gasification conducted in the moving bed reactor operated with higher oxygen carrier-to-fuel ratios. The heat demand for experiment conducted in the ADMBR was calculated to be 60% of output processing capacity due to the heat consumptions of fuel gasification. In sum, ADMBR is technically feasible to be a fuel reactor for partial oxidization of charcoal by CLG to achieve syngas production under appropriate operating conditions without auxiliary fuel.

Keywords: Chemical looping gasification (CLG); Char gasification; $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ composite oxygen carrier; Moving bed reactor.

INTRODUCTION

Syngas (CO/H_2) is an important raw material that can be further converted to a number of products, for instance hydrogen, liquid fuels, chemicals, and electricity (Bhattacharya, 2013). Syngas is mainly generated from natural gas reforming through steam methane reforming reaction, or from solid fuel gasification through water gas and Boudouard reactions. Solid fuels are more carbon intensive than methane; however, are much difficult to convert. In order to enhance the gasification of solid fuels, several gases, such as CO_2 and steam, are employed to facilitate gasification and improve the quality of syngas. However, the gasification of solid fuels with CO_2 or steam is endothermic and requires external heat supply to proceed. Hence, air (or O_2) is mixed with CO_2 or steam, is introduced to initiate the partial oxidization of solid fuels for providing heat for gasification (Wang *et al.*, 2008).

Chemical looping process (CLP) for fuel combustion has been actively studied and is considered to be a unique alternative to achieve efficient energy generation as well as inherent CO_2 capture (Richter *et al.*, 1983; Fan and Li, 2010; Figureoa *et al.*, 2008). Chemical looping gasification (CLG)

is an innovative application of chemical looping process to generate syngas through the partial oxidization of fuels with deficient oxygen carriers (Fan *et al.*, 2008). The reduced oxygen carrier is then oxidized and regenerated by air for heat generation to maintain heat balance of the process.

Metal oxides (called oxygen carriers) providing oxygen for fuel combustion by chemical looping process is rapidly developed recently. Cao *et al.* (2014) indicated that the agglomeration of copper-based oxygen carrier was avoided by using Al_2O_3 as support and promoted by lanthanum. In addition, the formation of a crystal phase (CuAl_2O_4), cross-linking CuO and $\gamma\text{-Al}_2\text{O}_3$, was supposedly to contribute to the stability of copper-based oxygen carrier, whereas the lanthanum contributed speeding the formation of the cross-linking between CuO and $\gamma\text{-Al}_2\text{O}_3$. Zhou *et al.* (2014) demonstrated that high CO_2 selectivity and CH_4 conversion for CLC operated in the batch fluidized bed reactor with NiO, and also reported that the operation time of approximately 6 min was achieved for 95% of NiO conversion by CLC operated in the fixed bed reactor, while the operation time of 95% of NiO conversion by CLC operated in the fluidized bed reactor reached lower than 3 min, indicating that the longer reaction times of the gas inside the reactor lead to faster conversions of the oxygen carrier. Wang *et al.* (2016) studied that the kinetic study of Mn-based oxygen carrier for oxygen release by chemical looping air separation (CLAS), and also reported that the first-order chemical reaction model (C1) and Avrami-Erofe'ev random nucleation and subsequence

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growth model (A2) are appropriate for the O₂ release of MnO₂ and Mn₂O₃, respectively. In addition, the activation energies of MnO₂ and Mn₂O₃ for oxygen release were determined to be 130 and 163 kJ mol⁻¹, respectively. Chiu *et al.* (2014) reported that Fe₂O₃/Al₂O₃ oxygen carriers containing 60wt% Fe₂O₃ sintered at 1300°C demonstrated reasonable oxygen conversion and delivered high CO₂ yields for chemical looping combustion of methane and syngas (CO/H₂) in a fixed bed reactor. Most Fe-based oxygen carriers demonstrate higher melting point, better mechanical strength, and lower cost than others. Therefore, various Fe-based carriers were developed and extensively employed for CLP in previous studies. Kuo *et al.* (2015) reported that the spinel structure of NiFeAlO₄ oxygen carriers presented high CO conversion and H₂ generation has been proved in fixed bed reactor for chemical looping hydrogen generation process (CLHG), because the ability of self-supported and agglomeration resistance were significantly enhanced. Chiu and Ku (2012) reported that the gasification of solid fuel in the fuel reactor is the rate limiting step for direct solid fuel combustion. The addition of gasification reactants, such as CO₂, H₂O and O₂ might enhance the gasification rate of the fixed carbons contained in these solid fuels.

Coal and petroleum coke are major fuels for power generation; however, combustion of coal and petroleum coke is also a major CO₂ emission source because of their high carbon contents (IPCC, 2007). Combustion of coal by chemical looping process is developed and considered to be an efficient alternative for power generation (Li and Fan, 2008). For direct coal combustion in the fuel reactor, a two-step mechanism is proposed, including gasification and combustion. Gasification of coal is a partial oxidation process that fixed carbon in the coal is partially oxidized by gasification reactants, such as O₂, H₂O and CO₂ to form CO and/or H₂ as gaseous fuels. The fixed carbon of coal is gasified to CO and H₂ (as H₂O employed to be the gasification reactant) by gasification reactants in the fuel reactor. The CO and H₂ from gasification process is immediately combusted by oxygen carriers in the same manner of gaseous combustion to yield H₂O and CO₂. However, gasification is a rate-limiting step in the fuel reactor to reduce the overall fuel combustion efficiency (Chiu and Ku, 2012). Therefore, retrofit the design of fuel reactor to extend the residence time of solid fuel in the fuel reactor is an alternative way to improve the limitation of low gasification rate for direct coal combustion by chemical looping process. The counter-flow current pattern of solid fuel and oxygen carriers was proposed as one of the engineering designs for better CO₂ yield and fuel conversion using Fe-based oxygen carriers (Li *et al.*, 2010).

Steam or CO₂ as gasification agent to the chemical looping process is widely studied by previous researchers employed with fluidized bed reactor and moving bed reactor (Berguerand *et al.*, 2010; Bayham *et al.*, 2013). However, application of steam/CO₂ mixture for charcoal gasification and combustion is rarely investigated. Hence, charcoal was selected to study its gasification with various gasification agents in a fixed bed. The performance of ADMBR using Fe-based oxygen carriers was also discussed in this study. In this study, pulverized charcoal was employed for chemical looping

gasification with Fe-based oxygen carriers in an annular dual-tube moving bed reactor (ADMBR). The compositions of flue gas were determined for experiments carried out at 900°C with varied oxygen carrier feeding rate. The fuel conversion and oxygen carrier conversion for charcoal gasification by CLG with 2.5% steam/CO₂ mixture and Fe₂O₃/Al₂O₃ oxygen carriers were evaluated by ADMBR. Heat analysis for CLG gasification of charcoal was employed to evaluate the heat balance of input and output processing capacities.

MATERIAL AND METHODS

Preparation and Characterization of Fe₂O₃/Al₂O₃ Oxygen Carriers

The oxygen carriers used in this study were composed of hematite (99.9% Fe₂O₃, China Steel) and alumina (99% Al₂O₃, Chin Jung). The Fe₂O₃/Al₂O₃ oxygen carriers were prepared with hematite and alumina at weight percentage of 60/40. Hematite and alumina particles of roughly 1 μm in diameter were mixed with deionized water at room temperature. The well-mixed slurry was then dried at 80°C for 6 hours and was subsequently pulverized and screened for sizes between 1.2 and 1.4 mm. The particles were later sintered at 1300°C for 2 hours in a muffle furnace. The crush strength of prepared Fe₂O₃/Al₂O₃ oxygen carriers ranged of 1.2 to 1.4 mm was determined to be approximately 22N by a texture machine (TA.XT plus) according to ASTM D4179-01. The reactivity and recyclability of prepared Fe₂O₃/Al₂O₃ oxygen carriers was analyzed by thermogravimetric analyzer (TGA), the phase transformation of prepared Fe₂O₃/Al₂O₃ oxygen carriers during redox cycle was characterized by X-ray diffraction (XRD), and surface morphology and interfacial behaviors of Fe₂O₃/Al₂O₃ oxygen carriers were examined by a field emission scanning electron microscope (FESEM) have been clearly described in previous publication. (Chiu *et al.*, 2014)

Characterization of Charcoal

Charcoal was pulverized and sieved for sizes between 1.2 and 2 mm before it was applied as solid fuels in this study. Proximate analysis of charcoal was conducted by a Netzsch STA 449F3 thermogravimetric analyzer (TGA) to determine the contents of moisture, volatile matters, fixed carbon and ash. Charcoal was heated in a TGA chamber for pyrolysis in nitrogen atmosphere, the temperature of TGA chamber was elevated with a ramping rate of 20°C min⁻¹ from room temperature to 700°C. Based on the TGA results, the contents of moisture and volatile matters were determined. Air was then introduced to the TGA chamber to combust the residues to determine the fixed carbon and ash contents of charcoal. Ultimate analysis of charcoal was analyzed by an elemental analyzer (Elementar vario EL III) to determine the elemental contents of C, H, O, N, and S.

Establishment of Fixed Bed Reactor System

The fixed bed reactor system employed in this study, demonstrated in Fig. 1, is composed of a 60 mm ID stainless steel tubular reactor and with a PID-controlled heating

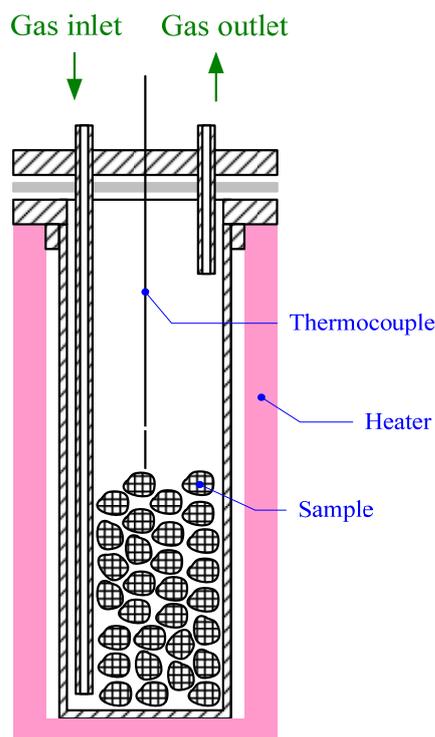


Fig. 1. Schematic diagram of the fixed bed reactor used in this study for charcoal gasification.

element covering 200 mm of reactor height. The thermocouple connected to the center of the top cover of the fixed bed reactor was composed of a 6.35 mm ID SS310 tube. Two 6.35 mm ID SS310 tubes were connected at the top cover of the fixed bed reactor for gas inlet and flue gas outlet, respectively. 75 g of Charcoals were gasified at 900°C by introducing gasification agents of various compositions. The outlet stream from the fixed bed reactor was passed through a cold trap to condense steam, and was consequently analyzed by a gas chromatography equipped with a thermal conductivity detector (GC-TCD, China Chromatography

2000) to detect carbon dioxide, carbon monoxide, methane, hydrogen, and oxygen. The detailed test conditions were listed in the Table 1.

Establishment of Moving Bed Reactor System

The schematic diagram of an annular dual-tube moving bed reactor (ADMBR) for charcoal gasification and combustion employed in this study is shown in Fig. 2. The ADMBR was composed of a 76.20 mm ID SS310S outer tube covered with an electric heating element to provide isothermally atmosphere, and a 25.40 mm ID SS310S inner gasification tube. For empty bed operations, 17.17 g min⁻¹ of charcoal was introduced into the gasification tube by a screw conveyor. Various flow rate of 2.5 mol.% steam/CO₂ mixture was also fed into the gasification tube to serve as gasification agent. The gaseous products generated by charcoal gasification along with steam and CO₂ were then left the gasification tube, and flew through the fuel reactor. The temperature for empty bed reactor system was controlled at 900°C, and the total flow rate of the 2.5 mol.% steam/CO₂ mixture was operated between 41.14 and 205.80 mmol min⁻¹. The char, residues and ash were collectively removed out of the gasification tube by a screw conveyor.

For continuously moving bed operations, roughly 2.0 kg of prepared Fe₂O₃/Al₂O₃ oxygen carriers was initially packed in the spacing between inner and outer tubes of the ADMBR. Fe₂O₃/Al₂O₃ oxygen carriers were then continuously fed into the packed reactor by a screw conveyor at flow rate operated between 11.48 and 29.67 g min⁻¹. The charcoal particles were fed into gasification tube through the screw conveyor, and 2.5 mol.% steam/CO₂ mixture was also introduced into the gasification tube at a molar flow rate of 164.66 mmol min⁻¹. All the operating flow rates were limited by the experimental equipment, such as syringe pump, mass flow controller and screw conveyor. The fuel gas generated by charcoal gasification was then passing through the bottom of gasification tube for consequent combustion with Fe₂O₃/Al₂O₃ oxygen carriers fed into and moved through the moving bed reactor. The reduced oxygen carrier was collectively removed out of the

Table 1. The operating conditions of charcoal gasification with various gasification agents in the fixed bed reactor.

Gasification agent	Inlet Concentration (mol.%)			The amount of Charcoal g	Reaction Temperature °C
	CO ₂	H ₂ O	N ₂		
CO ₂	2.5	0	97.5	75	900
	5	0	95		
	10	0	90		
	15	0	85		
	20	0	80		
steam	0	2.5	97.5	75	900
	0	5	95		
	0	10	90		
	0	15	85		
	0	20	80		
steam/CO ₂ mixture	97.5	2.5	0	75	900
	95	5	0		
	90	10	0		
	85	15	0		
	80	20	0		

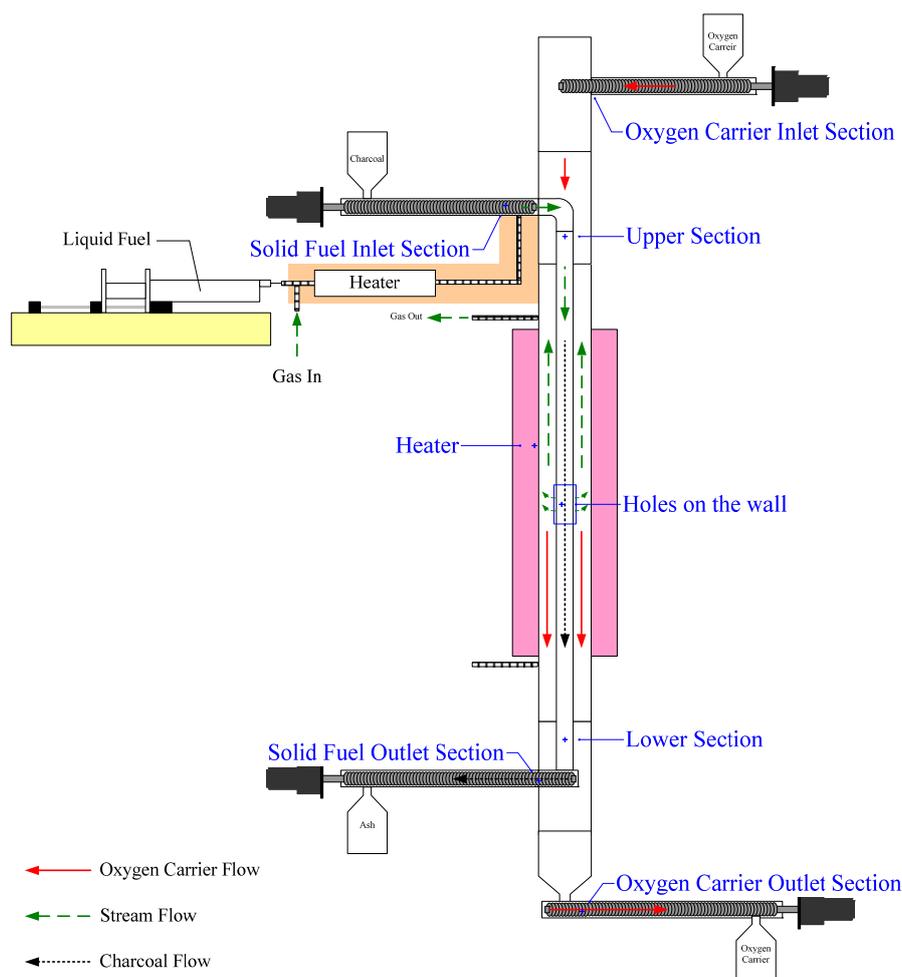


Fig. 2. Schematic diagram of the moving bed reactor system used in this study for charcoal combustion.

fuel reactor by a screw conveyor. The outlet stream from the moving bed reactor was cooled by a cold trap to condense and was afterward analyzed by a gas chromatography equipped with a thermal conductivity detector (GC-TCD, China Chromatography 2000) to detect carbon dioxide, carbon monoxide, methane, hydrogen, and oxygen. The detailed test conditions were listed in the Tables 2 and 3.

RESULTS AND DISCUSSION

Charcoal Gasification with Various Gasification Agents

The results of proximate and ultimate analyses for charcoal studied in this research are listed in Table 4. The content of volatile materials in charcoal was determined to be 21.14 wt%; while fixed carbon and ash contained in charcoal was 71.54 and 4.14 wt%, respectively. Based on the result of ultimate analysis, carbon and oxygen were the major elements in the charcoals. As also listed in Table 4, the higher heating value (HHV) of the charcoal was calculated to be 34.31 MJ kg^{-1} , demonstrating similar results reported by previous researchers (Bayham *et al.*, 2013).

Gasification is a rate-limiting step in the fuel reactor to reduce the overall fuel combustion efficiency. Hence, the performance of the charcoal gasification with various

gasification agents was investigated in a fixed bed. In this section, charcoal was gasified by CO_2/N_2 mixtures containing 2.5 to 20 mol% CO_2 in a fixed bed reactor at 900°C , to carry out the following inversed Bondouard reaction:



The outlet streams from the fixed bed reactor were composed mainly of CO, with minimum amounts of CO_2 , as illustrated in Fig. 3. Based on the carbon balance, the carbon gasification rate ($F_{c,\text{gasification}}$) is defined as:

$$F_{c,\text{gasification}} = (F_{\text{CO}_2,\text{out}} + F_{\text{CO},\text{out}}) - F_{\text{CO}_2,\text{in}} \quad (2)$$

where $F_{c,\text{gasification}}$ is the gasification rate of carbon of charcoal; $F_{\text{CO}_2,\text{in}}$ is the input molar flow rate of CO_2 which gasified with charcoal; $F_{\text{CO}_2,\text{out}}$ and $F_{\text{CO},\text{out}}$ are the output molar flow rate of CO_2 and CO, respectively. The concentrations of CO and carbon gasification rates were increased with increasing the inlet concentration of CO_2 , possibly because of the Le Chatelier's principle.

For gasification with steam, charcoal is gasified by 2.5 to 20 mol% steam based on N_2 through water gas and water gas shift reactions, as described by reactions (3) and (4).

Table 2. The operating conditions of charcoal gasification with 2.5 mol.% steam/CO₂ mixture in the empty bed reactor.

Gasification Agent	Flow rate (mmol min ⁻¹)			Flow rate of Charcoal g min ⁻¹	Flow rate of oxygen carrier g min ⁻¹	Reaction Temperature °C
	CO ₂	H ₂ O	Total			
steam/CO ₂ mixture (2.5 mol.%)	40.13	1.01	41.14	17.17	0	900
	80.25	2.03	82.28			
	120.38	3.14	123.51			
	160.50	4.15	164.66			
	200.63	5.17	205.80			

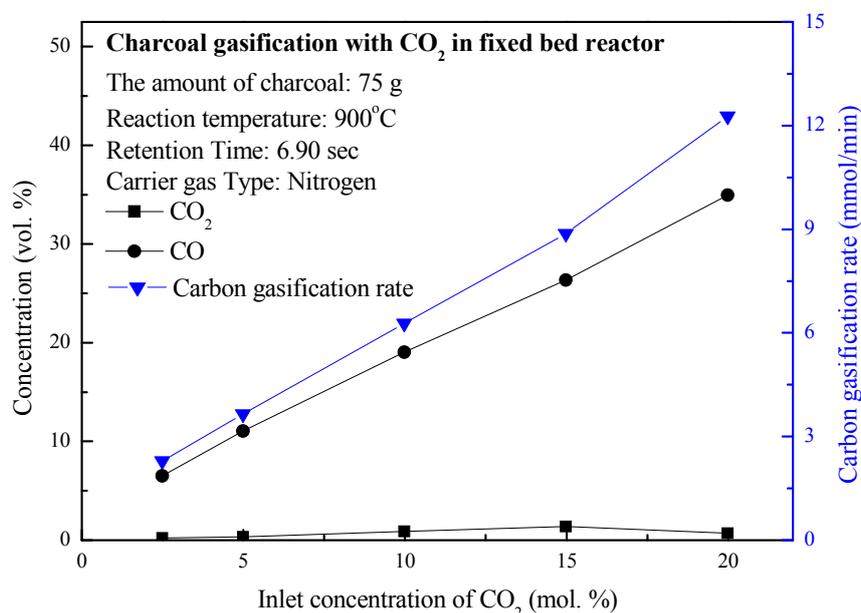
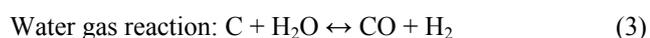
Table 3. The operating conditions of charcoal gasified for CLG operation in the moving bed reactor.

Gasification Agent	Flow rate (mmol min ⁻¹)			Flow rate of Charcoal g min ⁻¹	Flow rate of oxygen carrier g min ⁻¹	Reaction Temperature °C
	CO ₂	H ₂ O	Total			
steam/CO ₂ mixture (2.5 mol.%)	160.50	4.15	164.66	17.17	11.48	900
					17.67	
					24.05	
					29.67	

Table 4. Indexes for evaluation of oxygen carriers.

Fuel	Proximate Analysis (wt.%)				Ultimate Analysis (wt.%)					HHV (MJ kg ⁻¹)
	M	VM	FC	A	N	C	H	O	S	
Charcoal	3.19	21.14	71.54	4.14	0.33	73.30	8.50	12.50	0	34.31

M: Moisture; VM: Volatile Material; FC: Fixed Carbon; A: Ash; HHV: Higher Heating Value.

**Fig. 3.** Concentration of outlet gas stream obtained from charcoal gasification in fixed bed reactor under various inlet concentration of CO₂ based on nitrogen as carrier gas.

CO and H₂ are the major fuel gases generated during charcoal gasification with steam at 900°C, as illustrated in Fig. 4. CO and H₂ concentrations of the outlet gas stream

for charcoal gasification was found to be increased for experiments carried out with greater the inlet concentration of steam, whereas CO₂ concentrations decreased. The lower carbon gasification rate was observed for charcoal gasified by 2.5 to 15 mol.% steam than those by 2.5 to 15 mol.% CO₂, while higher carbon gasification rates was reached for experiments with 20 mol.% steam than those with 20

mol.% CO₂, as shown in the Figs. 3 and 4. As described by reaction (3), the gasification of charcoal at 2.5 to 15 mol.% steam may form CO and H₂, whereas the carbon gasification rate was increased for charcoal gasified by 20 mol.% steam possibly due to the more CO₂ was generated by water gas shift reaction for further charcoal gasification, similar results were reported by previous researchers (Berguerand *et al.*, 2010).

Charcoal gasification with steam/CO₂ mixture was also investigated in a fixed bed reactor. Outlet gas stream containing about 82% CO and 18% CO₂ were achieved for

charcoal gasification using pure CO₂. More combustible gas were observed in the outlet gas stream for experiments conducted with 2.5% steam/CO₂ mixture than those with only CO₂, possibly due to the occurrence of Boudouard and water gas reactions. However, CO concentration of the outlet gas stream was reduced to about 50 vol.% for experiments conducted with steam/CO₂ mixture containing more than 2.5 mol.% steam, as shown in Fig. 5. More CO₂ and H₂ were generated due to the occurrence of water gas shift reaction, as depicted by reaction (4), similar results were reported by Berguerand *et al.* (2010).

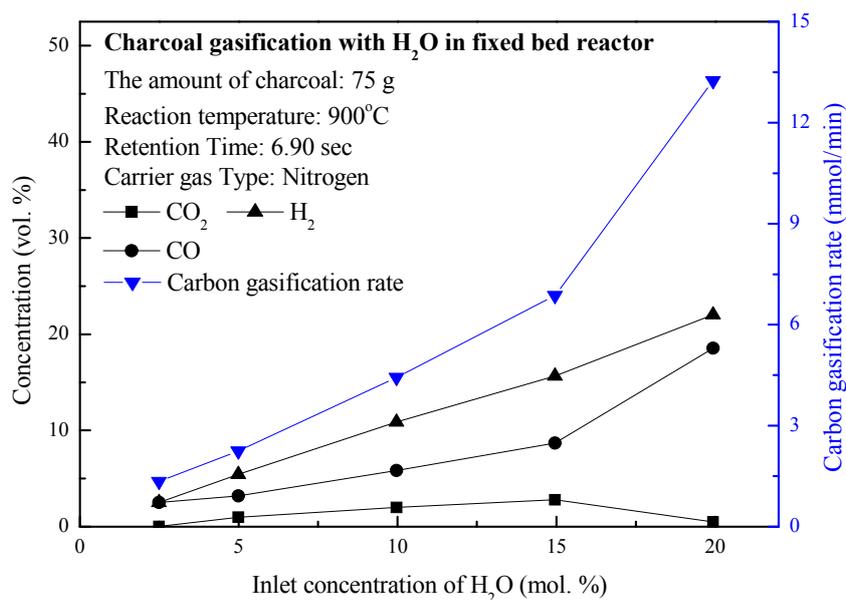


Fig. 4. Concentration of outlet gas stream obtained from charcoal gasification in fixed bed reactor under various inlet concentration of H₂O based on nitrogen as carrier gas.

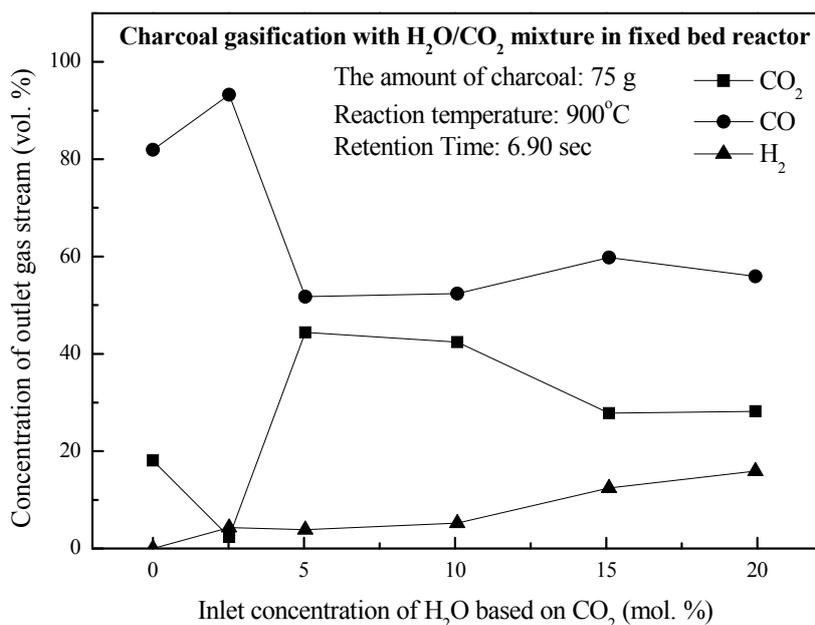


Fig. 5. Concentration of outlet gas stream obtained from charcoal gasification with steam/CO₂ mixture in fixed bed reactor under various inlet concentration of H₂O based on carbon dioxide.

Charcoal Gasification with Steam/CO₂ Mixture

According to the results of the section 3.1, 2.5% steam/CO₂ mixture was employed as gasification agent for consequent gasification of charcoal were conducted in the empty bed reactor and chemical looping gasification of charcoal were operated in an ADMBR with iron-based oxygen carrier. In this section, effect of 2.5% steam/CO₂ mixture flow rate on the combustible gas composition after charcoal gasification were investigated in an empty bed reactor. The gasification of charcoal were conducted in the empty bed reactor at 900°C by feeding charcoal particles at flow rate of 17.17 g min⁻¹ and steam/CO₂ mixture containing 2.5 mol.% steam and 97.5 mol.% CO₂ at flow rate from 41.14 to 205.80 mmol min⁻¹. The main components of outlet streams for charcoal gasification with steam/CO₂ mixture were determined to be CO, H₂, and CO₂, as illustrated in Fig. 6. The molar flow rate of outlet stream was increased with experiments conducted with increasing steam/CO₂ mixture flow rate. The yields of CO, H₂, and CO₂ in the outlet stream, Y_{CO} , Y_{H_2} , and Y_{CO_2} , were determined to be 1.63, 0.16, and 0.04, respectively, indicating CO₂ was majorly converted to CO.

The H₂/CO ratio was 1:1 through water gas shift reaction described by reaction (4); however, more CO was generated by the inversely Boudouard reaction described by reaction (1), whereas the amount of CO₂ was decreased. Therefore, the amount of CO was consequently reached approximately 10 times greater than H₂ based on CO and H₂ gas yields. The molar flow rate of fuel gas, $F_{Fuel\ gas}$, is described by Eq. (5), which is sum of F_{CO} and F_{H_2} for using charcoal as solid fuel.

$$F_{Fuel\ gas} = Y_g \cdot F_g \quad (5)$$

The fuel gas yield, Y_g , which is sum of Y_{CO} and Y_{H_2} , is

calculated as 1.79, indicating each CO₂ or H₂O molecule can be transformed to approximately 2 molecules of CO and/or H₂ for oxidization with oxygen carriers. According to mole balance for reactions (1) and (3), 2 moles of CO and/or H₂ by theoretical calculation would be generated by 1 mole of CO₂ and/or H₂O. However, more H₂ was generated from charcoal pyrolysis than those was generated from charcoal gasification with 2.5 mol.% steam/CO₂ mixture, because according to mole balance for reaction (3), 1 mole H₂ by theoretical calculation would be generated by 1 mole of H₂O, close to Y_{H_2} determine as only 0.025, which was lower than 0.16.

Charcoal Gasification in a Moving Bed Reactor

Chemical looping gasification of charcoal was conducted by feeding deficient Fe₂O₃/Al₂O₃ oxygen carriers into the ADMBR to provide lattice oxygen for production of syngas generated from charcoal. Effect of the oxygen carrier-to-fuel ratio on the combustible gas composition, fuel conversion and oxygen carrier conversion were investigated in an ADMBR. Chemical looping gasification of charcoal was conducted in the ADMBR at 900°C by feeding 17.17 g min⁻¹ charcoal particles and 164.66 mmol min⁻¹ gasification agent. For moving bed operations, 2.0 kg of Fe₂O₃/Al₂O₃ oxygen carriers were packed with 220 mm of bed height. The flow rate of Fe₂O₃/Al₂O₃ oxygen carriers feed into the moving bed reactor was operated between 11.48 and 29.67 g min⁻¹. In this study, the oxygen carrier-to-fuel ratio (ϕ) is the ratio of oxygen provision by Fe₂O₃/Al₂O₃ oxygen carrier and oxygen demand by fuel gas in the fuel reactor, as described by Eq. (6).

$$\phi = \frac{F_{Fe_2O_3}}{b \cdot F_{Fuel}} \quad (6)$$

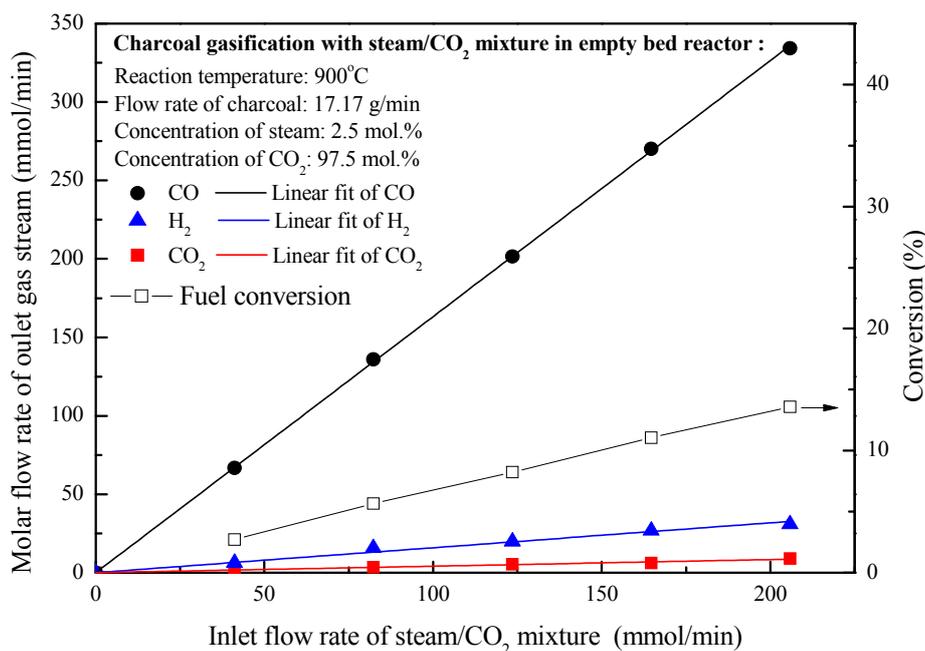
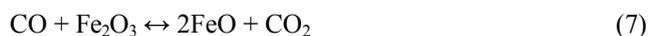


Fig. 6. Effect of gasification agent flow rate on the gasification of charcoal in empty bed.

where $F_{Fe_2O_3}$ is the molar flow rate of Fe_2O_3/Al_2O_3 ; F_{Fuel} is the molar flow rate of fuel gas; b is the stoichiometric coefficient of fuel gas combusted with Fe_2O_3 . Based on the result for charcoal gasification in an empty bed reactor, CO and H_2 are the major fuel gases generated; the stoichiometric coefficients for CO and H_2 combustion with Fe_2O_3 are both unity, as expressed by Eqs. (7) and (8).



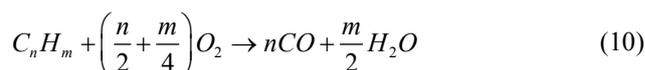
The oxygen carrier-to-fuel ratio is rearranged and rewritten as Eq. (9) for charcoal combustion with Fe_2O_3/Al_2O_3 oxygen carriers. Y_g is 1.79 based on the results of empty bed experiments. ϕ is determined to be in the range of 0.15 to 0.38.

$$\phi = \frac{F_{Fe_2O_3}}{b \cdot F_{Fuel}} = \frac{(x_{Fe_2O_3} \cdot \dot{m}_{OC} / M_{Fe_2O_3})}{b \cdot (Y_g \cdot F_g)} = 2.10 \times 10^{-3} \cdot \left(\frac{\dot{m}_{OC}}{F_g} \right) \quad (9)$$

where \dot{m}_{OC} is the mass flow rate of Fe_2O_3/Al_2O_3 oxygen carriers; $x_{Fe_2O_3}$ is the fraction of Fe_2O_3 contained in the oxygen carrier; $M_{Fe_2O_3}$ is the molecular weight of Fe_2O_3 .

CO and H_2 concentrations of the outlet gas stream from charcoal gasification were found to be increased with increasing ϕ , whereas CO_2 concentration was decreased, as demonstrated in Fig. 7. Hautman *et al.* (1981) reported that the oxidation of hydrocarbons was two-step reactions, as described in reactions (10) and (11), while the reaction of CO oxidized to CO_2 was slight slower. Hence, CO and H_2 might be formed from the charcoal gasified by CLG with

Fe_2O_3/Al_2O_3 oxygen carriers and steam/ CO_2 mixtures at ϕ lower than 1. Ge *et al.* (2015, 2016) reported that the maximum syngas (CO and H_2) yield of rice straw gasification reached about $0.33\text{--}0.74 \text{ Nm}^3 \text{ kg}^{-1}$ for experiments conducted at 750°C . In this study, the maximum syngas yield of around $0.28 \text{ Nm}^3 \text{ kg}^{-1}$ was achieved for the chemical looping gasification of charcoal with Fe_2O_3/Al_2O_3 flow rate of 29.7 g min^{-1} , much lower than those reported for rice straw and rice husk gasification, because fewer oxygen and volatile material were present in the charcoal.



Outlet gas stream comprised of 27.8 mol.% CO, 0.9 mol.% H_2 and 71.3 mol.% CO_2 were achieved for experiments conducted with the oxygen carrier-to-fuel ratio of 0.15. More CO and H_2 were generated for charcoal gasification conducted with higher oxygen carrier-to-fuel ratios because more oxygen was provided. Similar to the result reported by previous study (Cuadrat *et al.*, 2012) that coal gasification and combustion efficiencies were decreased for experiments conducted with the oxygen carrier-to-fuel ratio lower than 1.

The fuel conversion (X_{Fuel}) and oxygen carrier conversion (X_{OC}) for charcoal gasification by chemical looping were subsequently calculated by the following equations, respectively:

$$X_{Fuel} = \frac{(F_{CO_2, out, c} + F_{CO, out, c} - F_{CO_2, in})}{F_{C, in}} \quad (12)$$

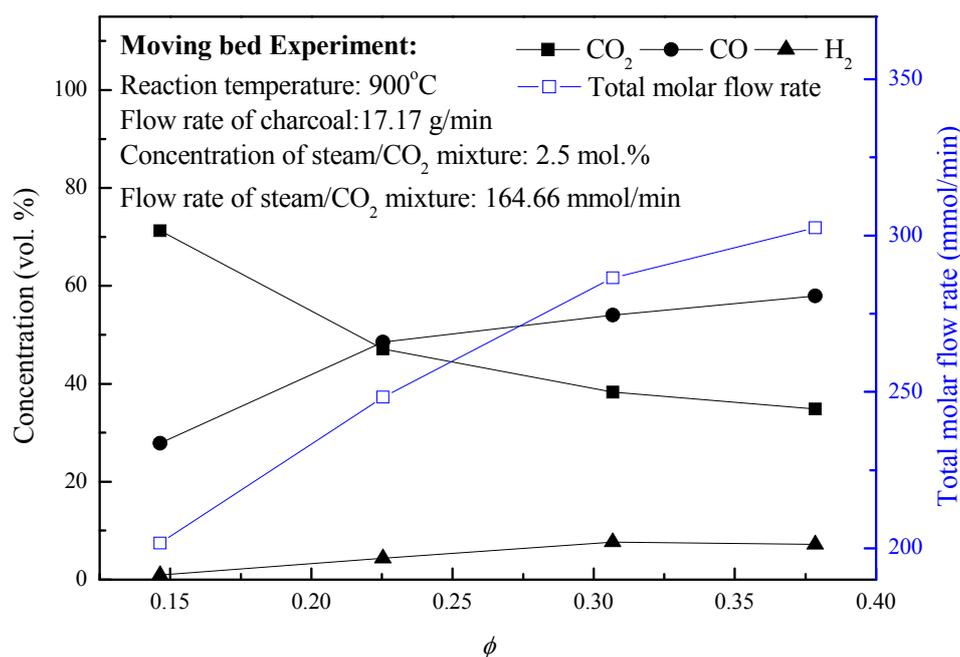


Fig. 7. Effect of oxygen carrier-to-fuel ratio on the CLG of charcoal in moving bed.

$$X_{OC} = \frac{(F_{CO_2,out,C} - F_{CO_2,in}) \times 2 + (F_{H_2O,out,C} - F_{H_2O,in}) + F_{CO,out,C}}{\left(\frac{x_{Fe_2O_3} \cdot \dot{m}_{OC}}{M_{Fe_2O_3}} \right) \times 1000 \times 3} \quad (13)$$

where $F_{C,in}$ is the inlet carbon mole flow rate of charcoal; $F_{CO_2,in}$ and $F_{H_2O,in}$ are the inlet molar flow rates of H_2O and CO_2 for charcoal gasification; $F_{CO_2,out,C}$, $F_{H_2O,out,C}$ and $F_{CO,out,C}$ are the outlet molar flow rates of CO_2 , H_2O and CO generated, respectively. Fuel reactor design for longer residence time of Fe-based oxygen carriers should be considered due to their low reactivity. However, as shown in Fig. 8, X_{Fuel} for charcoal gasification was slightly decreased for experiments conducted with decreasing oxygen carrier-to-fuel ratio, indicating insufficient oxygen was provided, similar to the results reported by previous study (Luo *et al.*, 2014). The conversion for Fe_2O_3/Al_2O_3 oxygen carriers was around 33.33% that corresponded to the amount of oxygen utilization from Fe_2O_3 to FeO . Approximately, 38% of the oxygen carrier conversions were maintained for charcoal gasification with oxygen carrier-to-fuel ratio from 0.15 to 0.38, demonstrating the iron-based oxygen carriers operated in a moving bed reactor was majorly reduced to FeO .

Heat Analysis

Heat balance and processing efficiency are analyzed for the charcoal gasification during CLG operation in this study. The input processing capacity (Q_{in}) is calculated as:

$$Q_{in} = \dot{m} \cdot \Delta H_{Fuel} \quad (14)$$

where \dot{m} and ΔH_{Fuel} are the mass flow rate ($g\ s^{-1}$) and the higher heating value of charcoal ($MJ\ kg^{-1}$), respectively. Thus, the Q_{in} is determined to be 9,818 W for experiments conducted with $17.17\ g\ min^{-1}$ charcoal. The heat balance

analysis is determined by the following equation:

$$Q_{in} = Q_{g,out} + Q_{C,out} + Q_{unC,out} \quad (15)$$

where $Q_{g,out}$ and $Q_{C,out}$ are the output processing capacity (W) for charcoal gasification and CLG, respectively; $Q_{unC,out}$ is the unburned processing capacity for charcoal, CO and H_2 . The output processing capacity for CLG and unburned was subsequently calculated by the following equation:

$$Q_{C,out} = \sum (F_{i,out,g} - F_{i,out,C}) \cdot \Delta H_{rxn,i} \quad (16)$$

$$Q_{unC,out} = \sum F_{i,out,C} \cdot \Delta H_{rxn,i} \quad (17)$$

where $F_{i,out,g}$ and $F_{i,out,C}$ are the molar flow rates of species i generated by charcoal gasification and CLG, respectively; $\Delta H_{rxn,i}$ is the enthalpy of species i ; i is denoted as CO , H_2 , O_2 and C .

The compositions in the outlet gas stream for charcoal gasification and charcoal combustion conducted with ϕ of 0.38 for moving bed operation at $900^\circ C$ were listed in Table 5, respectively. Hence, the $Q_{C,out}$, $Q_{unC,out}$ and $Q_{g,out}$ were determined to be 497 W, 9,602 W and -281 W, respectively, as calculated by Eqs. (15)–(17). $Q_{C,out}$ for chemical looping gasification of charcoal was slightly decreased for experiments conducted with higher ϕ , and reached to about 500 W, as shown in Fig. 9. However, $Q_{g,out}$ increased slightly with increasing ϕ , and enhanced to around -300 W, as shown in Fig. 9, indicating that above 60% of $Q_{C,out}$ generated was consumed for charcoal gasification in the ADMBR. Less heat was demanded for CLG of charcoal is possibly caused by the fuel gases combusted with Fe_2O_3/Al_2O_3 oxygen carrier, and more heat was generated for experiments carried out with greater ϕ . Therefore, ADMBR is technically feasible to be a fuel reactor for partial oxidization of charcoal by CLG

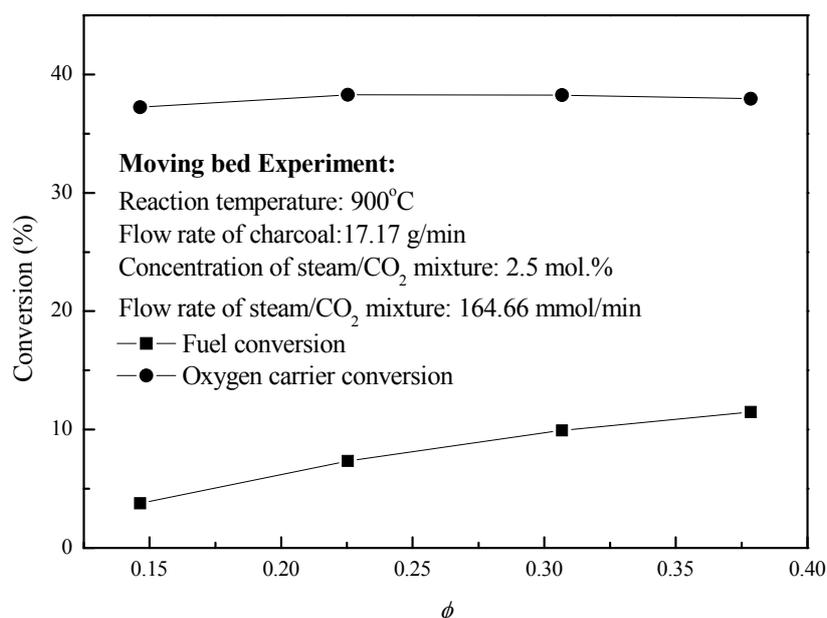
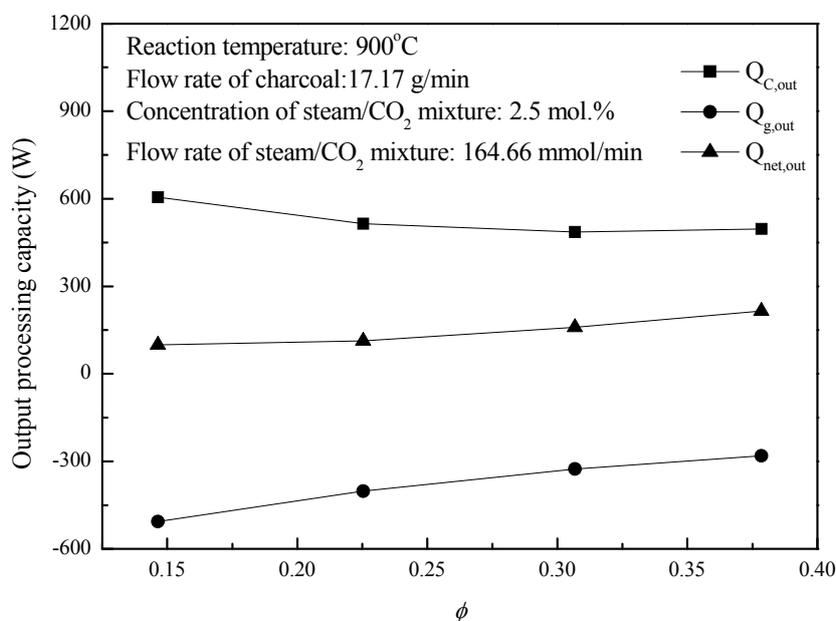


Fig. 8. Effect of oxygen carrier-to-fuel ratio on fuel and oxygen carrier conversions for CLG of charcoal in moving bed.

Table 5. Molar flow rates of gas component in the outlet streams from the decomposition and combustion of charcoal.

Operating condition	Molar flow rate (mmol min ⁻¹)				FeO generation (mmol min ⁻¹)	O ₂ demand (mmol min ⁻¹) ^a
	CO ₂	CO	H ₂	C		
Gasification	6.17	270.23	26.81	931.94	-	-
Combustion at $\phi = 0.38$	105.91	174.8	21.8	927.63	54.53	54.53

^aThe molar flow rate of O₂ demand for the oxidation of FeO with O₂.

**Fig. 9.** Effect of oxygen carrier-to-fuel ratio on output processing capacity for CLG of charcoal in moving bed.

to achieve syngas production under appropriate operating conditions without auxiliary fuel.

CONCLUSIONS

CO is the major fuel gases generated during charcoal gasification with CO₂ at 900°C. The carbon gasification rate of charcoal reached 12.27 mmol min⁻¹ for experiment conducted with the CO₂ at concentration of 20 mol.%. CO and H₂ are the major fuel gases generated from charcoal gasification with steam in fixed bed at 900°C. 13.25 mmol min⁻¹ of the carbon gasification rate of charcoal was achieved as the steam concentration reached 20 mol.% for charcoal gasification in fixed bed. By comparing with the CO₂ gasification of charcoal, the lower carbon gasification rate was observed for charcoal gasified by 2.5 to 15 mol.% steam than those by 2.5 to 15 mol.% CO₂, while higher carbon gasification rates was reached for experiments with 20 mol.% steam than those with 20 mol.% CO₂. Pure CO₂ was used to gasify the charcoal in fixed bed. Nearly 82% of CO concentration of charcoal gasification was achieved for experiments carried out with pure CO₂, while the CO₂ concentration was reached to about 18%. More combustible gas and fewer CO₂ were observed in the outlet gas streams for experiments conducted with steam/CO₂ mixture than those with only CO₂. However, the CO concentration of the outlet gas stream for experiment conducted with the inlet concentration of steam greater than 2.5 mol.%, and decreased

to about 50 vol.%. For empty bed operation, CO and H₂ are the major fuel gases generated during charcoal gasification prior to combustion with oxygen carrier at 900°C. The yields in the outlet stream were linearly increased with increasing steam/CO₂ mixture flow rate. Thus, the amounts of CO and H₂ generated by charcoal were estimated to modify the equation of oxygen carrier-to-fuel ratio (ϕ) for moving bed operation. CO and H₂ are the major components in the outlet gas stream generated from charcoal gasification with Fe₂O₃/Al₂O₃ oxygen carriers in the annular dual-tube moving bed reactor (ADMBR). Generation of CO and H₂ were enhanced for charcoal gasification conducted with higher oxygen carrier-to-fuel ratios. Output processing capacity estimated for CLG by employment of ADMBR as fuel reactor was slightly decreased for experiments conducted with higher ϕ , and reached to about 500W. About 300 W was required for charcoal gasification in the ADMBR, indicating that 60% of output processing capacity generated for charcoal gasification in the ADMBR. In sum, ADMBR is technically feasible to be a fuel reactor for partial oxidization of charcoal by CLG to achieve syngas production under appropriate operating conditions without auxiliary fuel.

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