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OPERATION OF A COUPLED FLUIDIZED BED SYSTEM FOR CHEMICAL LOOPING COMBUSTION OF SOLID FUELS WITH A SYNTHETIC CU-BASED OXYGEN CARRIER

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ABSTRACT

A copper-based oxygen carrier was successfully used for chemical looping combustion of coal. The two-stage fuel reactor design worked well, i.e. high CO₂ concentrations up to 94 vol.% and low concentrations of combustible gases below 1 vol.% in the dry fuel reactor off-gas were obtained. Based on solids samples withdrawn during operation the circulation rate was assessed by an oxygen balance for the air reactor. The circulation rate was in the range from 17 to 45 kg/m²s.

INTRODUCTION

Chemical-Looping Combustion (CLC) allows the inherent separation of CO₂, which is generated by the combustion of fossil fuels. In recent years CLC has attracted attention as an alternative conversion process for the carbon capture and storage (CCS) technology and is widely studied nowadays (e.g. 1,2,3). A key factor in the CLC performance is the oxygen carrier (OC), which is circulated between the reactors. It must fulfil several requirements, e.g. sufficient oxygen transport capacity, high reactivity for reduction and oxidation, resistance to attrition and cost-effectiveness (3). The question is whether it is advantageous to use a cheap natural ore which might lack the high reactivity or attrition resistance or to use a relatively more expensive synthetic oxygen carrier which offers a better reactivity and stability. Many potential natural and synthetic oxygen carrier materials have been tested on the scale from laboratory reactors up to pilot-scale plants (e.g. 4,5). However, besides the oxygen carrier the process design is important. The majority of process designs currently under investigation are systems of coupled fluidized beds which differ significantly in the flow regimes used in the individual reactors (e.g. both fuel and air reactor as circulating fluidized beds 6).

In the author's group a system of coupled fluidized beds for chemical looping combustion of solid fuels was recently erected and successfully commissioned (7). In the present work the results of the experiments with a synthetic oxygen carrier composed of Al₂O₃ and CuO are presented. Besides the combustion performance and the carbon slip, the circulation rate of the oxygen carrier and the loss of fuel and oxygen carrier particles with the flue gas were assessed.

EXPERIMENTAL

TUHH's Chemical-Looping Combustion facility

The unit consists in general of the riser of a circulating fluidized bed (CFB) acting as the air reactor (AR) and a bubbling fluidized bed used as the fuel reactor (FR). Different to other systems is the application of a two stage fuel reactor with the aim to increase the fuel conversion.

Table 1: Dimensions of the facility

	height [m]	diameter [m]
riser (air reactor)	8	0.1
fuel reactor	4	0.25
bed height per stage	0.6	
cyclone C1	0.34	0.21
standpipe SP1	1	0.07
standpipe SP2	2.5	0.07
standpipe SP3a	1.5	0.07
standpipe SP3b	1	0.11

A sketch of the experimental setup is shown in Figure 2. The dimensions of the unit are summarized in Table 1.

In the riser the oxygen carrier is oxidized and transported upwards by air. In the adjacent cyclone C1 the oxygen carrier is separated from the oxygen-depleted air and flows via the standpipe SP1 and the loop-seal S1 to the upper fuel reactor stage. The intention of the two-stage fuel reactor design is to enhance the conversion of combustible gases released in the lower fuel reactor stage by contacting them with freshly regenerated oxygen carrier in the upper stage. From the upper stage the oxygen carrier flows through the standpipe SP2 to the lower bed into which the solid fuel is fed. Finally, the reduced oxygen carrier is recycled to the air reactor via the standpipe SP3 and the siphon S2.

The whole unit is made of stainless steel (1.4841) without refractory lining. This allows a fast heating-up within 3 hours only and thus a day-wise operation without shift operation. The coupled fluidized bed system is installed inside an electrical furnace, which can heat the system up to 1000°C. The heating power of the heating segments can be independently adjusted on the fuel and air reactor side, respectively. During heating-up the fuel reactor, both siphons and the air reactor are fluidized with air.

Under CLC conditions the fuel reactor is fluidized with either steam, CO₂ or CO₂/steam mixtures. To avoid a dilution of the dry flue gas from the fuel reactor both siphons are fluidized with steam. The steam is supplied by three steam generators for the fuel reactor, the siphon S1 and the siphon S2, respectively.

The solid fuel is fed into the bottom zone of the lower fuel reactor bed 200 mm above the distributor plate. A screw feeder is used to control the mass flow. The mass flow of the solid fuel feed is determined by measuring the weight change of the feed hopper during operation time. From the outlet of the screw feeder the coal is pneumatically conveyed with CO₂ through a water-cooled tube into the fluidized bed. Cooling is necessary to avoid heating and consequently softening of the coal particles transported through the tube, which could lead to a blocking of the feeding line. The superficial gas velocity in the water-cooled injector tube is 7.6 m/s.

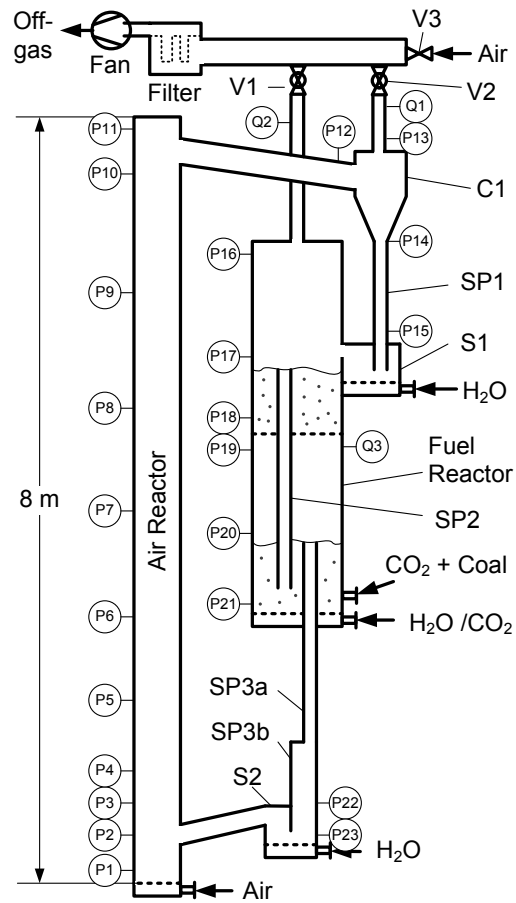


Figure 1: Sketch of the experimental setup

Fuel and oxygen carrier characteristics

Table 2: Fuel analysis (8)

Experiments were conducted using rhenish lignite dust with a surface mean diameter $x_{1,2}$ of 24.3 μm as fuel and a coarser copper-based oxygen carrier ($x_{1,2} = 284.6 \mu\text{m}$) which was prepared by the authors themselves. The oxygen carrier was made of commercial porous gamma alumina particles (Puralox NWA-155) supplied by Sasol Germany GmbH which was laden with 11.5 wt.% copper oxide. The impregnation with copper nitrite solution was done in a wurster coater (Glatt GF3, Glatt Ingenieurtechnik GmbH, Weimar, Germany) with a bottom spray nozzle. After impregnation the particles were dried at 80°C. The dried oxygen carrier was afterwards calcined at 800°C. The particle size and terminal velocity distributions of both materials are displayed in Figure 2. The intention to use a very fine fuel and a coarser oxygen carrier is that this enables the separation between the fuel and the oxygen carrier according to their different terminal velocities.

proximate analysis	wt.% (raw)
moisture	11
ash	4
volatiles	45
fixed carbon	40
ultimate analysis	wt.% (raw)
C	59.5
H	4.3
O	20.3
N	0.7
S	0.3

Furthermore, the fine coal dust has a shorter reaction time compared to larger coal particles which leads to a lower char holdup in the fuel reactor fluidized bed and consequently to a smaller carbon slip to the air reactor. The fuel composition is given in Table 2. It has a lower heating value of 22.2 MJ/kg (8).

Assessment of the attrition induced OC loss and entrainment of char

An important issue for the industrial realisation of the CLC technology is the attrition-induced loss of oxygen carrier. During operation fine oxygen carrier particles which are generated by attrition, ash and fine char particles are entrained with the flue gas from air and fuel reactor. These fines are collected in the filter. At the end of every experimental day the weight of the collected fines is measured and the water content w_{H_2O} and the ignition loss $w_{ignition,loss}$ of the collected fines are determined. The mass of carbon lost during the experiment is then calculated as follows

$$m_{\text{carbon,loss}} = m_{\text{fines}} \cdot (1 - w_{H_2O}) \cdot w_{\text{ignition,loss}} \quad (1)$$

The amount of oxygen carrier lost during the day $m_{\text{OC,loss}}$ is calculated from

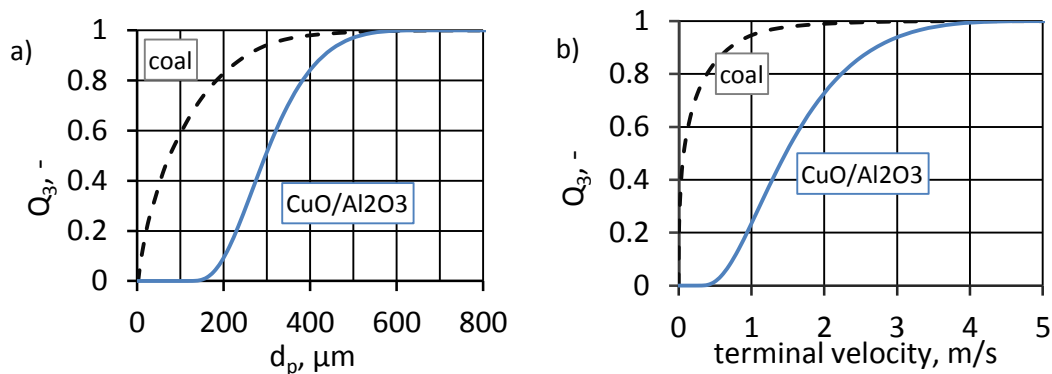


Figure 2: a) particle size and b) single particle terminal velocity distribution of coal and oxygen carrier

$$m_{OC,loss} = m_{fines} \cdot (1 - w_{H_2O}) \cdot (1 - w_{ignition,loss}) - m_{ash} \quad (2)$$

with m_{ash} the mass of ash in the fines which is assumed to be equal to the amount of ash introduced with the coal fed during the experiment.

Evaluation of combustion performance

Following Mendiara et al. (9) the carbon capture rate η_{CC} is defined as the molar flow of carbonaceous gases found at the FR exit minus the molar flow of carbonaceous fluidization gas entering the FR divided by the sum of molar flows of carbonaceous gases at the exits of FR and AR minus the molar flow of carbonaceous fluidization gas entering the FR,

$$\eta_{CC} = \frac{[\dot{n}_{CO_2} + \dot{n}_{CO} + \dot{n}_{CH_4}]_{FR,out} - [\dot{n}_{CO_2}]_{FR,in}}{[\dot{n}_{CO_2} + \dot{n}_{CO} + \dot{n}_{CH_4}]_{FR,out} - [\dot{n}_{CO_2}]_{FR,in} + [\dot{n}_{CO_2}]_{AR,out}} \quad (3)$$

Another important parameter is the dimensionless oxygen demand which is defined here as the molar flow of oxygen needed for complete conversion of both the combustible gases and the carbon loss leaving the FR divided by the molar flow of oxygen for complete conversion of the feed coal,

$$\Omega_{OD,mod} = \frac{[0.5 \cdot \dot{n}_{H_2} + 0.5 \cdot \dot{n}_{CO} + 2 \cdot \dot{n}_{CH_4}]_{FR,out} + \dot{n}_{carbon,loss}}{\dot{n}_{O_2,st}} \quad (4)$$

In a similar way the combustion efficiency $\eta_{FR,mod}$ of the FR is considering the slip of carbon from the FR into the AR,

$$\eta_{FR,mod} = 1 - \frac{[0.5 \cdot \dot{n}_{H_2} + 0.5 \cdot \dot{n}_{CO} + 2 \cdot \dot{n}_{CH_4}]_{FR,out} + \dot{n}_{carbon,loss}}{\dot{n}_{O_2,st} - \dot{n}_{carbon,slip}} \quad (5)$$

In the experiments the total flow rate of the dry off-gas is unknown and consequently the molar flow rates of the components at the FR outlet cannot be calculated directly from the measured concentrations. Therefore they are determined by solving an equation system containing the component balances for C, H, O in the FR together with the concentration measurements. Nitrogen and sulphur contents in the fuel are not considered in this calculation.

Measurement of the solids circulation rate

In the CLC process the solids circulation rate can be determined by an oxygen balance for the air reactor. For that the oxygen content of the solids and the gas composition at the air reactor entry and outlet have to be measured. To determine the solids oxygen content samples were taken from the siphons S1 and S2, which represent the air reactor outlet and inlet, respectively.

The oxygen mass m_{O_2} in the sample is measured by means of weight change during a complete reduction. In case of a gaseous fuel, the oxygen loading might alternatively be measured by a complete oxidation. For the operation with a solid fuel, there is always the risk of having char within the samples. In that case the oxygen consumption for full oxidation of the sample might be dominated by the oxygen needed for the combustion of the char.

Therefore, samples of 5 to 10 g are heated to 900°C in a lab-scale reactor which is flushed with nitrogen. Then the samples are reduced in an atmosphere of 4 vol.% H_2 and 96 vol.% N_2 for 3 h. During cooling down the gas flow consists again of nitrogen to avoid any oxidation.

The oxygen mass fraction w_{O_2} is defined as

$$w_{O_2} = \frac{m_{O_2}}{m_{OC,red}} = \frac{m_{O_2}}{m_{sample} - m_{O_2} - m_{char}} \quad (6)$$

where $m_{OC,red}$ is the mass of reduced oxygen carrier in the sample, m_{sample} is the mass of the analysed sample, m_{O_2} is the measured oxygen mass in the sample and m_{char} is the char mass in the sample. The char mass in the sample is not measured directly, but it is assessed by relating the carbon slip mass flow to the circulation rate of reduced oxygen carrier $\dot{m}_{OC,red}$. This gives

$$w_{O_2} = \frac{m_{O_2}}{m_{sample} - m_{O_2}} \cdot \left(1 + \frac{\dot{m}_{carbon,slip}}{\dot{m}_{OC,red}} \right) \quad (7)$$

The circulation rate of the reduced oxygen carrier $\dot{m}_{OC,red}$ is calculated as follows.

$$\dot{m}_{OC,red} = \frac{\dot{m}_{O_2,Air \rightarrow OC}}{(w_{O_2,S1} - w_{O_2,S2})} = \frac{(\dot{V}_{in}[O_2]_{in} - \dot{V}_{out}[O_2]_{out}) \cdot M_{O_2}}{(w_{O_2,S1} - w_{O_2,S2})} \quad (8)$$

where w_{O_2} is the oxygen mass fraction measured at siphon S1 and S2, respectively, $[O_2]$ is the molar oxygen concentration and \dot{V} is the volumetric flow rate of air at the air reactor inlet and outlet, respectively.

RESULTS & DISCUSSION

Attrition and char entrainment with flue gas

In Table 3 operational parameters and analysis results of the fines collected in the filter during four days of operation are summarized.

The oxygen carrier loss rate is displayed in Figure 3. The loss rate decreases from over 7 % of the inventory per 24 hours in the first experiment to around 1 % of the inventory per 24 hours in the last experiment.

This decrease in the loss rate

Table 3: Operational parameters and analysis results of fines collected in the filter. (T = 900°C)

day		1	2	3	4
u_{FR}	m/s	0.17	0.17	0.14	0.1
operating hours		9	12	11	10.5
coal feeding hours		4	6	6	6
m_{fines}	kg	2	2.07	1.9	2.1
w_{H_2O}	wt.% (raw)	9.5	9.5	4	5.18
$w_{ignition,loss}$	wt.% (wf)	18	27	37	36
m_{coal}	kg	6.0	10.3	17.1	25.4
m_{ash}	kg	0.24	0.41	0.68	1.02
$m_{OC,loss}$	kg	1.24	0.96	0.47	0.26
$r_{OC,loss}$	wt.%/24h	7.4	4.2	2.3	1.1
$r_{carbon,loss}$	wt. %	13.6	12.3	9.9	7.1

arises from an elutriation of fines present in the fresh material during the first experiments as well as from a change in the material's attrition propensity. With increasing operating time the particles become rounder and smoother due to the abrasion of surface roughness and consequently they become more resistant towards abrasion (10). Considering the decrease of the loss rate it can be deduced that the steady-state loss rate will be lower than the loss rate measured during the last day.

Based on the ignition loss and the total coal fed during the experimental day the carbon loss per kilogram fixed carbon (C-fix) fed is calculated. In the first two tests more than 12 % of the C-fix fed is lost with the flue gas. In the following experiments the fluidizing gas flow in the fuel reactor was reduced which led to a reduction of the carbon loss rate to 7.1 wt.%. An explanation for this is that due to the smaller gas velocity in the fuel reactor less carbon is entrained. The loss in thermal power which results from carbon loss with the flue gas is between 4 to 8 %.

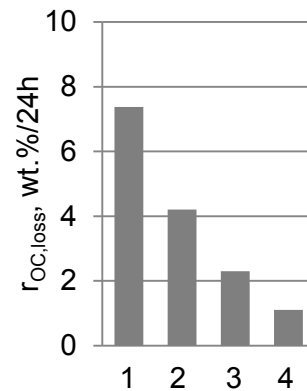


Figure 3: Loss rates measured during an experimental day

However, in the present experimental setup no cyclone is installed downstream of the fuel reactor and therefore the entrainment rates with the flue gas are comparatively high. Besides the installation of a cyclone a coal with a larger particle size could be used in order to reduce the char loss with the flue gas. However, the usage of larger coal particles will presumably lead to an increase of the carbon slip from the fuel to the air reactor.

Combustion performance

During operation the composition of the fuel and air reactor off-gas is measured by online analysers. For better comparison between different operating conditions the concentrations of the fuel reactor off-gas have been corrected by subtraction of the CO_2 which is used for fluidization and coal injection. High CO_2 concentrations above 99 vol.% can be achieved. The fraction of combustible gases is below 0.5 vol.%. In case of the experiment with the lowest CO_2 concentration of 91.3 vol.% a high oxygen concentration (around 3 vol.%) together with H_2 and CO was measured. However, the high oxygen concentration was only measured during the first experiments and it decreased to values below 0.1 vol.% O_2 . The oxygen fraction measured in the first test is due to the oxygen uncoupling ability of the copper oxide. An explanation for the low oxygen concentration in the following tests is the loss of the oxygen uncoupling ability which may be due to an interaction between the alumina support and the copper oxide to give CuAl_2O_4 . This was reported in literature (e.g. 11) for copper based oxygen carriers with alumina as support.

Throughout all experiments the CO_2 concentration in the air reactor off-gas was small (below 0.3 vol.%). This means that only a small carbon slip from the fuel to the air reactor occurred (average value 2.7 wt.% per kg fixed carbon fed).

In Figure 4 the performance parameters as defined above are presented for the experiments conducted with the copper-based OC and additionally with the results obtained previously in the same facility using Australian ilmenite (7). It can be seen that for both oxygen carriers the carbon capture rate is high ($> 96\%$). This is attributed to the very fine coal dust which is gasified extremely fast and is rather entrained from the lower fuel reactor bed with the flue gas instead of being carried over with the oxygen carrier to the air reactor. The oxygen demand is significantly lower for the copper-based OC compared to the ilmenite. In case of the copper-based material the oxygen demand is mainly attributed to the entrainment of carbon with the fuel reactor off-gas. Accordingly, the combustion efficiency in the fuel reactor is high for the copper-based material but again the efficiency loss is attributed to the loss of char.

Effect of the second stage on fuel conversion

In order to investigate the effect of the second fuel reactor stage on the fuel conversion gas samples were taken after the first and second fuel reactor stage for offline gas chromatographic analysis. In Figure 5 the dry gas composition measured with the GC are shown for two different coal feeding rates. In all samples a fraction of 2 to 7 vol.% nitrogen was measured which may originate

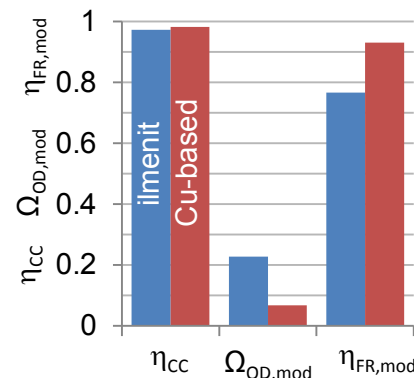


Figure 4: Performance parameters η_{CC} , $\Omega_{OD,mod}$, $\eta_{FR,mod}$. ($T = 900^\circ\text{C}$, $r_{\text{carbon,loss}} = 10 \text{ wt.}\%$)

from leakage-air introduced during sampling, the nitrogen introduced with coal and the nitrogen introduced with gas leakage from the air reactor to the fuel reactor. After the first stage the CO_2 concentration is low and high H_2 and CO concentrations were measured. An explanation for this can be the gasification of char in the freeboard of the first stage. After the second stage the CO_2 concentrations are significantly increased and reach values up to 95 vol.%. The H_2 , CH_4 and CO concentrations are reduced significantly to values below 1 vol.%. Thus the second stage has a significant effect on the conversion of combustible gases.

Circulation rates

During three test days several solids samples were withdrawn from the siphons S1 and S2. The maximum oxygen content of the oxygen carrier is 2.3 wt.%. The fraction of chemically bound oxygen in the samples from siphon S1 is in most cases close to the maximum oxygen content. After passage through the fuel reactor the oxygen content is decreased significantly to values below 1 % for a coal feeding rate of 3,7 kg/h and to values below 0.5 % for the coal feeding rate of 4.3 kg/h. Based on the oxygen balance for the air reactor the circulation rates are calculated and displayed in Figure 6. The error bars represent the standard deviation of the measurement. The circulation rates are in the range from 17 to 45 $\text{kg/m}^2\text{s}$. With increasing superficial gas velocity in the riser the circulation rate increases. Compared to fluidized bed combustors the circulation rates are higher.

CONCLUSIONS

A system of coupled fluidized beds for chemical looping combustion of coal using a copper-based oxygen was successfully operated. The two-stage design of the fuel reactor worked well, i.e. the second stage has a significant effect on the conversion of combustible gases. High CO_2 concentrations in the dry fuel reactor off-gas (up to 94 vol.%) were achieved. The concentrations of combustible gases were below 1 vol.%. Consequently the oxygen demand was low around 6 % and is mainly attributed to the entrainment of carbon with the fuel reactor flue gas. The carbon slip to the air reactor is low which yields a high carbon capture rate with values above 97 %. An explanation for this is the fine coal which is gasified extremely fast and/or is rather entrained from the lower fuel reactor bed with the flue gas instead of being carried over with the oxygen carrier to the air reactor. Compared to results from previous experiments with ilmenite the performance of the copper-based oxygen carrier is much better. The oxygen carrier loss rate was found to be below 1.1 wt.% per 24 hours under steady state attrition conditions.

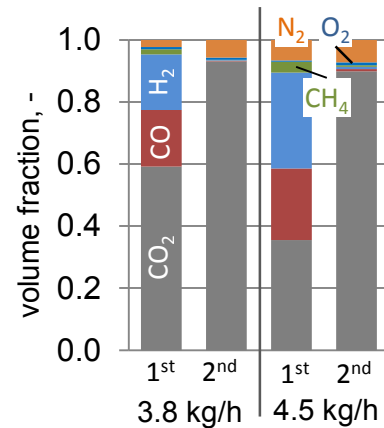


Figure 5: Dry gas composition above first and second stage of the fuel reactor. ($T = 900^\circ\text{C}$)

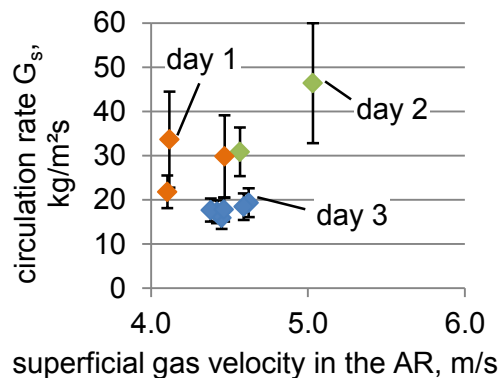


Figure 6: Circulation rates measured during operation. ($T = 900^\circ\text{C}$)

By means of an oxygen balance for the air reactor the circulation rate was measured with values between 17 to 45 kg/m²s. Further work will focus on reduction of the char loss with the flue gas. Possible strategies are for example to increase the coal particle size, to improve the char mixing into the lower fluidized bed or to install a cyclone downstream of the fuel reactor.

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NOTATION

G_s	cross-sectional mass flow in the riser	kg/m ² s	u	gas velocity	m/s
\dot{m}	mass flow	kg/s	\dot{V}	volumetric flow rate	m ³ /s
M	molar weight	mol/kg	w	oxygen mass fraction	-
\dot{n}	molar flow rate	mol/s	η_{CC}	carbon capture efficiency	-
p	pressure	bar	η_{FR}	FR combustion efficiency	-
r	loss rate	wt.%/h	Ω_{OD}	oxygen demand	-
T	temperature	°C			

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