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Chemical looping gasification of torrefied woodchips in a bubbling fluidized bed test rig using iron-based oxygen carriers

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A B S T R A C T

Chemical looping gasification is an efficient technology to convert biomass into valuable syngas. The iron-based oxygen carriers are a promising option for large-scale commercial applications due to their low cost and environmentally-friendly properties. The present study aims at evaluating the performance of the syngas production from the chemical looping gasification of torrefied woodchips in a pilot-scale bubbling fluidized bed reactor using iron ore and ilmenite as oxygen carriers. The effects of the operating parameters were investigated in this study. The results show that an increase in operating parameters could favor the process performance. Carbon conversion efficiency and the yields accelerate at high operating conditions. Carbon conversion efficiency showed a maximum value of 91.42% for iron ore at the ratio of oxygen carrier-to-biomass of 6, while the gas yield reaches the peak at SBR of 1.4 for ilmenite. The addition of steam in biomass chemical looping gasification improves hydrogen production and syngas quality in the product gas. Despite ilmenite provides better performance for hydrogen production, it characterizes by a lower reactivity compared to iron ore. It is also found that iron ore performs better at lower values of steam-to-biomass ratios and temperatures, while ilmenite shows good results at higher those parameters.

1. Introduction

Biomass, a feedstock derived from lignocellulosic matter is a promising renewable energy source for the production of heat, electricity, hydrogen, chemicals, and liquid fuels [1,2] despite some challenges from biomass's inherent properties such as low energy density, high moisture content, and complex ash components, biomass is abundant, widely available, and renewable. Moreover, the utilization of biomass for power and heat production has an advantage over other renewable sources such as solar energy, wind energy, and hydropower, etc. due to its low dependence on site and climate [3].

Chemical looping gasification (CLG) is a novel concept to gasify feedstocks into syngas, which can be used to generate power or produce chemicals and fuels. Biomass gasification using chemical looping technology is an innovative biomass technology due to its advantages such as high-quality syngas production, lower CO_2 emissions, and higher hydrogen production efficiency. Biomass chemical looping gasification (BCLG) shares the principles with chemical looping technology. A simplistic mechanism of biomass chemical looping gasification is illustrated in Fig. 1.

The BCLG system mainly consists of two reactors: the air reactor and the fuel reactor. The metals/metal oxides work as oxygen carriers, circulating between two reactors to transport oxygen and heat to solid feedstock. Biomass is partially oxidized in the fuel reactor at sub-stoichiometric quantities of metal oxides (Me_xO_y) to produce a mixture of gases, including H_2 and CO. Steam or CO_2 can be supplied to the fuel reactor to enhance reforming reactions and char gasification. In the air reactor, the reduced form of oxygen carrier (Me_xO_{y-1}) from the fuel reactor is oxidized by oxygen from air. The general chemical reactions that take place in the air reactor and the fuel reactor are presented in Reaction (R1) and (R2), respectively.

Air reactor: $2Me_xO_{y-1} + O_2 \rightarrow 2Me_xO_y$ (R1)

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Abbreviations

AR	Air reactor
BCLG	Biomass chemical looping gasification
BFB	Bubbling fluidized bed
CCE	Carbon conversion efficiency
CFD	Computational fluid dynamics
CGE	Cold gas efficiency
CLG	Chemical looping gasification
DIN	Deutschen Instituts für Normung
FR	Fuel reactor
H/C	Hydrogen-to-carbon ratio
LHV	Lower heating value
OBR	Oxygen carrier-to-biomass ratio
OC	Oxygen carrier
O/C	Oxygen-to-carbon ratio
OTC	Oxygen transport capacity
PI	Pressure indicator
Syngas	Synthesis gas
SBR	Steam-to-biomass ratio
TI	Temperature indicator

$$\text{Fuel reactor: Biomass} + Me_xO_y \xrightarrow{H_2O/CO_2} CO + H_2 + CO_2 + CH_4 + \text{tar} + Me_xO_{y-1} + \quad \text{(R2)}$$

Fluidized bed reactors are advantageous for the power generation and production of chemicals due to their continuous operation and process scalability. Bubbling fluidized bed gasifiers have high simplicity in configuration and process operation, and it is suitable for various particle sizes and types of feedstock. In bubbling fluidized bed reactors, the solid biomass material is introduced into a reactor through which is fluidized using an upward flow (air, oxygen, steam, carbon dioxide, or mixture at a sufficient flow rate to support their weight (incipient fluidization)). The longer residence time of fuel particles and the lower particle entrainment offers a certain advantage over the other types of fluidized bed reactors.

Many previous studies have been carried out to evaluate the performance of oxygen carrier materials in the BCLG process [4–11]. Various transition metal oxides and metal sulfates such as Ni, Cu, Co, Mn, Fe show good characteristics as feasible oxygen carriers for BCLG due to their favorable reductive/oxidative thermodynamic properties [12]. Compared to other oxygen carriers, the iron-based oxygen carriers are the most attractive oxygen carriers due to their low cost, environmentally-friendly issues, high mechanical strength, and high-temperature stability [13,14]. Furthermore, metallic iron is expected to promote C-C and C-H bond cleavage [15], resulting in more tar decomposition in the presence of iron oxide. Iron ore and ilmenite are both iron-based oxygen carriers that have been widely used as an oxygen carrier in various

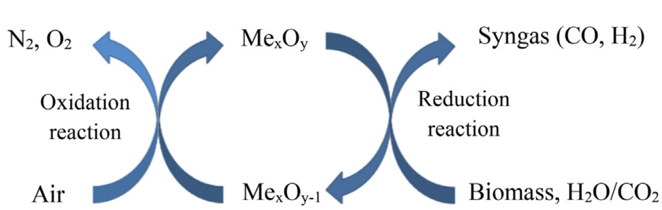

Fig. 1. Schematic diagram of Biomass chemical looping gasification process.

chemical looping conversion processes (mainly in the combustion process). Iron ore with Fe_2O_3 as the active component (>80 wt%) is an abundant low-cost source. The iron ore was applied as an oxygen carrier for CLG of biomass char [16], improving the char conversion rate and showing stable reactivity after 20 cycles. In the chemical looping conversions of solid fuels, Fe_2O_3 is mostly reduced to Fe_3O_4 in a fluidized bed reactor due to thermodynamic limitation, and its relatively low oxygen transfer capacity [17,18]. The ilmenite is an iron-titanium oxide mineral, basically composed of iron and titanium with the idealized formula $FeTiO_3$ ($FeO.TiO_2$). The iron oxides and titanium oxide can be considered as the active component and support material in ilmenite. The ilmenite mainly contains Fe^{2+} and can be fully oxidized to Fe^{3+} in the air at 900–1200 °C to improve its oxygen transfer capacity (OTC). Calcination temperature could influence the ilmenite transformation. The temperatures below 800 °C could favor the formation of Fe_2O_3 and TiO_2, while Ilmenite could be transformed into pseudobrookite Fe_2TiO_5 and TiO_2 at temperatures above 900 °C [19,20]. $Fe_3Ti_3O_{10}$ ($Fe_3O_4.3TiO_2$) could be the possible intermediate phases of ilmenite and pseudobrookite [21]. The ilmenite is intensively used as oxygen carrier, showing good stability and reactivity in chemical looping combustion applications [21–26].

Biomass gasification has emerged as a promising pathway to generate valuable products from biomass. Many problems and lack of understanding of the behavior of oxygen carriers in the gasifier have hindered its large-scale commercial applications. Tars released from biomass gasification, the effects of operating parameters in a fluidized bed gasifier on the behavior of oxygen carriers as well as the performance of BCLG, and the feasibility of biomass-based CLG using Fe-based oxygen carriers, etc. have been concerned. However, there are a limited number of studies on biomass chemical looping gasification in fluidized bed reactors in the literature, especially using torrefied biomass as a feedstock. Additionally, very few studies on fluidization regimes and the effect of gas velocity in BCLG can be found.

In the present work, experimental investigations of chemical looping gasification of torrefied woodchips were carried out in a bubbling fluidized bed test rig at a negative gauge pressure. Iron ore and ilmenite were selected as an oxygen carrier in this study. A series of CLG investigations were performed to evaluate the influences of gasification temperature, steam-to-biomass mass ratio (SBR), oxygen carrier-to-biomass ratio (OBR), and superficial velocity on the hydrogen production and the process performance. The results of this study can provide a better understanding of the behavior of iron-based oxygen carriers in a bubbling fluidized bed gasifier towards renewable energy generation and syngas production from biomass. The objectives of this study are listed as follows:

- Given current challenges for hydrogen production based on renewable sources, this work investigates the CLG of torrefied woodchips using steam as a gasifying agent and an iron-based oxygen carrier (Iron ore and ilmenite) in a bubbling fluidized bed reactor. The woodchips were first torrefied and the produced solid fuel was characterized. Then, CLG investigations were carried out in a pilot-scale bubbling bed test rig at different operating conditions, providing relevant measurement data to the most important parameters in the process.
- The performance of the BCLG is evaluated through the variation of operating parameters (the ratio of oxygen carrier-to-biomass, the ratio of steam-to-biomass, the gasification temperature, and the superficial velocity). Furthermore, detailed comparative performance of two oxygen carriers is carried out.
- The feasibility of hydrogen production using torrefied biomass as a feedstock is evaluated through experimental results (CLG of

torrefied woodchips). The presented measurements are of high importance for the validation of numerical models.

This manuscript is structured in the following manner. The setup of the test facility and its measurement systems are described. Then, the measurement data are presented with discussion and justification. Finally, the conclusions and outlooks are summarized in the last section of this manuscript.

2. Materials and method

2.1. Materials

Woodchips, torrefied at 250 °C and atmospheric pressure, were used as feedstock in the experimental investigations. Detailed information on the biomass torrefaction experimental setup has been described in a dissertation [27]. The torrefied woodchips were ground and sieved to a particle size of 200–850 μm. The proximate analysis of all samples was conducted following the DIN norms 18122, 18123, and 18134 standard test methods for ash, volatile matter, fixed carbon, and moisture determination, respectively. The ultimate analysis was carried out using an elemental analyzer (Elementar vario MACRO cube, measurement error < 0.1%). The feedstock characteristics are illustrated in Table 1. The determination of the heating value of the feedstock was performed in an isoperibolic, according to the DIN norms 51900 standard test method.

Ilmenite and iron ore are used as oxygen carriers in the investigations. To improve the reactivity of oxygen carrier materials, the ilmenite was calcinated at 850 °C in the air atmosphere for about 2 h in a bubbling bed reactor, while the iron ore has been crushed, dried, and calcinated at 950 °C [24]. The physical properties and chemical composition of these oxygen carriers are shown in Table 2.

The bed materials are used in a fluidized bed reactor to create fluidizing fundamentals. In the biomass gasification investigation (oxygen carrier-to-biomass ratio (OBR) of 0), silica sand is selected as an inert bed material due to its mechanical properties and neutral role in biomass gasification. The used F34 quartz sand of Quarzwerke company has particle diameters in the range of 125–355 μm and a density of 2650 kg/m^3. A reduced form of oxygen carriers is used in the BCLG as bed materials in the bubbling fluidized bed test rig.

2.2. Fluidized bed gasifier

The steam gasification experiments were carried out in a pilot-scale bubbling bed reactor, which is schematically shown in Fig. 2. The experimental pilot is equipped with a complete control system including flow control, feeding control system, pressure control, electrical heating system, temperature measurement points inside the reactor. The gasifier consists of a circular column with an internal diameter of 54.5 mm and a height of 550 mm, and a porous plate as gas distribution at the bottom. Temperature and pressure are measured at heights of 90 mm, 350 mm, and 550 mm. The reactor is externally heated by two electrical heating elements. The feedstock is continuously fed from a hopper into the reactor at 90 mm height through a screw feeder. A mixture of gases is preheated to 300 °C and injected into the reactor through a porous plate. The product gas on the top of the reactor is heated up to 110 °C to prevent the moisture and tars from condensing. A small amount of the product gas extracted from the top of the reactor is to measure continuously the volume fraction of the major components at a gas analysis unit. A jet pump to maintain negative gauge pressure inside the reactor spews the rest of the product gas out.

2.3. Experimental procedure

The torrefied woodchips and oxygen carriers are mixed at a known ratio and contained in a hopper, in which the agitation and screw feeder is set to the desired feed rate. Meanwhile, 0.05 Nm^3/h of N_2 is injected into the hopper to create an inert environment inside the hopper. Before starting the experiment, a negative gauge pressure inside the reactor is generated by turning the jet pump on. The reactor is filled up with 800 g of sand (for OBR of 0) or with the reduced form of oxygen carrier as bed material and fluidized with a stream of N_2 during the heating period up to the experiment temperature. When the desired temperature is reached, water is evaporated for steam generation, and N_2 is added to yield a total gas flow. The mixture of steam and N_2 is pre-heated to 300 °C before injection into the reactor. As soon as the temperature and pressure in the reactor reach a stable condition, the feedstock is fed continuously at 1 g/min of biomass flow rate. The steam-to-biomass mass ratio can be varied by changing the mass flow rate of steam while keeping the biomass flow rate constant. Once stable gas compositions have been achieved for 30 min, all data are recorded. The reported volume fractions of the gas composition are the average values on a dry and nitrogen-free basis.

In this study, torrefied woodchips are gasified with steam as gasification agent, and ilmenite and iron ore as oxygen carriers. Additionally, steam gasification of torrefied biomass is also conducted at 850 °C with oxygen carrier-to-biomass ratio (OBR) of zero and sand as bed material. The experiments are carried out to investigate the effect of operating parameters such as the ratio of steam-to-biomass (SBR), operating temperature, the ratio of oxygen carrier-to-biomass (OBR), and superficial velocity on hydrogen

Table 1
Main characteristics of the torrefied woodchips.

	Properties	Value	Comment
Proximate analysis [wt.%]	Moisture	5.28	As received
	Volatile matter	70.75	As received
	Fixed carbon	22.82	As received
	Ash	1.15	As received
Ultimate analysis [wt.% daf]	C	54.46	Dry basis
	H	5.99	Dry basis
	O	39.31	Dry basis
	N	0.24	Dry basis
	S	0.00254	Dry basis
HHV [MJ/kg]		20.97	As received
LHV [MJ/kg]		19.26	As received
Bulk density [kg/m^3]		161.71	As received
Mean particle diameter [μm]		296.65	Mass-weighted average diameter

Table 2
Oxygen carriers, * numbers were provided by suppliers [24].

Oxygen carrier	Ilmenite	Iron ore
Supplier, country	Titania AS, Norway	Promindsa, Spain
Mass weight mean diameter [μm][a]	98	183
Bulk density [kg m^{-3}]	2533	1823
Main composition, [wt.%]	TiO_2, 44	α-Fe_2O_3, 80 ± 1.5
	Total Fe, 35	$Ca(Mg,Fe)(CO_3)_2 \leq 11$
	MgO,4	$KAl_2[(Si_3Al)O_{10}](OH)_2$, ≤ 10
	SiO_2, 3.2	α-SiO_2, ≤ 4
	Accessory minerals, ≤ 2	Accessory minerals, ≤ 1

[a] As received.

production and the process performance. The operating conditions of the experiments are summarized in Table 3.

2.4. Data evaluation

The gasification performance is evaluated through key variables such as the calorific value of the product gas, hydrogen fraction and yield, and carbon conversion efficiency, etc. These variables can be derived from the data obtained during gasification.

The outlet volume fraction of gas species obtained from the gas analysis unit was calculated to ratios of H_2/CO and H_2/CO_2 by the following equations [28]:

$$\frac{H_2}{CO}=\frac{C_{H_2}}{C_{CO}}, \tag{1}$$

$$\frac{H_2}{CO_2}=\frac{C_{H_2}}{C_{CO_2}} \tag{2}$$

where C_i denotes the volume fraction of the component i recorded by the gas analysis unit. Since N_2 was used in this study as an inert tracer gas, the volume flow rate of other components can be calculated:

$$F_{i,out}=C_i \times \frac{F_{N_{2,in}}}{C_{N_2}} \left[Nm^3\ h^{-1}\right] \tag{3}$$

The lower heating value (LHV) of syngas, one of the most key parameter to evaluate syngas quality, is calculated using the following relation:

$$LHV_{syngas}=(30.18\times\ C_{CO}+25.76\times\ C_{H_2}+85.78\times\ C_{CH_4}) \times \frac{4.2}{1000}\left[MJ\ Nm^{-3}\right] \tag{4}$$

The cold gas efficiency (CGE) is defined as the ratio of the low heating value of product gas to the low calorific value of the corresponding used biomass, as shown by the following equation:

$$CGE=\frac{LHV_{syngas}\times\ V_{syngas}}{LHV_{biomass}}\times 100[\%] \tag{5}$$

Where the LHV_{syngas} is the lower heating value of the syngas in MJ/Nm^3, the symbol V_{syngas} represents the syngas yields Nm^3/kg$_{biomass}$ feedstock, the $LHV_{biomass}$ is the lower heating value of the biomass feedstock in MJ/kg.

The carbon conversion efficiency (CCE) is used as a key figure on the performance of biomass gasification in fluidized beds. It is defined as the ratio of the converted carbon to the carbon of biomass fed to the reactor.

$$CCE=\frac{(N_{CO,out}+N_{CO_2,out}+N_{CH_4,out})\times 12}{m_C\times\ \%C}\times 100[\%] \tag{6}$$

with the outlet molar flow rate of gas species $N_{i,\ out}$ in kmol/h, the mass flow rate of biomass m_c in kg/h, and the carbon content in biomass feedstock %C.

The gas yield (Y_{Gas}, Nm^3 kg^{-1}) represents the total gas volume (H_2, CO, CO_2, CH_4) obtained per mass of biomass fed to the reactor:

$$Y_{Gas}=\frac{V_{H_2,out}+V_{CO,out}+V_{CO_2,out}+V_{CH_4,out}}{m_{Biomass}} \tag{7}$$

3. Results and discussion

The experiments were performed using a pilot-scale bubbling fluidized bed reactor, as shown in Fig. 2, to investigate the gasification performance under various oxygen carrier-to-biomass ratios (OBRs), steam-to-biomass ratios (SBRs), gasification temperatures, and superficial velocities. Experimental setups are listed in Table 3.

The variations of operating parameters in the bubbling fluidized bed reactor influence strongly the output of the process through a series of complex and competing reactions in the presence of steam or CO_2. These main reactions are summarized here as follows [29–31]:

$$Biomass \xrightarrow{Heat} H_2+CO+CO_2+CH_4 + \text{light and heavy hydrocarbon}+\text{Tar}+\text{char} \tag{R3}$$

Homogeneous reactions:

$$\text{Water-gas shift reaction: } CO+H_2O\rightarrow CO_2+H_2 \tag{R4}$$

$$\text{Steam reforming of methane } CH_4+H_2O\rightarrow CO+H_2 \tag{R5}$$

Heterogeneous reactions:

$$\text{Boudouard reaction } C+CO_2\rightarrow 2CO \tag{R6}$$

$$\text{Water-gas reaction } C+H_2O\rightarrow CO+H_2 \tag{R7}$$

$$\text{Oxygen carrier reduction } CO+Me_xO_y\rightarrow CO_2+Me_xO_{y-1} \tag{R8}$$

$$\text{Oxygen carrier reduction } H_2+Me_xO_y\rightarrow H_2O+Me_xO_{y-1} \tag{R9}$$

$$\text{Oxygen carrier reduction } CH_4+Me_xO_y\rightarrow 2H_2+CO+Me_xO_{y-1} \tag{R10}$$

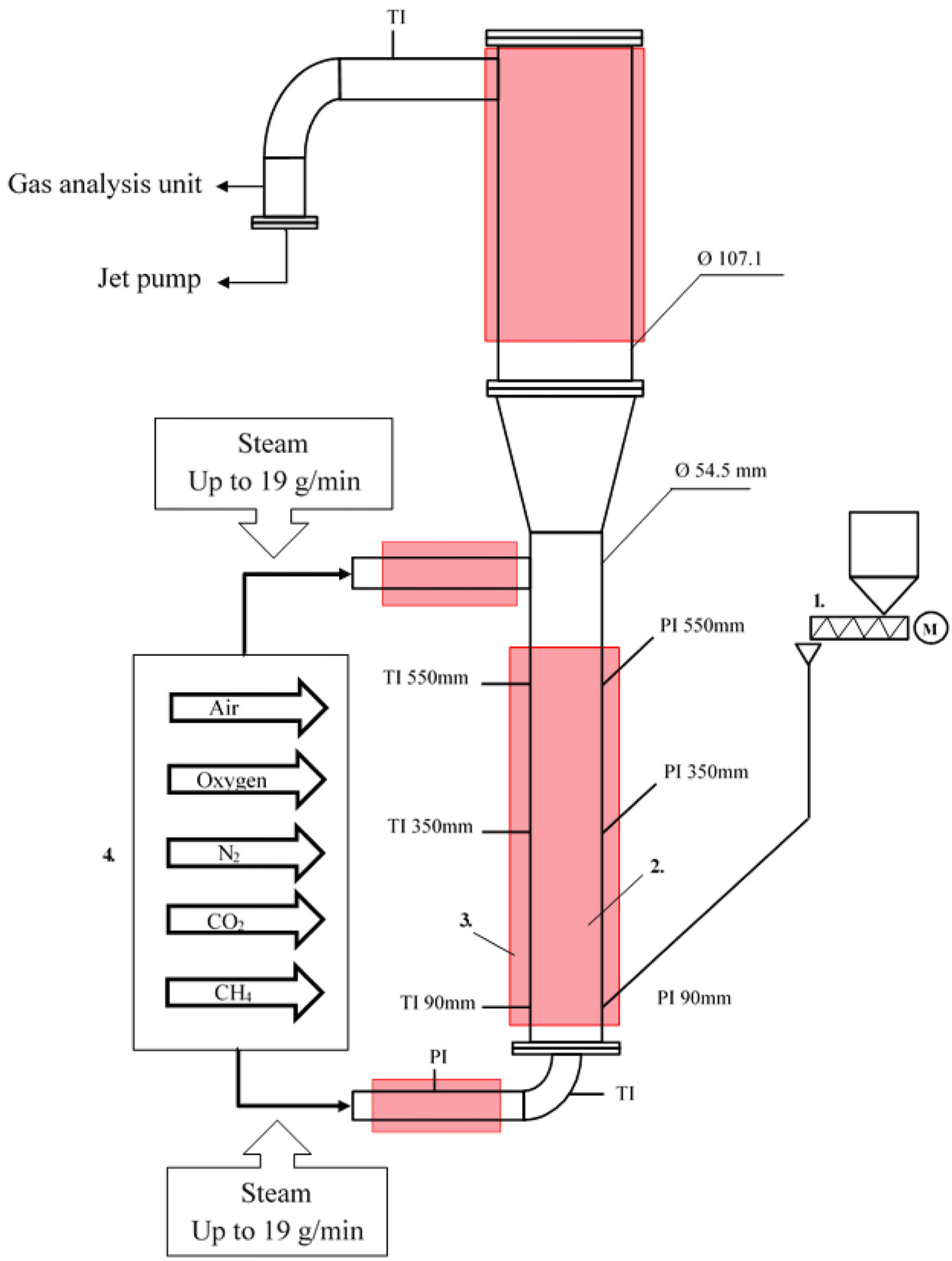

Fig. 2. Configuration of the fluidized bed reactor. 1 – screw conveyor for feeding fuel; 2 – bubbling fluidized bed reactor; 3 – electrical heater; 4 – gas distribution system.

3.1. Effect of the ratio of OC-to-biomass

Oxygen carrier plays a key role as the chemical intermediate to indirectly transfer pure oxygen from the air to the fuels via the oxidation-reduction (redox) reactions in the chemical looping gasification. In this study, iron ore and ilmenite were selected as oxygen carriers in the BCLG experiments. The mass ratio of oxygen carrier -to-biomass (OBR) is defined as the ratio of the mass of oxygen carrier to the mass of biomass used. Various OBRs are investigated to analyze the effect of oxygen carriers on BCLG's performance. The OBR is varied in the range of 0–6 by changing the mass of oxygen carrier used while keeping the torrefied woodchips mass at a constant in these experiments. In this section, the SBR and gasification temperature were set at 1.0 and 850 °C, respectively.

Fig. 3 and Table 4 show the effect of OBR on the BCLG's performance with iron ore as oxygen carrier. As can be seen in Fig. 3, the OBR shows a strong impact on the gas composition in the product gas. The combustible components display a downward trend with

Table 3
Matrix of experiments for BCLG.

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14
T [°C]	850	850	850	850	850	850	750	800	900	850	850	850	850	850
P [mbar]	−80	−80	−80	−80	−80	−80	−80	−80	−80	−80	−80	−80	−80	−80
Bed material [g]	800	800	800	800	800	800	800	800	800	800	800	800	800	800
Biomass [g/min]	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Steam [g/min]	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	0.9	1.26	1.4	1.08	1.08
OBR	0	2	3	4	5	6	3	3	3	3	3	3	3	3
N_2 [Nm^3/h]	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.17	0.18	0.16	0.15	0.17	0.17

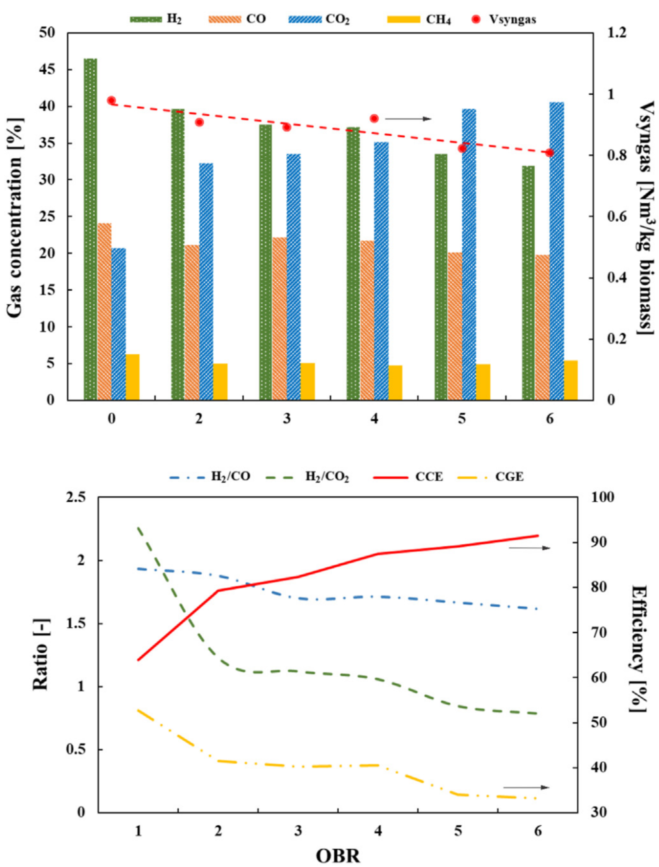

Fig. 3. Effects of OBR (iron ore) on (top) the relative content of the product gas, syngas yield, and (bottom) ratios and efficiencies.

increasing the OBR, while the content and yield of CO_2 increase by 19.88% and 0.0186 Nm^3/h, respectively. On the contrary, the H_2 content and yield decrease significantly to 31.97% and 0.0271 Nm^3/h at OBR of 6, respectively, whereas there is a slight reduction in CO concentration with a 4.33% decline over the range of OBRs. The concentration of CH_4 is relatively lower with maintaining around 5–6%. These trends lead to a fall in the ratios of H_2/CO and H_2/CO_2 as well as syngas production and LHV. Syngas yield drops considerably from 0.98 to 0.81 [Nm^3/kg biomass], while LHV decreases from 10.36 to 7.9 [MJ/Nm^3]. As a result, the cold gas efficiency (CGE) falls by 19.55% in the range of OBRs. However, an increase of OBR enhances the carbon conversion efficiency and gas yield, reaching a peak of about 91.42% and 1.4146 [Nm^3/kg biomass] at OBR of 6, respectively.

The influence of OBR on the syngas production from the BCLG using ilmenite as oxygen carrier shows a similar tendency. According to Fig. 4 and Table 5, the H_2 content reduces significantly by 12.83%, while the CO_2 increases sharply, reaching a peak of 39.55% at an OBR of 6. Consequently, a decrease in syngas yield and gas yield is found with an increase of OBR due to a gradual decrease in yields of CO and CH_4. The result also indicates that the carbon conversion efficiency rises in the range of OBR. At OBR of 0, the carbon conversion efficiency is about 63.95%, and this figure increases gradually, reaching 83.99% at OBR of 4, to a peak of 85.52% at OBR of 6. Whereas the cold gas efficiency drops considerably by around 20% in the same period.

The result of this investigation shows that the amount of oxygen carriers used in the BCLG significantly influences the process performance, especially the H_2 production. Both BCLG tests using the two oxygen carriers reveal a considerable reduction in the yield and concentration of H_2 as well as a great increase in those of CO_2 with an increase of OBR. This can be explained by the higher amount of oxygen carrier used that can provide more oxygen source for

Table 4
Experimental results of the BCLG using Iron ore as oxygen carrier.

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14
T [°C]	850	850	850	850	850	850	750	800	900	850	850	850	850	850
OBR	0	2	3	4	5	6	3	3	3	3	3	3	3	3
SBR	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	0.9	1.26	1.4	1.08	1.08
u_f [m/s]	0.132	0.132	0.132	0.132	0.132	0.132	0.12	0.127	0.138	0.132	0.132	0.132	0.106	0.158
H_2/CO	1.93	1.88	1.7	1.72	1.67	1.62	2.5	2.11	1.62	1.65	1.91	2.15	1.9	1.73
H_2/CO_2	2.25	1.23	1.12	1.06	0.85	0.79	1.36	1.35	1.21	1.08	1.2	1.4	1.17	1.19
V_{H2} [Nm^3/h]	0.0356	0.0329	0.0311	0.0323	0.0283	0.0271	0.0368	0.035	0.035	0.031	0.0346	0.0396	0.032	0.0339
V_{CO} [Nm^3/h]	0.0184	0.0175	0.0183	0.0188	0.0169	0.0168	0.0147	0.0166	0.0216	0.0188	0.0181	0.0185	0.0169	0.02
V_{CO2} [Nm^3/h]	0.0158	0.0267	0.0277	0.0305	0.0333	0.0344	0.0271	0.026	0.029	0.0287	0.0287	0.0283	0.0275	0.0285
V_{CH4} [Nm^3/h]	0.0048	0.0042	0.0042	0.0041	0.0041	0.0046	0.0033	0.0039	0.0047	0.0042	0.0042	0.0046	0.004	0.0041
V_{syngas} [$Nm^3/kg_{biomass}$]	0.9802	0.9091	0.893	0.9205	0.822	0.8079	0.9125	0.9236	1.0228	0.9	0.9483	1.0437	0.8833	0.9585
V_{gas} [$Nm^3/kg_{biomass}$]	1.2736	1.3811	1.3783	1.4444	1.4013	1.4146	1.3915	1.3831	1.5358	1.3963	1.4547	1.5393	1.3648	1.4642
LHV [MJ/Nm^3]	10.36	8.78	8.69	8.49	7.96	7.9	8.41	8.76	8.93	8.65	8.66	8.95	8.63	8.68
CCE [%]	63.95	79.35	82.28	87.48	89.19	91.42	73.18	76.05	90.79	84.78	83.69	84.17	79.33	85.48
CGE [%]	52.71	41.43	40.31	40.52	33.98	33.16	39.85	42.03	47.43	40.44	42.63	48.51	39.59	43.17
u_f/u_{mb} [a]	2.41	1.68	1.68	1.68	1.68	1.68	1.53	1.60	1.75	1.68	1.68	1.68	1.34	2.01

[a] u_f is superficial velocity, u_{mb} is minimum bubbling velocity.

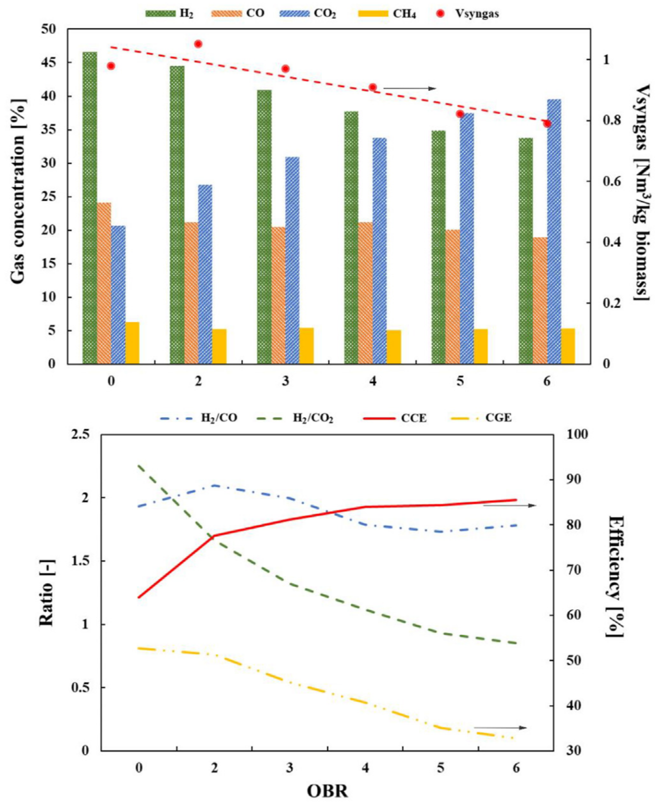

Fig. 4. Effects of OBR (ilmenite) on (top) the relative content of the product gas, syngas yield, and (bottom) ratios and efficiencies.

oxidation reactions (R8-R10) in the reactor, resulting in more combustible gas components consumed and more CO_2 generated. Additionally, an increase of CO_2 and H_2O contents in the reactor can favor the char gasification reactions (R6 and R7) and cracking reactions, which enhance biomass conversion or carbon conversion efficiency. Therefore, it can be suggested that high syngas production is obtained at low OBRs.

It is noteworthy that the rate of decrease in the concentration of H_2 is higher than that of CO and CH_4. These figures are 12.83%, 5.14%, and 0.93% for the investigations with ilmenite and 14.62%, 4.33%, and 0.89% for the tests with iron ore corresponding to H_2, CO, and CH_4, respectively. This is attributed to the difference in the reaction rate of Fe_2O_3 with various fuels. Generally, the reactivity of Fe_2O_3 with those gaseous fuels has the following order: $H_2 > CO > CH_4$ [17]. Therefore, the amount of H_2 oxidized by Fe_2O_3 is higher than the others. Although the theoretical oxygen transport capacity of iron ore is lower than that of ilmenite (~3.3% and ~4%), the carbon conversion efficiencies for the BCLG with iron ore are higher than those with ilmenite, while a greater hydrogen production is obtained with ilmenite in terms of concentration and yield. This is related to the calcination temperature of oxygen carriers. Ilmenite has been pre-oxidized at 850 °C, whereas the calcination temperature of iron ore is 950 °C.

3.2. Effect of gasification temperature

The gasification temperature is crucial for the performance of the BCLG process. In this study, the experiments were carried out at four temperatures in the range of 750 °C–900 °C with 50 °C increments. Due to the small reactor diameter and long operating time, the OBR of 3 was selected in the variation of temperatures, and SBR of 1.0 was used for these investigations. The effects of gasification temperature on the performance of the BCLG using iron ore and ilmenite as oxygen carriers are given in Tables 4 and 5, respectively. Additionally, Fig. 5 and Fig. 6 show the variations of the gas concentrations and syngas yield as a function of gasification temperature.

Generally, these figures show that the concentration of H_2 from the BCLG with iron ore and ilmenite decreases slightly, while there is an increase in CO content in both cases corresponding to elevated temperature in the reactor. It can be observed that higher gasification temperatures generate more syngas yield and gas yield, which reach maximum values of 1.023 $Nm^3/kg_{biomass}$ and 1.536 $Nm^3/kg_{biomass}$ from tests using iron ore and 1.098 $Nm^3/kg_{biomass}$ and 1.559 $Nm^3/kg_{biomass}$ in the case of ilmenite at 900 °C. It is also noteworthy that the gasification temperature shows little impact on the outlet CH_4 concentration in the investigations of two oxygen carriers. The CH_4 concentration increases slightly by 0.88% in the range of temperature for the BCLG using iron ore, whereas this figure from ilmenite tests drops from 7.19% at 750 °C to 5.43% at 900 °C. Furthermore, the elevated temperature significantly improves both carbon conversion efficiency and cold gas efficiency. There is a considerable rise in carbon conversion efficiency with 17.62% and 25.21% in cases of iron ore and ilmenite, respectively. While the result shows a lower increase in cold gas efficiency with 7.58% and 14.98% in the temperature range.

The above-mentioned variations of the performance of the BCLG

Table 5
Experimental results of the BCLG using ilmenite as oxygen carrier.

Run	1	2	3	4	5	6	7	8	9	10	11	12	13	14
T [°C]	850	850	850	850	850	850	750	800	900	850	850	850	850	850
OBR	0	2	3	4	5	6	3	3	3	3	3	3	3	3
SBR	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	1.08	0.9	1.26	1.4	1.08	1.08
u_f [m/s]	0.132	0.132	0.132	0.132	0.132	0.132	0.12	0.127	0.138	0.132	0.132	0.132	0.106	0.158
H_2/CO	1.93	2.1	1.99	1.79	1.73	1.78	2.25	1.83	1.65	1.77	2.04	2.2	1.96	1.78
H_2/CO_2	2.25	1.66	1.32	1.12	0.93	0.85	1.37	1.2	1.43	1.34	1.47	1.53	1.30	1.32
V_{H2} [Nm^3/h]	0.0356	0.0395	0.0357	0.0322	0.0285	0.0276	0.0291	0.0279	0.0378	0.0339	0.0408	0.0432	0.0343	0.0359
V_{CO} [Nm^3/h]	0.0184	0.0188	0.0179	0.018	0.0165	0.0155	0.013	0.0159	0.023	0.0192	0.02	0.0196	0.0175	0.02
V_{CO2} [Nm^3/h]	0.0158	0.0238	0.027	0.0288	0.0307	0.0323	0.0212	0.0242	0.0265	0.0254	0.0277	0.0283	0.0263	0.0272
V_{CH4} [Nm^3/h]	0.0048	0.0047	0.0047	0.0044	0.0043	0.0044	0.0049	0.0049	0.0051	0.0047	0.0052	0.0054	0.0049	0.005
V_{syngas} [$Nm^3/kg_{biomass}$]	0.9802	1.0507	0.9705	0.9103	0.8215	0.7905	0.785	0.8329	1.0979	0.9646	1.1011	1.138	0.9447	1.0168
V_{gas} [$Nm^3/kg_{biomass}$]	1.2736	1.4788	1.4522	1.4217	1.3637	1.3617	1.1522	1.2676	1.5587	1.4063	1.5931	1.6425	1.3974	1.492
LHV [MJ/Nm^3]	10.36	9.41	8.97	8.61	8.22	7.98	9.53	9.15	9.45	9.26	9.25	9.26	9.17	9.19
CCE [%]	63.95	77.54	81.22	83.99	84.32	85.52	64.23	72.55	89.44	80.87	86.78	87.52	79.82	85.7
CGE [%]	52.71	51.36	45.21	40.7	35.06	32.76	38.86	3888.57	53.84	46.38	52.85	54.68	44.97	48.51
u_f/u_{mb} [a]	2.41	3.53	3.53	3.53	3.53	3.53	3.21	3.37	3.68	3.53	3.53	3.53	2.82	4.23

[a] u_f is superficial velocity, u_{mb} is minimum bubbling velocity.

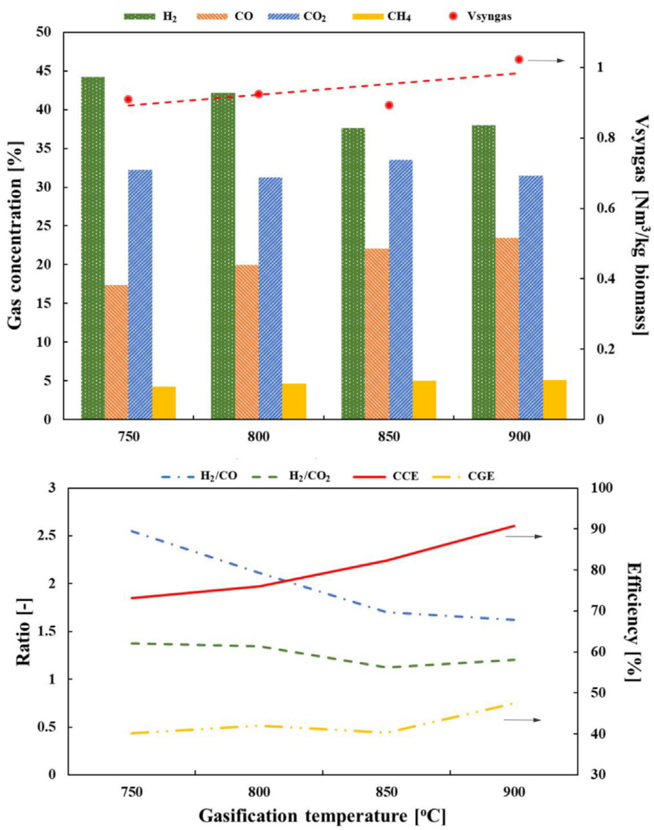

Fig. 5. Effects of temperature (iron ore) on (top) the relative content of the product gas, syngas yield, and (bottom) ratios and efficiencies.

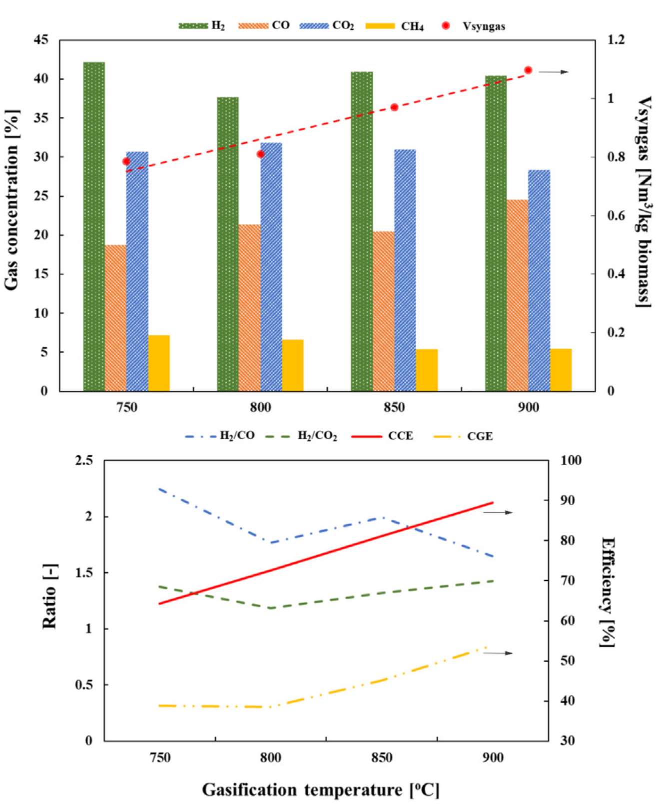

Fig. 6. Effects of temperature (ilmenite) on (top) the relative content of the product gas, syngas yield, and (bottom) ratios and efficiencies.

using two types of oxygen carrier at various temperatures can be well explained due to a series of complex and completing reactions including exothermic and endothermic reactions as well as solid/gas and gas/gas reactions in the BCLG [31,32]. It can be seen that the CO concentration rises, while there is a slight decrease in the contents of H_2 and CO_2 with the temperature increase. This can be attributed to Le Chatelier's principle (elevated temperatures favor the reactants in exothermic reactions and the products in endothermic reactions). Therefore, high temperature promotes the endothermic reactions (R5-R7), resulting in the enriched H_2 and CO contents and the reduction in CO_2. Additionally, combustible gases can be also oxidized by iron ore and ilmenite through R8−R10 to produce CO_2 and H_2O. However, it is due to the stronger reducibility of oxygen carriers with H_2, an amount of H_2 oxidized is more than that of CO and CH_4. Therefore, the content of H_2 decreases relatively compared to other components. Furthermore, the increasing temperature can strengthen the decomposition reactions of heavier hydrocarbons, which enhance the cracking of heavier hydrocarbons into the product gas. As a result, there is a considerable rise in yields of gas components, and the decreasing residual solid leftover at accelerated temperatures.

The gasification temperature shows a great effect on the performance of the BCLG in both cases of iron ore and ilmenite. The elevated temperature significantly enhances the yields of syngas and the product gas as well as the carbon conversion efficiency and the cold gas efficiency. Moreover, the quality of the product gas is improved at higher temperatures. A comparison of the performance of two oxygen carriers at different temperatures is also considered to evaluate their behavior in BCLG at various temperatures. It should be noted that ilmenite shows a better performance at higher temperatures, whereas iron ore performs a greater result at lower temperatures. However, the behavior of ilmenite and iron ore at various investigated temperatures is still unclear due to the lack of understanding of the reaction mechanism in the BCLG process, further studies on their reaction mechanism at different temperatures would be necessary.

3.3. *Effect of steam-to-biomass ratio*

The steam-to-biomass mass ratio (SBR) refers to the amount of steam per mass of biomass fed into the reactor [31]. Besides the gasification temperature, SBR is a key parameter influencing strongly on the performance of the BCLG, especially H_2 production [33]. In the CLG of solid fuels, steam is used as a gasification agent, it provides not only hydrogen for high-quality syngas production but also molecular oxygen for char conversion. In this study, the SBR is varied in the range of 0.9−1.4 by changing the mass flow rate of steam, while keeping the biomass-feeding rate constant at 1 g/min. The gasification temperature was fixed at 850 °C and OBR was at 3.

Fig. 7 and Table 4 show the results obtained from the BCLG using iron ore as oxygen carrier. Generally, the content of H_2 has been trending upward over the range of SBR from 37.08% to 42.89%, whereas the fractions of CO and CO_2 slightly fall by 2.46% and 3.63%, respectively. Additionally, there is a gradual rise in carbon conversion efficiency, reaching 84.17% at SBR of 1.4. It is noteworthy that increasing the SBR improves the ratios of H_2/CO_2 and H_2/CO (the rates of increase accelerate, being about 1.4 for H_2/CO_2 and 2.15 for H_2/CO at SBR of 1.4). This trend indicates that the fraction of H_2 increases relatively in the product gas compared to the other species corresponding to a higher amount of steam used. The yields of syngas and product gas obtained are improved considerably with about 15.9% and 10.2% at SBR of 1.4 higher than those at SBR of 0.9. These increases are due to the significant rise in the yields of H_2 and CH_4 despite a slight reduction in the yields of CO and CO_2. Moreover, the rise in the contents of H_2 and CH_4 results in an increase in

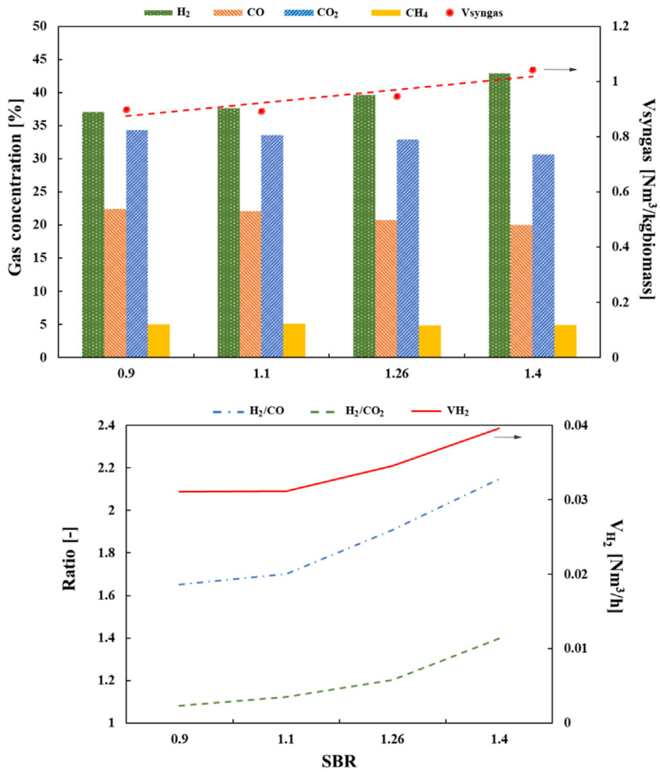

Fig. 7. Effects of SBR (iron ore) on (top) the relative content of the product gas, syngas yield and (bottom) ratios and H_2 yield.

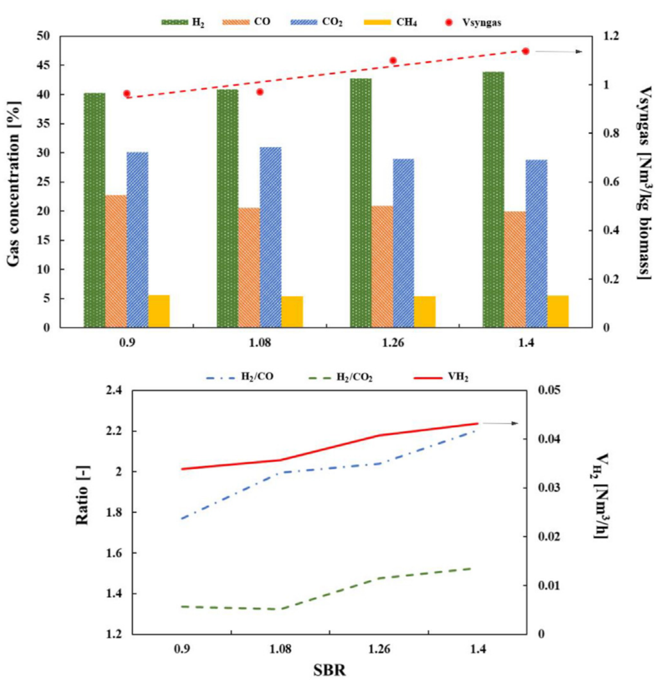

Fig. 8. Effects of SBR (ilmenite) on (top) the relative content of the product gas, syngas yield and (bottom) ratios and H_2 yield.

the lower heating value and the cold gas efficiency, which reach their maximum values of 8.95 [MJ/Nm3] and 48.51% at the SBR of 1.4, respectively.

The experimental results using ilmenite as oxygen carrier are presented in Fig. 8 and Table 5. Overall, the presence of steam shows a strong influence on syngas production. The content of H_2 increases by about 3.63%, while its yield at SBR of 1.4 is 27.32% higher than that at SBR of 0.9. Furthermore, the ratios of H_2/CO and H_2/CO_2 increase rapidly to about 2.2 and 1.53 at SBR of 1.4, respectively. It is attributed to the reduction in the fractions of CO and CO_2 in the product gas, despite their yields obtained a slight rise with an increase of SBR. Moreover, a high amount of steam used also promotes the yields of syngas and product gas. It is found that the yields of syngas and product gas obtained are getting 17.97% and 16.8% increase over the range of SBR, respectively. As a result, the carbon conversion efficiency and the cold gas efficiency increase continuously, reaching a peak of 87.82% and 54.68% at SBR of 1.4, respectively. However, the LHV maintains at around 9.2 MJ/Nm^3 in the range of SBR.

Those trends mentioned above regarding the content of steam in the gasifier are attributed to a series of reactions in the gasification process. The reactions (R4, R5, R7) with the increase of steam content toward the right side based on Le Chatelier's Principle. As a result, there is a considerable increase in H_2 production and a relative reduction in the concentrations of other gas species. Additionally, the water-gas shift reaction is promoted by the higher steam content that would be accompanied by a reduction in the fraction of CO. It is noted that there is little variation in the content and yield of CH_4 in the range of 0.9–1.4 because its fraction is very small compared to other components and it mainly derives from the devolatilization of torrefied woodchips. The char gasification reactions and the heavier hydrocarbon cracking reactions are favored by the high content of steam in the reactor, increasing the carbon conversion efficiency and the gas yield. Therefore, the steam content in the gasifier strongly influences the H_2 production, the syngas quality, and the char conversion. However, the adding of excess steam may cause a reduction in the temperature of the BCLG since the steam absorbs a lot of heat, resulting in a decline in BCLG performance.

It is noted that the investigation using ilmenite performs better in terms of H_2 production, gas yield, LHV, and efficiencies compared to those from BCLG using iron ore. Interestingly to note that the carbon conversion efficiency from the test using iron ore is higher at low SBR, but ilmenite shows better performance at a higher amount of steam. Additionally, the test with ilmenite also shows a higher rate of increase in gas yield with 16.82% in the range of SBR compared to that using iron ore with 10.24%. It could be concluded that the steam content strongly affects the performance of ilmenite in the BCLG process.

3.4. Effect of superficial gas velocity

The superficial velocity is one of the key factors, which define the hydrodynamics of bed material in a bubbling fluidized bed reactor. The variation of the superficial velocity significantly influences the gas-solid contact, heat and mass transfer, and the performance of the BCLG in a bubbling bed reactor. Three input total gas flow rates were selected at 0.2, 0.25, and 0.3 Nm^3/h, corresponding to the superficial velocity of 0.106, 0.132, and 0.158 m/s, respectively. The operating conditions were fixed at 850 °C, SBR of 1.08, and OBR of 3.

The results of these investigations are shown in Fig. 9 and Table 4 for iron ore as well as Fig. 10 and Table 5 for ilmenite. It is noted that a similar phenomenon is observed in the results of the two oxygen carriers. There is a small variation in the contents of gas species. This variation could be neglected compared to other operating parameters in the previous sections. However, the carbon conversion efficiency increases from about 79% at 0.106 m/s to 85% at 0.158 m/s, while the cold gas efficiency enhances by about 3.5%

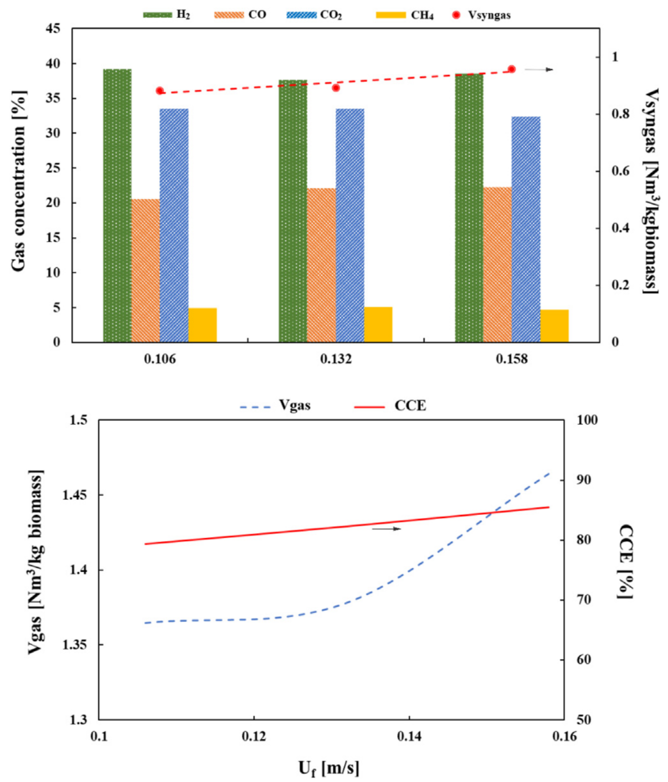

Fig. 9. Effects of superficial velocity (iron ore) on (top) the relative content of the product gas, syngas yield, and (bottom) yield of the product gas and CCE.

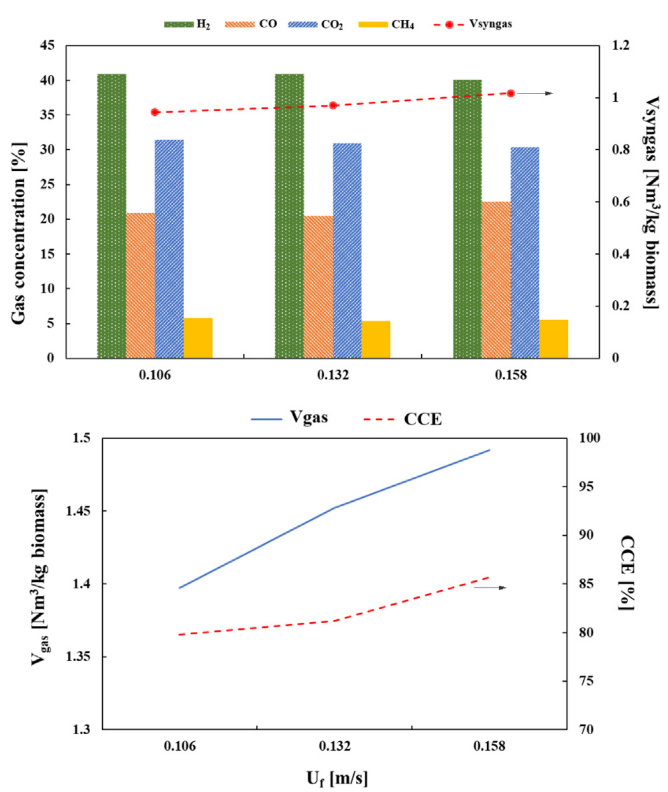

Fig. 10. Effects of superficial velocity (ilmenite) on (top) the relative content of the product gas, syngas yield, and (bottom) yield of the product gas and CCE.

over the range of gas velocity. Additionally, all yields of gas components obtained are higher at higher gas velocities, resulting in about 0.07 $Nm^3/kg_{biomass}$ and 0.09 $Nm^3/kg_{biomass}$ increase of syngas and product gas. It can be concluded that the superficial velocity has a small effect on the fraction of species in the product gas, but the carbon conversion of biomass gasification and the yield of gas is improved. As the same tendency with other variables, the results with ilmenite indicate better performance in terms of H_2 production and gas yield in every gas velocity.

Those trends may be attributed to the effect of superficial velocity on the hydrodynamics of bed material in the BCLG. In this investigation, only the gas velocity varied, while other variables were fixed. Therefore, there is a limiting factor, which can affect chemical equilibrium in the BCLG. Consequently, the variation of component concentrations in the product gas can be neglected. As discussed above, an increase in gas velocity can enhance the gas-solid mixing, the heat and mass transfer in a bubbling bed reactor [34], the temperature distribution along the reactor, and the solid fuel conversion. The char gasification reactions are favored at high gas velocities, resulting in a slight increase in the content of CO and gas yield, and a small reduction in CO_2 concentration. However, when the gas velocity is too high, the bed material can transit into slugging, turbulent, or fast fluidization regimes. Therefore, the evaluation of the effect of gas velocity in a bubbling bed reactor on the performance of the BLCG is crucial to select the suitable gas velocities for stable operations while achieving the desired results.

3.5. Evaluation of iron ore and ilmenite performance

This section compares the performance of two oxygen carriers in the BCLG process through their results evaluated in the previous sections. Generally, the ilmenite performs better than the iron ore in terms of the content and yield of H_2 with a greater percentage of H_2 content from 0.98 to 4.84%, whereas the iron ore produces more CO_2 in the product gas with around 1–5.48% for all operating parameters (OBR, SBR, gasification temperature, and superficial velocity). Additionally, carbon conversion efficiency for the iron ore is higher than that with ilmenite in a range of 1.06–8.94%, excluding the case of SBR. Therefore, it may be concluded that the reactivity of the iron ore is higher than that of the ilmenite in this work. According to the previous studies, iron ore as an oxygen carrier has a theoretical oxygen transport capacity (OTC) of around 3.3%, which is lower compared to that of the ilmenite with 4% [24]. However, the study's results show here the opposite trend. It can be attributed to the calcination temperature of the ilmenite, which strongly influences its reactivity (ilmenite was oxidized in air at 850 °C, while iron ore was calcinated at 950 °C). The iron ore mainly consists of Fe_2O_3 as the active component with < 80 wt%. In a fluidized bed reactor, the iron ore is mainly reduced from Fe_2O_3 to Fe_3O_4 by solid fuels because of thermodynamic limitation [17]. The ilmenite mainly contains iron oxides and titanium oxide as the active components. The raw ilmenite largely comprises Fe^{2+}, which can be converted into Fe^{3+} after the calcination process to form a composite of Fe_2O_3/TiO_2. Some previous studies found that the calcination temperature could significantly influence the ilmenite transformation. The calcination of ilmenite at a temperature below 800 °C could promote the formation of Fe_2O_3 and TiO_2, while ilmenite can be transformed to pseudobrookite Fe_2TiO_5 at temperatures above 900 °C. In the range between 770 and 900 °C, the $Fe_2Ti_3O_9$ phase is existent after the oxidation process [17,20]. Yamaguchi et al. [19] found that pseudo-brookite (Fe_2TiO_5) performed lower reduction kinetics, but it showed a greater OTC compared to other ilmenite phases. Their results also indicated that the highest redox activity was obtained for the ilmenite calcinated at 1000 °C. Moreover, the reactivity and redox performance of ilmenite is also affected during the calcination due to its crystalline properties and its surface area. As a result, the calcination temperature strongly influences the performance of ilmenite in the chemical looping gasification process. The effect of oxygen carrier on the BCLG on the H_2 content is the greatest with 12.83–14.62%, while the content of CH_4 shows the lowest difference with around 0.9% in the range of OBR in the cases of two oxygen carriers. The reaction rate of H_2 with iron-based oxygen carriers is higher than that of CO. By contrast, the CH_4 shows the lowest reactivity with this type of oxygen carrier. This order is in good agreement with the literature data [12,17].

4. Conclusion

Chemical looping gasification is considered as a potential process to produce high-quality syngas from biomass. Among various types of oxygen carriers, iron-based oxygen carriers have been intensively used in chemical looping conversion processes due to their low price, environmentally-friendly issues, high mechanical strength, and high-temperature stability, despite the relatively low kinetics and low oxygen transport capacity. In this study, the influence of process parameter variations on the performance of the bubbling fluidized CLG using torrefied woodchips was evaluated experimentally. The highlighted remarks of this study are as follows:

1. The oxygen carrier is a key factor in the BCLG process. The amount of oxygen carrier used in the gasifier strongly affects the performance of the CLG process. An increase in OBR causes a reduction in H_2 production and an upward trend in carbon conversion efficiency. Moreover, OBR also does not favor syngas yield in a CLG conversion. Interestingly to note that the reactivity of gaseous fuels with iron-based oxygen carriers has the following order: H_2 > CO > CH_4.
2. The gasification temperature is a key factor in the BCLG for iron-based oxygen carriers. The increment of temperature significantly enhances the gas yields and the process efficiencies. It is found that the ilmenite shows a better performance at high temperatures, while the iron ore performs greater results at lower temperatures. However, the detailed evaluation of the effect of gasification temperature on the BCLG process is limited by the unavailability of the reaction mechanism of these types of oxygen carriers at different temperatures. Therefore, further studies on this topic would be necessary to clarify those phenomena discussed in the previous section.
3. The ratio of steam-to-biomass is crucial for H_2 production in the BCLG process. The content of H_2 has been trending upward with the steam amount used, reaching a peak of about 42.89% for the iron ore and 43.87% for the ilmenite at SBR of 1.4. Additionally, higher SBRs also enhance the syngas yield as well as the gas yield and process efficiencies. Interestingly to note that the carbon conversion efficiency obtained for the iron ore is higher at lower SBRs, but the ilmenite shows better performance at a higher amount of steam used in the gasifier. However, excess steam may cause a decline in the BCLG performance due to heat loss in the gasifier.
4. The superficial velocity significantly influences the gas-solid contact as well as heat and mass transfer in a bubbling fluidized bed reactor. In this study, the results show that there is a minor variation in the fractions of gas species recorded, but the carbon conversion efficiency increases from about 79% at 0.106 m/s to 85% at 0.158 m/s. Additionally, the yield of the product gas increases by 0.09 $Nm^3/kg_{biomass}$ over the range of the superficial velocities.
5. The performance of the iron ore and ilmenite in the BCLG is evaluated through the data obtained in this study. Ilmenite gives averagely a better result than the iron ore in terms of H_2 production with a greater percentage of H_2 content between 0.98 and 4.84%, while the carbon conversion efficiency for the iron ore is higher with about 1.06–8.94%. Interestingly to note that the calcination temperature strongly influences the reactivity of ilmenite in the BCLG. Ilmenite performs low reactivity compared to iron ore in this investigation. This is since the ilmenite was oxidized in air at 850 °C, whereas the iron ore was oxidized at 950 °C.

The present study gives an insight into the chemical looping gasification of torrefied woodchips using iron-based oxygen carriers. All operating parameters investigated in this study have a strong effect on the performance of the BCLG. Furthermore, it was shown that the iron-based oxygen carriers have been proved as a suitable option for the chemical looping gasification of biomass to produce high-quality syngas.

CRediT authorship contribution statement

Nhut M. Nguyen: is responsible for Administration, Conceptualization, the original draft, and the applied methodology, The experimental investigations were conducted. **Falah Alobaid:** supported the writing process with his reviews and edits. **Bernd Epple:** supervised the research progress and the presented work, All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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