Development and Validation of a 1D Process Model with Autothermal Operation of a 1 MW_{th} Chemical Looping Pilot Plant

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Abstract

Chemical Looping Combustion (CLC) has been extensively investigated up to pilot scale. Despite promising results, this CO₂ capture technology has to be further developed towards a potential industrial application. In order to accelerate the scale up of the process, it is essential to simulate CLC with process simulation software (Aspen Plus® V8.8). In this study, a process simulation model of the CLC pilot plant at Technische Universität Darmstadt is developed. The air reactor and the fuel reactor are integrated in the process model to calculate the conversion of the oxygen carrier and gases. The solids distribution and also the chemical conversion of gases and solids are implemented by user-defined functions programmed with FORTRAN. These codes are based on mathematical equations for fluidized beds and kinetic data of the chemical reactions taken into consideration. For this reason, dedicated thermal gravimetric analysis (TGA) experiments were carried out to determine both kinetics of redox reactions of oxygen carrier and gasification kinetics of the coal used in the 1 MW_{th} CLC unit. The one-dimensional solids distributions and gas/solid mixing are calculated from empirical correlations according to Kunii and Levenspiel. The models are validated by means of experimental data obtained from the the 1 MW_{th} CLC pilot plant with ilmenite as oxygen carrier and Russian hard coal (“Taldinsky”) as fuel. Among others, pressure profiles and gas concentrations at reactor exits are calculated for various operational points with autothermal operation. The results show good agreement with the experimental data. The process model was applied to optimize the operational conditions of the pilot plant.

Keywords

- Chemical Looping Combustion (CLC)
- CO₂ capture
- Kinetic measurements
- 1 MW_{th} pilot
- Process simulation
- Sensitivity analysis

Highlights:

- Coal CLC process simulation model is developed
- Main reaction kinetics for coal CLC are measured using TGA experiments
- Good agreement between the simulation results and experimental data from 1 MW_{th} CLC unit
- Sensitivity analyses show that the specific inventory should be as high as possible

1 Introduction

The reduction of carbon dioxide (CO₂) emissions in power generation is one of the most difficult and important challenges nowadays. There are different possibilities to reduce these emissions like reduction in electricity consumption, efficiency improvements, or CO₂ capture. Various technologies have been investigated to avoid the CO₂ emissions during combustion of fossil fuels. Among others, Chemical Looping Combustion (CLC) is an emerging CO₂ capture technology that is characterized by a low energy penalty, low carbon dioxide capture costs, and low environmental impact (Adanez et al., 2012; Kunze and Spliethoff, 2012; Wang et al., 2015). In CLC, the furnace of a conventional coal fired power plant is substituted by two circulating fluidized bed reactors (air reactor and fuel reactor). The oxygen needed for oxidation of the fuel is provided by an oxygen carrier. Typical oxygen carriers are metal oxides (e.g. ilmenite, iron ore or copper oxide) (Abad et al., 2007; Cho et al., 2004; Ströhle et al., 2015). The oxygen carrier circulates between the air reactor and the fuel reactor. In the air reactor the solid material (a reduced form of a metal oxide in this case) becomes oxidized with oxygen from the air.

After oxidation, the oxygen carrier enters the fuel reactor. In the fuel reactor, different processes take place simultaneously: After drying and pyrolysis of coal, char particles are gasified by steam and CO₂ that are used for fluidization.

Products from pyrolysis and gasification (mainly CO, H₂, CH₄) react with the solid oxygen carrier forming the main products steam and CO₂:

A concurrent reaction is the water-gas shift reaction:

The relevant gaseous products of the fuel reactor are CO₂ and H₂O, but some unconverted gases leave the fuel reactor due to bad contact of gases and oxygen carrier as well as due to gasification along the total height of the reactor. These gases (mainly CH₄, CO, H₂) are oxidized in the post oxidation chamber (POC) downstream the fuel reactor cyclone. After the condensation of steam, the remaining pure CO₂ can be compressed and stored (Epple and Ströhle, 2008). The reduced oxygen carrier particles (Me_xO_{y-1}) are transported to the air reactor and are oxidized again. Unconverted char particles that enter the air reactor are burned with air leading to non-captured CO₂ (Ohlemüller et al., 2017):

Experimental results have been collected during various tests in different CLC units, e.g. the 100 kW_{th} unit at Chalmers university of technology (Sweden) (Markström et al., 2013), the 50 kW_{th} unit at ICB-CSIC (Spain) (Abad et al., 2015), or the 10 kW_{th} CLC reactor at Southeast University (China) (Shen et al., 2009). Literature overviews are given by Adanez (Adanez et al., 2012; Adánez et al., 2018), Wang (Wang et al., 2015), and Lyngfelt (Lyngfelt, 2014). Beside experimental studies, mathematical models contribute to a better understanding of the processes, their capabilities and limitations and play an important role for process optimization. The process modelling of the chemical looping combustion is indispensable for the further

development, but detailed information such as oxygen carrier and gasification kinetics as well as hydrodynamic is required for the model build-up. Furthermore, appropriate experimental data is needed for model validation. Publications of coal gasification (Cuadrat et al., 2012), oxygen carriers (Abad et al., 2011), model development (Abad et al., 2013a; Abad et al., 2013b; Ohlemüller et al., 2015) and pilot operation (Ohlemüller et al., 2016; Ohlemüller et al., 2017) provide specific information about thematic focusses in this work.

In this work, a coal CLC process simulation model (Ohlemüller et al., 2015) was further developed and validated against experimental data from the CLC pilot plant at Technische Universität Darmstadt (Ohlemüller et al., 2016; Ohlemüller et al., 2017). Dedicated TGA experiments were carried out to determine both kinetics of redox reactions of the oxygen carrier and gasification kinetics of the coal used in the 1 MW_{th} CLC unit. Ten operational points were selected for model validation. The predictions of the model are in good agreement with experimental data. Sensitivity analyses were carried out using the validated process model. According to our best knowledge, there is no comparable comprehensive study available in literature for the validation of a theoretical model including both fuel and air reactors with coal at MW_{th} scale.

2 Experimental

2.1 Results from 1 MW_{th} CLC pilot

The 1 MW_{th} Chemical Looping plant at Technische Universität Darmstadt was originally designed and operated by Ströhle et al. (Ströhle et al., 2014). During previous tests, some operational problems occurred, mainly due to the high losses of pulverized coal (Ströhle et al., 2015). Further tests with ilmenite as oxygen carrier ($d_{p50} = 154 \mu\text{m}$) and a coarse hard coal (“Taldinsky”, $d_{p50} = 3100 \mu\text{m}$) with low ash content and a high amount of volatiles were performed and autothermal operation was achieved (Ohlemüller et al., 2016; Ohlemüller et al., 2017). A detailed description of the experimental setup (cf. Figure 1) and obtained data can be found in literature. The main dimensions of the reactors are shown in Table 1. The fuel reactor was designed conically close to the nozzle plate. The reactor diameter is 0.28 m at the height of the nozzle plate and 0.4 m from a height of 1.145 m. Data for model validation were collected during 10 h of operation.

Table 1: Dimensions of the reactors

Dimension	Unit	Fuel reactor	Air reactor
Height	m	11.35	8.66
Inner diameter	m	0.28 - 0.4	0.59
Outer diameter	m	1	1.3

Figure 1: Experimental setup of the pilot plant

The boundary conditions for ten selected operational points (OPs) are summarized in Table 2, including e.g. temperature, pressure drop and mass flow (Ohlemüller et al., 2016; Ohlemüller et al., 2017). The basic condition for the selection of OPs was steady-state operation for at least 10 minutes. However, some OPs lasted about one hour. The dry outlet concentrations of CO₂, CO, H₂ and CH₄ for the fuel reactor as well as CO₂ and O₂ for the air reactor are continuously measured and provide the most appropriate information for model validation (cf. Table 3).

Table 2: Boundary conditions of the operational points I-X

Value	Unit	I	II	III	IV	V	VI	VII	VIII	IX	X
<i>time</i>	min	10	30	10	10	70	20	50	50	50	10
<i>Ap_{AR}</i>	mbar	90	91	90	88	86	78	77	70	63	57
<i>Ap_{FR}</i>	mbar	61	60	62	64	65	66	71	86	101	115
<i>T_{AR}</i>	°C	1029	1033	1042	1044	1053	1040	1046	1056	1060	1073
<i>T_{FR}</i>	°C	917	926	936	939	948	930	936	947	945	941
<i>Propane_{AR}</i>	kg/h	9	6	-	-	-	-	-	-	-	-
<i>Coal_{FR}</i>	kg/h	101	99	112	114	115	111	117	120	116	126
<i>P_{Coal}</i>	MW	0.70	0.69	0.78	0.79	0.80	0.77	0.81	0.83	0.81	0.88
<i>AirI_{AR}</i>	kg/h	647	734	840	841	840	841	841	841	842	830
<i>AirII_{AR}</i>	kg/h	258	169	63	63	63	63	63	63	63	141
<i>N₂ to AR</i>	kg/h	44	44	43	43	43	44	43	43	43	43
<i>Steam to FR</i>	kg/h	214	214	215	215	215	195	195	195	195	194
<i>CO₂ to FR</i>	kg/h	63	63	70	69	-	-	-	-	-	-
<i>N₂ to FR</i>	kg/h	120	120	120	120	161	161	146	148	149	123

Table 3: Gas compositions at the outlet of air and fuel reactor

Species	Unit	I	II	III	IV	V	VI	VII	VIII	IX	X
CO₂, AR	Vol.-%	11.2	10.5	10.1	10.3	10.1	10.1	10.0	9.6	9.3	9.2
O₂, AR	Vol.-%	2.4	3.3	3.6	3.3	3.2	3.4	3.1	2.8	3.0	2.7
CO, FR	Vol.-%	4.3	4.3	4.8	4.8	4.0	3.0	3.2	3.1	3.1	4.3
CO₂, FR	Vol.-%	38.1	38.1	38.2	38.7	21.7	21.6	24.6	26.4	27.2	35.3
CH₄, FR	Vol.-%	2.5	2.5	2.8	2.8	2.5	2.3	2.5	2.3	2.2	2.9
H₂, FR	Vol.-%	4.8	4.7	5.1	5.0	5.3	5.2	5.7	5.8	6.0	8.4

2.2 Gasification kinetics of Taldinsky Coal

The conversion of coal in a solid fueled CLC system goes through devolatilization and char gasification in the fuel reactor. Very fast devolatilization is expected for small particles (< 8 mm) as those used in CLC (Agarwal et al., 1984; Pillai, 1981). However, the coal char gasification reaction rates have one important effect on the process performance. Thus, the kinetics of the gasification reactions of Taldinsky coal char with H₂O and CO₂ were determined by TGA experiments. The analysis of the char gasification both with steam and CO₂ was performed, considering a complete scheme of reactions involved in coal conversion in the fuel reactor. The ultimate and proximate analyses and the heating value of the fuel are gathered in Table 4. The coal particle size used for this study was 100-200 µm.

Table 4: Proximate and ultimate analyses and lower heating value of “Taldinsky” coal

Proximate analysis	Unit	Value
Humidity	wt.-%	5.8
Ash	wt.-%	10.1
Volatile matter	wt.-%	32.0
Fixed carbon	wt.-%	52.1

Ultimate analysis	Unit	Value
C	wt.-%	65.8
H	wt.-%	4.0
N	wt.-%	2.0
S	wt.-%	0.5
Lower Heating Value	kJ/kg	26640

Experiments were carried out in a TGA CI Electronics type. A detailed description of the TGA facility can be found elsewhere (de Diego et al., 2014). Kinetic determination was performed at conditions, in which the chemical reaction is the controlling step in the reaction rate. For the reactivity experiments, about 50 mg of coal particles were loaded in the platinum basket. Heating was done in a N₂ atmosphere from room temperature until the desired temperature at a constant rate of 20 K/min. Thus, the char was generated just before reaction, by devolatilization of coal in the TGA. The gasification rate of remaining char was determined at different temperatures and gas mixtures (H₂O/H₂/N₂ or CO₂/CO/N₂).

In gasification of char, whose main component is carbon, the most common gasification agents are steam and CO₂, through which H₂ and CO are generated by reactions (2) and (3). For kinetics determination, conversion vs. time curves obtained by TGA tests at different temperatures (1173, 1223 and 1273 K), gasification agent concentrations (i.e. 20-80 vol.-% O or CO₂) and gas product concentrations (i.e. 0-40 vol.-% H₂ or CO) were obtained. Totally, 96 gasification tests were carried out to determine the gasification kinetics. Thus, the gasification kinetic parameters were obtained taking into account the inhibitory effect of H₂ and CO on the gasification rate. The experimental work for char gasification was developed in conditions, where the homogeneous solid reaction model with control by chemical reaction was fulfilled. Thus, the gasification reaction rate, r_g , is constant with the char conversion, X_C , and it is defined by the following equation, both for steam and CO₂ gasification.

$$(-r_g) = -\frac{1}{m_c} \left[\frac{dm_c}{dt} \right] = \frac{1}{1 - X_c} \left[\frac{dX_c}{dt} \right] \quad (9)$$

Furthermore, the effect of the gasifying agent concentration, as well as the inhibitory effect of the product gas, was included considering a Langmuir-Hinshelwood reaction model. Thus, the net gasification rate with CO_2 and H_2O is calculated by:

$$(-r_{g,\text{CO}_2}) = \frac{k_{c,\text{CO}_2} \cdot p_{\text{CO}_2}}{1 + K_{\text{CO}_2} \cdot p_{\text{CO}_2} + K_{\text{CO}} \cdot p_{\text{CO}}} \quad (10)$$

$$(-r_{g,\text{H}_2\text{O}}) = \frac{k_{c,\text{H}_2\text{O}} \cdot p_{\text{H}_2\text{O}}}{1 + K_{\text{H}_2\text{O}} \cdot p_{\text{H}_2\text{O}} + K_{\text{H}_2} \cdot p_{\text{H}_2}} \quad (11)$$

By integration of equation (9) the following equation is obtained:

$$-\ln(1 - X_c) = k'_i \cdot t \quad (12)$$

The term k'_i comprises the right side term in equations (10) and (11) and can be determined by the slope when fitting the data $-\ln(1 - X_c)$ vs. time obtained from experiments in TGA. The kinetic constant $k_{c,i}$ and the adsorption constant for the gasification gas, i.e. $K_{\text{H}_2\text{O}}$ or K_{CO_2} , were calculated from tests with $p_{\text{H}_2} = 0$ or $p_{\text{CO}} = 0$, as shown in Figure 2. The parameter $k_{c,\text{H}_2\text{O}}$ can be obtained as the inverse of the slope in the linear fitting of plotting $1/k'_{\text{H}_2\text{O}}$ vs. $1/p_{\text{H}_2\text{O}}$, as showed in Figure 2 (a). After that, $K_{\text{H}_2\text{O}}$ can be calculated from the y-intercept of the line at $1/p_{\text{H}_2\text{O}} = 0$. Equally, $k_{c,\text{H}_2\text{O}}$ and K_{CO_2} can be calculated from linear fitting of $1/k'_{\text{CO}_2}$ vs. $1/p_{\text{CO}_2}$, as showed in Figure 2 (b). All these parameters were calculated at 1173, 1223 and 1273 K.

Figure 2: Plots of $1/k'_{H_2O}$ vs. $1/p_{H_2O}$ and $1/k'_{CO_2}$ vs. $1/p_{CO_2}$ for calculations of the kinetic parameters $k_{c,i}$ and K_i , i being H_2O or CO_2

The inhibitory effect of H_2 or CO during H_2O or CO_2 gasification is included in the kinetic model by the presence of the adsorption parameters K_{H_2} and K_{CO} . These parameters were calculated by using the values of k'_{H_2O} and k'_{CO_2} obtained for different partial pressures of H_2 and CO , respectively. The adsorption parameter K_{H_2} can be calculated as the slope in the linear fitting of Y_{H_2O} vs. p_{H_2} , see Figure 3 (a). Y_{H_2O} was calculated by:

$$Y_{H_2O} = \left[\frac{k_{c,H_2O}}{k'_{H_2O}} - K_{H_2O} \right] p_{H_2O} - 1 \quad (13)$$

Similar procedure was used to obtain K_{CO} by plotting Y_{CO_2} vs. p_{CO} , see Figure 3 (b).

Figure 3: Plots of Y_{H_2O} vs. p_{H_2O} and Y_{CO_2} vs. p_{CO_2} for calculations of the kinetic parameters $k_{c,i}$ and K_i , i being H_2O or CO_2

The kinetic parameters for steam and CO₂ gasification were calculated at 1173, 1223 and 1273 K. All them assuming to be Arrhenius type dependent with temperature, the kinetics parameters were calculated as shown in Table 5.

Table 5: Kinetic parameters for “Taldinsky” coal char gasification

	Gasification agent		
	H ₂ O	CO ₂	Unit
$k_{0,c}$	$1.1 \cdot 10^3$	$1.3 \cdot 10^3$	s ⁻¹ atm ⁻¹
E_c	120.4	141.8	kJ/mol
$K_{0,i} (i=H_2O \text{ or } CO_2)$	$4.1 \cdot 10^{-4}$	$3.9 \cdot 10^{-5}$	atm ⁻¹
$E_i (i=H_2O \text{ or } CO_2)$	-88.3	-112.7	kJ/mol
$K_{0,i} (i=H_2 \text{ or } CO)$	$1.0 \cdot 10^{-5}$	$2.9 \cdot 10^{-6}$	atm ⁻¹
$E_i (i=H_2 \text{ or } CO)$	-151.9	-154.7	kJ/mol

2.3 Ilmenite kinetics

The reactivity of ilmenite particles increases during the first redox cycles until a roughly constant reactivity was reached in the so-called “activated” state. The activation process undergone by ilmenite occurs after a low number of redox cycles (Adánez et al., 2010). Thus, kinetics of activated ilmenite can be considered to be included in a reactor model. Table 6 shows the chemical composition for activated ilmenite.

Table 6: Composition of calcined and activated ilmenite (wt.-%)

	Unit	Activated ilmenite
XRD (main species)		Fe ₂ TiO ₅ , Fe ₂ O ₃ , TiO ₂
Fe₂O₃	wt.-%	22.0
Fe₂TiO₅	wt.-%	38.5
TiO₂	wt.-%	34.0
Inerts	wt.-%	5.5

Kinetics of reduction of ilmenite with CH₄, CO and H₂, as well as oxidation with O₂, is presented in (Abad et al., 2011). The grain model with uniform reaction in the particle describes the evolution of ilmenite conversion with time as following:

$$\frac{t}{\tau_{chr}} = 1 - (1 - X_i)^{\frac{1}{3}}, \quad \tau_{chr} = \frac{\rho_m r_g}{b k_s C_g^n} \quad (14)$$

The dependence on the temperature of the kinetic constant is assumed to be Arrhenius type, as follows:

$$k_s = k_{0,s} \cdot e^{-\frac{E_{A,i}}{RT}} \quad (15)$$

The values of the kinetic parameters finally obtained for the reduction and oxidation of the activated ilmenite are given in Table 7. The oxygen transference rate is defined by both the reactivity and the oxygen transport capacity of the oxygen carrier:

$$r_{O_2} = \frac{d\omega}{dt} = R_{0,ilm} \left(\frac{dX_{ilm}}{dt} \right) \quad (16)$$

The reaction rate of activated ilmenite, dX_{ilm}/dt , can be calculated by using kinetic parameters in equation (14). The actual oxygen transport capacity of ilmenite particles in the CLC unit, $R_{0,ilm}$ in equation (16), is $R_{0,ilm} = 4.0$ wt.% (Cuadrat et al., 2011).

Table 7: Kinetic parameters for ilmenite reduction (H₂, CO and CH₄) and oxidation (O₂)

Kinetic parameters	Unit	H ₂	CO	CH ₄	O ₂
ρ_m	mol m ⁻³	13590	13590	13590	31100
r_g	m	1.25 10 ⁻⁶	1.25 10 ⁻⁶	1.25 10 ⁻⁶	1.20 10 ⁻⁶
$\bar{b}$	-	1.45	1.45	5.78	4
k_{s0}	mol ¹⁻ⁿ m ³ⁿ⁻² s ⁻¹	6.2·10 ⁻²	1.0·10 ⁻¹	9.8	1.9·10 ⁻³
E_{ks} (kJ/mol)	kJ mol ⁻¹	65.0	80.7	135.2	25.5
n	-	1	0.8	1	1

2.4 Evaluation parameter

There are two common evaluation parameters for CLC of solid fuels, the oxygen demand and the oxide oxygen fraction (Berguerand and Lyngfelt, 2008; Markström et al., 2014). The oxygen demand, Ω_{OD} , is the fraction of oxygen lacking for a complete conversion of gases formed by coal pyrolysis and gasification. The oxygen demand is calculated according to Equation (17). Φ_0 is the ratio of moles of oxygen needed to convert the fuel completely per moles of carbon in the fuel ($\Phi_0 = 1.176$ for Taldinsky coal (Ohlemüller et al., 2016)). The oxide oxygen fraction, η_{OO} , is calculated by the ratio of oxygen needed for oxidizing the oxygen carrier in the AR divided by the total amount of oxygen consumed.

$$\Omega_{OD} = \frac{(0.5 \cdot y_{CO} + 0.5 \cdot y_{H_2} + 2 \cdot y_{CH_4})_{FR,out}}{\Phi_0 \cdot (y_{CO_2} + y_{CO} + y_{CH_4})_{FR,out}} \quad (17)$$

$$\eta_{OO} = \frac{(0.21 - y_{O_2} - y_{CO_2})_{AR,out}}{(0.21 - y_{O_2} - 0.21 \cdot y_{CO_2})_{AR,out}} \quad (18)$$

Two further evaluation parameters are the oxygen demand of the fuel reactor, Ω_{ODFR} (Equation (19)), and the carbon capture efficiency, η_{CC} (Equation (20)) (Ohlemüller et al., 2017). Some additional values (e.g. the loss of fixed carbon at the fuel reactor cyclone, additional propane feed to the air reactor, CO₂ for fluidization of the fuel reactor (cf. Table 2)) can be considered using these equations. Based on mass balances, the efficiency of the fuel reactor cyclone can be assumed to be ~ 95 % for char particles (C_{fix}).

$$\Omega_{ODFR} = \frac{(0.5 \cdot \dot{n}_{CO} + 0.5 \cdot \dot{n}_{H_2} + 2 \cdot \dot{n}_{CH_4} + 0.05 \cdot \dot{n}_{C_{fix}})_{FR,out}}{\Phi_0 \cdot [(\dot{n}_{CO_2} + \dot{n}_{CO} + \dot{n}_{CH_4} + \dot{n}_{C_{fix}})_{FR,out} - (\dot{n}_{CO_2})_{FR,in}]} \quad (19)$$

$$\eta_{CC} = 1 - \frac{(\dot{n}_{C_{fix}})_{FR \text{ to } AR}}{(\dot{n}_{C_{total}})_{fuel \text{ feed}}} \quad (20)$$

3 Modelling

3.1 Description of the process flow sheet

The CLC process model is based on the 1 MW_{th} unit erected at Technische Universität Darmstadt. A simplified flow sheet was presented in Figure 1, and the corresponding Aspen Plus® simulation model is shown in Figure 4. All important components and streams are described below:

- The coal (COAL) that is fed into the system is decomposed (DECO) into its products from the pyrolysis (DECO-OUT, see section 3.2).
- All products from pyrolysis including moisture and char (DECO-OUT), the oxidized oxygen carrier (OCO-TOFR) from the air reactor, steam and CO₂ (STEAMCO2) for the gasification of the coal as well as nitrogen (FR-N2) for the fluidization of the L-valve and the purge of the burner and coal system are combined into one stream (FR-IN) before entering the fuel reactor (FR).

- Inside the fuel reactor, char is gasified and the products from pyrolysis and gasification are converted by the active oxygen carrier following Equations (2) - (7). The characteristics of a fluidized bed and the kinetics of the reactions are calculated by a FORTRAN code (see section 3.3). The main output of this code is the conversion of solids and gases corresponding to reactions mentioned above.
- Products from the fuel reactor (FR-OUT) are separated into gases (FR-FLUE) and solids (TOASHSEP) using a cyclone (FR-CYCL, separation efficiency 100 %). During the first calculation step an initial mass flow (INIT) specifies the total solids circulation. A percentage of 1 wt.-% of the circulating oxygen carrier is removed from the process in a second separation unit (ASHSEP, OCLOSS) and 1 wt.-% of the initial mass flow is fed to the air reactor (AR, MAKEUP) to maintain the specified circulating mass flow. The amount of 1 wt.-% loss and makeup was chosen arbitrary to achieve fast calculations. Ashes are removed (ASH).
- Propane (PROPANE) that was needed for some operational conditions (OP I and OP II) is burned with air (COMB-AIR) in a separate reactor (COMB) following Equation (21). This reactor equals the start-up burner shown in Figure 1. Products from combustion (COMB-OUT), makeup (MAKEUP), primary air (AIR) and nitrogen needed for fluidization of the loop seal below the fuel reactor cyclone (AR-N2, cf. Figure 1) enter the air reactor (AR, AR-IN) together with the reduced oxygen carrier (OCR-TOAR).

- The reduced oxygen carrier and unconverted char particles (OCR-TOAR) from the fuel reactor enter the air reactor. Inside the air reactor, the oxygen carrier is oxidized with air and the char is burned following Equations. (1) and (8). The conversion of the solid oxygen carrier is calculated by a FORTRAN code considering kinetics and hydrodynamics of the circulating fluidized bed (see section 3.4).
- Solids and gases downstream of the air reactor (AR-OUT) are separated by means of the air reactor cyclone (AR-CYCL, separation efficiency 100 %). The oxidized oxygen carrier (OCO-TOFR) are transferred to the fuel reactor.
- Heat streams from combustion of propane (Q-COMB) and decomposition of coal (Q-DECOMB) are added to the air and the fuel reactor.

Figure 4: Aspen Plus® flow sheet of the 1 MW_{th} CLC pilot

3.2 Decomposer

The conversion of coal in the fuel reactor can be divided in three steps: Rapid drying of coal, pyrolysis, and gasification of char particles. The composition after devolatilization is dependent on the coal. Merrick (Merrick, 1983a, b) developed a model to predict the product distribution of coal devolatilization out of the proximate and ultimate analysis of the coal, which was further validated by Matthesius (Matthesius et al., 1987). This model was applied in the present study. Tar and C₃H₆ are considered to be transformed to methane and reformed to carbon monoxide and hydrogen by steam and carbon dioxide. This assumption is supported by experiments where only small amounts of C₃H₆ and tar were found (Cuadrat et al., 2012). The products from devolatilization of Taldinsky coal are summarized in Table 8.

Table 8: Products after the pyrolysis of Taldinsky hard coal

Product	Mass fraction	Unit
Char	46.28	wt.-%
CH ₄	9.18	wt.-%
CO	23.16	wt.-%
CO ₂	1.33	wt.-%
H ₂	2.68	wt.-%
H ₂ O	5.78	wt.-%
N ₂	1.81	wt.-%
SO ₂	0.60	wt.-%

3.3 Fuel reactor

The model of the fuel reactor was described in detail in a former work (Ohlemüller et al., 2015). It included the hydrodynamics of a fluidized bed, the gasification of char as well as reactions of intermediate products (CH₄, CO, H₂) with the oxygen carrier. In this work, some minor changes as well as improvements were incorporated and are described as follows:

The fuel reactor was divided in ten reaction zones (2 dense zones at the bottom of the reactor and 8 lean zones above) and the conical shape of the 1 MW_{th} unit was taken into consideration. The bottom bed of the reactor consists of two dense zones with high solid fractions and formation of bubbles (Pallarès and Johnsson, 2006). The calculation of the volumetric fraction of bubbles in the dense zone, δ_b , was improved considering the gas velocities that are higher in the 1 MW_{th} unit compared to the 100 kW_{th} unit modelled in the former work. A calculation method from Abad et al. (Abad et al., 2013b) is implemented in the FORTRAN code for the fuel reactor following Equations (22) - (24), where the fraction of bubbles in the bed, δ_b , is depending on the saturation porosity of the bed (ε_{bsat}) and in case of minimum fluidization conditions (ε_{mf}).

$$\delta_b = \frac{\varepsilon_{bsat} - \varepsilon_{mf}}{1 - \varepsilon_{mf}} \quad (22)$$

$$\varepsilon_{bsat} = 0.5452 + \frac{495.5}{\Delta p_0} + \frac{4.9 \cdot 10^{-6}}{d_p} \quad (23)$$

$$\varepsilon_{mf} = 0.586 \cdot 0.7^{-0.72} Ar^{-0.029} \left(\frac{\rho_g}{\rho_s} \right)^{0.021} \quad (24)$$

Additionally, the conversion of gases by the water-gas shift reaction (WGS, cf. Equation (7)) is involved in the fuel reactor model. The conversion is calculated according to Equation (25) (Graven and Long, 1954).

$$\frac{d_{WGS,i}}{dV_j} = (1 - \varepsilon_j) \cdot k_{0,fWGS} \cdot e^{-E_{fWGS}/RgT} \cdot C_{CO}^{0.5} \cdot C_{H_2O} \quad (25)$$

Here, ε_j is the porosity of the bed in the region j with a volume V_j . The constant is $k_{0,fWGS} = 7.97 \cdot 10^9 \text{ (m}^3/\text{mol)}^{0.5} \cdot \text{s}^{-1}$, and the activation energy is $E_{fWGS} = 274.5 \text{ kJ/mol}$ (Abad et al., 2013a). Large coal particles were used in the pilot as described above. Two assumptions have to be made:

- Instantaneous devolatilization can be assumed by comparing devolatilization time ($\sim 10 \text{ s}$) vs. residence time of char in the FR ($> 100 \text{ s}$).
- Gasification is controlled by kinetics of chemical reaction.

3.4 Air reactor

The oxidation of unburned char and reduced oxygen carrier with air take place in the air reactor (cf. Equations (1) and (8)). The air reactor was assumed as a stoichiometric reactor without any hydrodynamic or kinetic model in a former work (Ohlemüller et al., 2015) because of the high air-to-fuel ratio of ~ 2 of the air reactor of the CLC unit erected at Chalmers (Markström et al., 2013). However, the air-fuel ratio was low during the relevant tests (Ohlemüller et al., 2016; Ohlemüller et al., 2017). Thus, the oxidation reaction of ilmenite was modeled, while the conversion of char was set to 100 %. This can be justified because the amounts of carbon monoxide (CO) and char at the AR outlet were low. Hydrodynamics and kinetics were integrated in the air reactor with a FORTRAN code. The AR model is described in the following sections:

The height of the lean zone is calculated by a numerical approximation described in a former work (Ohlemüller et al., 2015). The solids inventory ε_{sd} in the dense zone is constant and $\overline{\varepsilon_{sl}}$ is the average value of the volume of solids in the lean zone of the circulating fluidized bed, calculated by Equation (26). The solid fraction at reactor exit ε_{se} can be calculated by Equation (27) (Kunii and Levenspiel, 1991). The saturation carrying capacity of solids in the gas flow is

ε_s^* , a is the decay constant for solid fraction in the lean region and H_l is the height of the lean zone, cf. (Ohlemüller et al., 2015)

$$\overline{\varepsilon_{sl}} = \varepsilon_s^* + \frac{(\varepsilon_{sd} - \varepsilon_{se})}{aH_l} \quad (26)$$

$$\varepsilon_{se} = \varepsilon_s^* + (\varepsilon_{sd} - \varepsilon_s^*)^{-aH_l} \quad (27)$$

The inventory of solids in the air reactor, m_{inv} , is equal to the sum of the solids in the dense and the lean region, $m_{inv,d}$ and $m_{inv,l}$, respectively. These quantities depend on the area of the reactor (A_R), the density of solids (ρ_s), the solids fraction (ε_s) and the height (H) of the corresponding zone, and are calculated by the following equations (Lasheras et al., 2011).

$$m_{inv,d} = A_R \cdot \rho_s \cdot H_d \cdot \varepsilon_{sd} \quad (28)$$

$$m_{inv,l} = A_R \cdot \rho_s \cdot H_l \cdot \overline{\varepsilon_{sl}} \quad (29)$$

The conversion rate of ilmenite oxidation was described above (cf. section 2.3) and is calculated by Equation (30), where $R_{OC,0}$ and R_{OC} were 4.0 wt.-% (Abad et al., 2011; Cuadrat et al., 2011).

$$\frac{dX_{OC}}{dt} = \left[\frac{3}{\tau_i} (1 - X_{OC})^{2/3} \right] \left[\frac{R_{OC,0}}{R_{OC}} \right], \quad \tau_i = \frac{q_m \cdot r_g}{b_i \cdot k_i \cdot C_i^n} \quad (30)$$

The oxidation reaction of ilmenite with oxygen is a first order gas-solid reaction. The reaction rate of oxygen consumption can be expressed by (Kunii and Levenspiel, 1991):

$$-\frac{dn_{O_2}}{dt} \frac{1}{V_{OC}} = K_r \cdot C_{O_2} \quad (31)$$

The consumption of oxygen and oxidation of ilmenite occur concurrently:

$$-\frac{dn_{O_2}}{dt} = \frac{1}{b_{O_2}} \cdot \frac{dn_{OC}}{dt} = \frac{n_{OC,total}}{b_{O_2}} \frac{dX_{OC}}{dt} \quad (32)$$

Equations (30) - (32) are rearranged as follows to calculate the overall oxidation rate of oxygen carrier (K_r):

$$K_r \cdot C_{O_2} \cdot V_{OC} = -\frac{dn_{O_2}}{dt} = \frac{n_{OC,total}}{b_{O_2}} \left[\frac{3 \cdot b_{O_2} \cdot k_{O_2} \cdot C_{O_2}^n}{q_m \cdot r_g} (1 - X_{OC})^{2/3} \right] \left[\frac{R_{OC,0}}{R_{OC}} \right] \quad (33)$$

$$n = 1, \quad \frac{n_{OC,total}}{V_{OC}} = \varrho_m, \quad R_{oc,0} = R_{oc} \quad (34)$$

$$K_r = \left[\frac{3 \cdot k_{O_2}}{r_g} (1 - X_{OC})^{2/3} \right] \quad (35)$$

The gas/solid contact is derived from Kunii and Levenspiel (Kunii and Levenspiel, 1991), previously used for a Calcium Looping (CaL) process model developed by Lasheras et al. (Lasheras et al., 2011). Considering the bottom bed zone an overall rate constant K_{ff} can be calculated as follows:

$$K_{ff} = \gamma_{core} \cdot K_r + \left[\frac{1}{1/K_{be} + 1/(\gamma_{wall} \cdot K_r)} \right] \quad (36)$$

where K_r is the reaction rate (cf. Equation (35)) and K_{be} is the gas-interchange coefficient between the bubble and emulsion phases in the bottom bed zone and can be calculated from Equations (37) and (38) (Abanades et al., 2004; Kunii and Levenspiel, 1991):

$$K_{be} = 4.5 \cdot \frac{u_{mf}}{d_b} \quad (37)$$

with (Abad et al., 2013b):

$$d_b = 0.54 \cdot (u_0 - u_{mf})^{0.4} \left(\frac{H_d}{2} + 4\sqrt{A_0} \right)^{0.8} g^{-0.2} \quad (38)$$

The solid fractions at the core and at the reactor wall, γ_{core} and γ_{wall} , are set to 0.01 and 0.15 and are derived from experimental data (Kunii and Levenspiel, 1991; Lasheras et al., 2011). A fractional expression of the oxygen concentration at the reactor inlet, C_0 , and at the top of the bottom bed, C_d , can be derived as:

$$\ln \left(\frac{C_0}{C_d} \right) = \frac{K_{ff} \cdot \delta_d \cdot H_d}{u_0} \quad (39)$$

The fractional value of oxygen concentration at the bottom bed zone and the reactor outlet, C_l , can be calculated from the following expression (Lasheras et al., 2011):

$$\ln\left(\frac{C_d}{C_l}\right) = \frac{(1 - \varepsilon_f)_{bed} \cdot K_r}{U_0 \cdot a} \cdot \left[(1 - e^{-a \cdot H_l}) - \frac{1 - \eta_{bed}}{1 + \left(\frac{a'}{a}\right)} \cdot (1 - e^{-(a' + a) \cdot H_l}) \right] \quad (40)$$

where a' is a model parameter set to 6.62 m^{-1} (Lasheras et al., 2011), a is the decay constant, H_l is the height of the lean zone of the fluidized bed, and u_0 is the superficial gas velocity. The parameter ε_f is the void fraction at the top of the bottom bed, and η_{bed} is the contact efficiency at the top of the bottom bed, are calculated as:

$$1 - \varepsilon_f = (1 - \delta_l) \cdot (1 - \varepsilon_{mf}) \quad (41)$$

$$\eta_{bed} = \left[\gamma_{core} + \frac{1}{K_r/K_{be} + 1/\gamma_{wall}} \right] \cdot \frac{\delta_d}{1 - \varepsilon_f} \quad (42)$$

The core area in the dense zone δ_d and in the lean zone δ_l can be calculated from Equations (43) and (44), respectively (Kunii and Levenspiel, 2000). The fraction of solids in the wall zone is estimated with $\varepsilon_w = 0.3$ (Kunii and Levenspiel, 1991, 2000).

$$\delta_d = \frac{\varepsilon_w - \varepsilon_{sd}}{\varepsilon_w - \varepsilon_s^*} \quad (43)$$

$$\delta_l = \frac{\varepsilon_w - \overline{\varepsilon_{sl}}}{\varepsilon_w - \varepsilon_s^*} \quad (44)$$

From equations (39) and (40) the conversion of oxygen by the oxygen carrier in the dense and lean zone can be calculated according to Equation (45).

$$X_{O_2} = \left[1 - \frac{C_l}{C_0} \right] \quad (45)$$

If the conversion of oxygen X_{O_2} is known the conversion of oxygen carrier can be calculated. However, the oxygen needed for char oxidation, $\dot{n}_{O_2,Char}$, should be considered in this calculation because char oxidation occurs concurrently. Thus, the total conversion of oxygen carrier was derived following Equation (46). In this formula, the average available oxygen needs to be taken into account. Hence, half of the oxygen needed for char oxidation is subtracted from the total oxygen introduced. This calculation follows the assumption that both reactions (char and oxygen carrier oxidation) take place simultaneously along the height of the air reactor.

$$\Delta X_{OC} = \frac{b_{O_2} \cdot \left(\dot{n}_{O_2,in} - \frac{\dot{n}_{O_2,char}}{2} \right) \cdot X_{O_2}}{\dot{n}_{OC,in}} \quad (46)$$

Results and discussion

In this section the results of the CLC process simulation model are compared with experimental data described above. Evaluation parameters are the gas concentrations downstream the FR and AR cyclones as well as oxygen demand (Ω_{OD}), oxygen demand of the fuel reactor (Ω_{ODFR}), oxide oxygen fraction (η_{OO}), and carbon capture efficiency (η_{CC}).

4.1 Validation of hydrodynamic model

To fit the solid distribution in the fuel reactor, the calculated pressure distribution was compared with experimental data. The decay constant (a) and the solid fraction in the dense zone (ε_{sd}) were determined. Appropriate values were found for both the air reactor and the fuel reactor (cf. Table 9). The corresponding graphs for one exemplary operational point (OP V) are shown in Figure 5. Similar results were achieved for other operational conditions. The solid fraction in the dense zone of the fuel reactor is smaller than it is described in the literature $0.16 < \varepsilon_{sd} < .22$ (Kunii and Levenspiel, 1991). Comparatively high superficial gas velocities due to the conical part of the fuel reactor (cf. section 2.1) can explain the small solid fraction.

Table 9: Values for decay constant and solid fraction in the dense zone for both reactors

Found values	Fuel reactor	Air reactor
Decay constant a (m ⁻¹)	5.5	4
Solid fraction in the dense zone ε_{sd} (-)	0.07	0.16

Figure 5: Pressure profile from air reactor (a) and fuel reactor (b) for OP V. Diamonds: Experimental results; dashed lines: Model predictions

4.2 Gas concentrations and evaluation parameter

The residence time of char particles in the fuel reactor is not exactly known. However, it has been found by iterative calculations using the process model that the average residence time of char particles was ~ 5 times the residence time of OC particles. This can be explained by the low entrainment of coal/char particles due to their large particle size leading to an accumulation of char particles in the FR bed. The circulation of the oxygen carrier was iteratively calculated by the saturated mass flux of solids G_s^* (cf. (Ohlemüller et al., 2015)) and a heat balance of the whole setup. A mass flow of 7500 – 8500 kg/h was estimated for all operation conditions.

The dry concentrations of the gases CO_2 and O_2 downstream the AR as well as CO_2 , CO , H_2 and CH_4 downstream the FR are graphically shown in Figure 6 (a-c). The corresponding evaluation parameters are depicted in the same Figure (d-f). Experimental results are also shown in order to evaluate the accuracy of the modelling results. In general, the calculated dry gas concentrations follow the experimental data. The chronological developments of the results depending on the operational points with different conditions are described as follows:

- The first operational point (OP I) was characterized by the co-combustion of propane in the air reactor and the lowest temperature of fuel and air reactor (917 and 1029 °C). The fuel feed was 101 kg/h (cf. Table 2) and the fuel reactor was fluidized with steam, CO_2 , and N_2 (purge). Oxygen from air was consumed by various processes in the AR, namely the oxidation of the oxygen carrier (ilmenite) and the combustion of propane (AR start

up burner) and char particles leaving the FR. The dry concentration of CO₂ was greater than 11 Vol.-% (dry basis) which was the highest value of the present study.

- An amount of $\sim 70 \text{ kg h}^{-1}$ of combustion air of the air reactor start-up burner ($AirII_{AR}$) was replaced by preheated air ($AirI_{AR}$, $\sim 400 \text{ }^{\circ}\text{C}$) that enters the AR via the nozzle grid. Furthermore, propane feed to the AR was reduced. This resulted in higher temperatures of FR and AR as well as in a lower CO₂ concentration at the AR outlet. The dry concentration of O₂ at the air reactor outlet increased concurrently. There are some deviations between simulation and experimental findings (OP I and II): Dry concentrations of H₂ and CO₂ at the FR outlet are underpredicted and CH₄ is overpredicted. There are different possible reasons for this behavior, e.g. some slight deviations of the product distribution of pyrolysis or processes that cannot be depicted in a 1D model.
- The following changes were done between OP II and OP III: Propane feed to the air reactor was stopped; combustion air of the air reactor start-up burner ($AirII_{AR}$) was again reduced; the fuel feed as well as the CO₂ feed to the FR were slightly increased. This resulted in similar measured dry gas concentrations (AR and FR), but a better match of the modelled and measured evaluation parameters (i.e. the oxygen demand of the FR, Ω_{ODFR}) was obtained compared to OP I and II. This is mainly due to the more accurate agreement of the measured and modelled CO₂ concentrations of the FR off gas.
- Only slight increase of the reaction temperature can be observed between OP III and OP IV, leading to minor changes of the results.
- The greatest impact on the results was the stop of CO₂ feed to the FR (OP IV $\rightarrow$ OP V). The dry CO₂ concentration (FR) dropped from 38.7 % to 21.7 %. Furthermore the oxygen demand (Ω_{OD}) increases due to this measure. However, it was explained in section 2.4 that the common evaluation parameters are not appropriate for the present process configuration. The oxygen demand of the fuel reactor (Ω_{ODFR}) is rather constant between OP IV and V and seems to be a good indicator of the conversion of unburned components.
- Only minor changes were done between OP V and OP VI: Less steam was used to fluidize the FR, temperatures are slightly lower. The decrease of the hydrogen concentration could be due to lower steam content. It is overestimated by the process model.

- Before OP VII, N₂ feed to the FR (purge) was reduced. This resulted in higher dry concentrations of CO₂, H₂, CO and CH₄ downstream the FR. The main reason is the smaller dilution of the off gas.
- A transition of solids from AR to FR was an effect of the reduced fluidization velocity of the fuel reactor. The pressure drop of the fuel reactor was increased from 71 mbar (OP VII) to 101 mbar (OP IX). Furthermore, temperatures of the reactors were higher than before. Due to this facts, gas conversion in the fuel reactor was enhanced that can be observed by increasing dry CO₂ concentrations downstream the FR and decreasing oxygen demand. Furthermore, the carbon capture efficiency was enhanced resulting in less CO₂ in the AR off gas. As can be seen from e.g. the dry concentration of CH₄ (downstream FR) and the oxygen demand of the FR, Ω_{ODFR} , the described effect was overpredicted by the model.
- OP X: Due to a further decrease of the N₂ purge, the above described effects (increase of FR pressure and reactor temperatures) were repeated. There strong discrepancy of the measured dry H₂ concentration and the result of the simulation can be explained by the fact that OP X was very short.

Some general points are summarized as follows. The model results show lower dry O₂ concentrations of AR flue gas compared to the measurements for OP VII – X. This can be explained by overpredicted gas-solid reactions. However, it should be noted that the difference of the oxygen conversion is still small.

CO₂ at the fuel reactor outlet is the target product of the CLC process. Between OP IV and V the fluidization of the fuel reactor was changed from steam/CO₂ to only steam. This resulted in a significant reduction of CO₂ downstream the reactor. The unconverted gases that leave the CLC process are CO, CH₄ and H₂. The corresponding dry gas concentrations are depicted in Figure 6 (b)-(c). The simulated concentrations of CO are in good agreement with experimental values, the slight overprediction for OP V – X could be explained by an underpredicted water-gas-shift. CH₄ is a product from pyrolysis and reacts with ilmenite forming CO₂ and H₂O. The process model overpredicts it for OP I-VII. Possible reasons could be overestimation of CH₄ production during pyrolysis or an underprediction of the gas-solid reaction of CH₄ and ilmenite. Hydrogen is slightly under-predicted by the model for operational points VI-IX. The significant underprediction for OP X can be explained by the fact that this OP was short.

Figure 6 (d)-(f) show the oxide oxygen fraction, η_{OO} , the oxygen demand, Ω_{OD} , carbon capture efficiency, η_{CC} , and the oxygen demand of the fuel reactor, Ω_{ODFR} . Models predictions are in

good agreement with experimental data. The oxygen demand and the oxygen demand of the fuel reactor are overestimated for OP I-II and OP VI (oxygen demand). This can be explained by the underestimation of CO_2 (OP I-II) and slight overestimations of unconverted gases (OP VI). This is due to an underestimation of the conversion of unconverted gases by the model. Factors like high temperatures, high FR inventory and low amount of N_2 purge have a positive influence on the conversion of solids and gases.

Figure 6: (a) Dry concentrations of CO_2 and O_2 downstream the AR; (b) dry concentrations of CO_2 and CO downstream the FR; (c) dry concentrations of CH_4 and H_2 downstream the FR; (d) oxygen demand Ω_{OD} and oxide oxygen fraction η_{OO} ; (e) carbon capture efficiency η_{CC} ; (f) oxygen demand of the fuel reactor Ω_{ODFR} . Experimental data: Black squares; modelling results: Red dots

4.3 Sensitivity analyses

Sensitivity analyses regarding the influence of different boundary conditions have been carried out. The oxygen demand of the fuel reactor and the carbon capture efficiency were selected for the purpose of comparison. OP V was chosen as basic point because most of the evaluation parameters are well estimated for these conditions. The influence of the thermal power (corresponding to the fuel feed), the solids inventory of the fuel reactor (corresponding to the pressure drop of the fuel reactor), the temperature of the fuel reactor, and the circulation of oxygen carrier were defined as potential optimization parameters. The predictions of the process model are described below:

- An increase of the thermal power from 0.3 to 0.9 MW_{th} leads to higher oxygen demand. This is due to the decreasing inventory-to-fuel ratio. The decreasing carbon capture efficiency is mainly influenced by the gasification reaction that is slowed down by intermediates (H₂, CO), cf. Eqs. (10) and (11). (Reference: OP V: 0.8 MW_{th})
- An increase of the solids inventory of the FR (pressure drop, 50 to 150 mbar) leads to significantly higher carbon capture efficiency. The main reason is the longer residence time of char that enables higher conversion. The lower oxygen demand is due to the higher inventory-to-fuel ratio that enhances the conversion of gases (CH₄, CO, H₂). (Reference: OP V: 65 mbar)
- Higher carbon capture efficiency can also be observed with higher temperature (910 to 990 °C) of the fuel reactor. It is again associated with lower oxygen demand. This can be explained by faster gas-solid reactions that lead to better conversion of char (carbon capture) and intermediate products (oxygen demand). (Reference: OP V: 948 °C)
- The circulating mass of oxygen carrier has a low influence on the evaluation parameter. (Reference: OP V: 8350 kg h⁻¹). However, the circulation is an important value regarding the heat balance of the system, because the oxygen carrier is also a thermal carrier that provides the heat for the endothermic reactions inside the fuel reactor. This means that this parameter should be taken into account within a scale-up study.

These trends also agree with experimental findings (Ohlemüller et al., 2017). Some process optimizations like a secondary fluidization of the fuel reactor above the dense phase, a second fuel reactor downstream the first fuel reactor, a carbon stripper, or the use of an oxygen carrier with CLOU properties were proposed in literature (Abad et al., 2012; Gayán et al., 2013; Ohlemüller et al., 2016) and can be confirmed by the modelling results. The carbon capture efficiency should be at least 90 % to provide a comparative technology. However, this capture

rate has already been achieved in other CLC units (Abad et al., 2012; Adánez et al., 2018; Markström et al., 2013).

Figure 7: Influence of the thermal power (fuel feed) (a), the solids inventory of the fuel reactor (b), the temperature of the fuel reactor (c) and the circulation of oxygen carrier (d) on the carbon capture efficiency (blue triangles) and the oxygen demand of the fuel reactor (orange inverted triangles)

5 Conclusions

A process simulation model (Ohlemüller et al., 2015) that has previously been validated by results of a 100 kW_{th} plant was further developed and validated against experimental data from the CLC unit at Technische Universität Darmstadt. For this reason, kinetics of the gasification reactions with H₂O and CO₂ for “Taldinsky” coal was obtained by TGA analysis. The homogeneous reaction model with control by chemical reaction and taking into account the inhibitory effect of H₂ and CO was used to obtain the kinetics parameters. Dedicated TGA

experiments are described to determine kinetics of redox reactions of ilmenite. The determined kinetic parameters were introduced in mathematical models to predict the performance of a CLC unit under different operating conditions, and therefore to optimize the operational conditions. Ten operational points from the 1 MW_{th} unit at Technische Universität Darmstadt were selected for model validation. The predictions of the model are in good agreement with experimental data. Simulations of ten operational points were performed using different mass flows of coal, different compositions of the medium of fluidization and various other changes. The validated model was used to study the influences of thermal power, pressure drop of the fuel reactor, temperature of the fuel reactor, and circulation of oxygen carrier on the oxygen demand of the fuel reactor and the carbon capture efficiency. This developed CLC process model can be considered as basis for further investigations and as a promising tool for scale-up studies. Finally, it should be mentioned that in addition to the 1D process simulation models, the 3D computational fluid dynamics (CFD) models should be developed concurrently to support the progress of the CLC technology (Alobaid et al., 2015; May et al., 2016; Sharma et al., 2017). The advantage of 3D models is the generation of spatial data about e.g. mass flows or concentrations of solids and gases.

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Nomenclature

a	Decay constant for solid fraction in the lean region (m^{-1})
a'	Decay constant of clusters in the freeboard (m^{-1})
A	Area (m^2)
A_0	Area of the gas-distributor per nozzle (m^2 per nozzle)
Ar	Archimedes number (-)
AR	Air reactor
b_i	Stoichiometric coefficient for reaction of solid with gas i (-)
C_i	Concentration of gas i ($\text{mol} \cdot \text{m}^{-3}$)
d_b	Bubble diameter (m)
d_p	Average diameter of particles (m)

E_{ch}	Activation energy of the chemical reaction rate constant (J mol^{-1})
FR	Fuel reactor
H	Height (m)
k_s	Chemical reaction kinetic constant ($\text{mol}^{1-n} \text{m}^{3n-2} \text{s}^{-1}$)
$k_{s,0}$	Pre-exponential factor for chemical kinetic constant ($\text{mol}^{1-n} \text{m}^{3n-2} \text{s}^{-1}$)
K_{be}	Overall gas interchange coefficient between bubbles and emulsion phase (s^{-1})
K_{eq}	Equilibrium constant (-)
K_{ff}	Overall reaction rate for fast fluidization (s^{-1})
K_r	Overall oxidation rate of oxygen carrier in the emulsion phase (s^{-1})
m	Mass of the sample at each time in TGA (kg)
m_{inv}	Mass inventory (kg)
m_{ox}	Mass of the oxygen carrier sample fully oxidized (kg)
m_{red}	Mass of the oxygen carrier sample fully reduced (kg)
n	Reaction order (-)
P	Thermal power (MW)
r_g	Characteristic radius of the grain (m)
R_g	Gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
R_0	Oxygen transport capacity (-)
$(-r_i)$	Reaction rate of reduction (s^{-1})
t	Time (s)
T	Temperature (K or $^{\circ}\text{C}$)
u_0	Superficial gas velocity (m s^{-1})
u_{mf}	Minimum fluidization velocity (m s^{-1})
V_{OC}	Volume of the oxygen carrier (m^3)
X_{OC}	Oxygen carrier conversion (-)
X_{ox}	Oxygen carrier oxidation conversion (-)
X_{red}	Oxygen carrier reduction conversion (-)

Greek symbols

γ_{core}	Fraction of solids in the core of the reactor (-)
γ_{wall}	Fraction of solids in the wall region of the reactor (-)
δ_b	Volumetric fraction of bubbles in the bottom bed (-)
δ_d	Volumetric fraction of the core region of the dense zone (-)
δ_l	Volumetric fraction of the core region of the lean zone (-)

Δp	Pressure drop (mbar)
ε_{bsat}	Bed porosity at saturation conditions (-)
ε_f	Void fraction in a fluidized bed (-)
ε_{mf}	Porosity at minimum fluidization conditions (-)
ε_{sd}	Volume fraction of solids in the dense zone (-)
ε_{sl}	Volume fraction of solids in the lean zone (-)
ε_s^*	Saturation carrying capacity of solids in the gas flow (-)
ε_w	Volume fraction of solids in the wall region (-)
η_{bed}	Contact efficiency (-)
η_{CC}	Carbon capture efficiency (%)
η_{OO}	Oxide oxygen fraction (%)
ρ_m	Molar density of reacting compound (mol m ⁻³)
ρ_s	Density of solids (kg m ⁻³)
τ_{ch}	Time for complete reaction under chemical reaction control (s)
Φ_0	Ratio of moles of oxygen needed to convert the fuel completely per moles of carbon in the fuel (-)
Ω_{OD}	Oxygen demand (%)
Ω_{ODFR}	Oxygen demand of the fuel reactor (%)

Subscripts

0	Initial conditions
C _{fix}	Fixed carbon, char particles
d	Dense phase
l	Lean phase
OC	Oxygen carrier

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