**MODELLING CHEMICAL-LOOPING ASSISTED BY OXYGEN
UNCOUPLING (CLaOU): ASSESSMENT OF NATURAL GAS
COMBUSTION WITH CALCIUM MANGANITE AS OXYGEN CARRIER**

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Abstract

Chemical-Looping Combustion (CLC) is a promising technology for performing CO₂ capture in combustion processes at low cost and with lower energy consumption. Fuel conversion modelling assists in optimizing and predicting the performance of the CLC process under different operating conditions. For this work, the combustion of natural gas was modelled using a CaMnO₃-type perovskite as oxygen-carrier and taking into consideration the processes of fluid dynamics and reaction kinetics involved in fuel conversion. The CLC model was validated against experimental results obtained from the 120 kW_{th} CLC unit at the Vienna University of Technology (TUV). Good agreement between experimental and model predictions of fuel conversion was found when the temperature, pressure drop, solids circulation rate and fuel flow were varied. Model predictions showed that oxygen transfer by means of the gas-solid reaction of the fuel with the oxygen-carrier was relevant throughout the entire fuel-reactor. However, complete combustion could be only achieved under operating conditions where the process of Chemical-Looping *assisted* by Oxygen Uncoupling (CLaOU) became dominant, i.e. a relevant fraction of the fuel was burnt with molecular oxygen (O₂) released by the oxygen-carrier. This phenomenon was improved by the design configuration of the 120 kW_{th} CLC unit at TUV, in which oxidized particles are recirculated to the upper part of the fuel-reactor. Thus, the validated model identified the conditions at which complete combustion can be achieved, demonstrating that it is a powerful tool for the simulation and optimization of the CLC process with the CaMnO₃-type material.

Keywords: CO₂ capture; Chemical-Looping Combustion; methane; modelling; perovskite.

Nomenclature

d_p	particle diameter (m)
e	relative error (%)
f_s	solids fraction (-)
F_{exc}	excess flow generated in the emulsion with respect to minimum fluidization (mol/s)
$F_{j,i}$	molar flow of gas i in the j phase (mol/s)
m_{FR}	specific mass of oxygen-carrier in the fuel-reactor (kg/MW)
$\dot{m}_{OC}$	solids circulation flow rate (kg/s)
Q_i	volumetric flow of gas i (m ³ /h S.T.P.)
$R_{OC,ou}$	oxygen transport capacity for the oxygen uncoupling reaction (kg oxygen per kg solids)
$R_{OC,t}$	total oxygen transport capacity (kg oxygen per kg solids)
T_{FR}	fuel-reactor temperature (K)
u_g	gas velocity (m/s)
X_{CH_4}	methane conversion (-)
$X_{OC,k}$	oxygen-carrier conversion for reaction k (-)
z	position in the axial direction (m)

Greek symbols

ΔP_{FR}	pressure drop in the fuel-reactor (Pa)
ϕ	oxygen-carrier-to-fuel ratio (-)
η_{comb}	combustion efficiency (-)
ρ_{OC}	solids density (kg/m ³)

Subscripts

j	phase (<i>db</i> : dense bed; <i>cl</i> : cluster; <i>tr</i> : transport; <i>dil</i> : dilute; <i>b</i> : bubbles; <i>e</i> : emulsion)
in	inlet
ILS	internal loop seal

out outlet

USL upper loop seal

Acronyms

CLaOU Chemical-Looping *assisted* by Oxygen Uncoupling

CLC Chemical-Looping Combustion

DCFB Dual Circulating Fluidised Bed

fWGS forward Water Gas Shift

TUV Vienna University of Technology

1. Introduction

Chemical-Looping Combustion (CLC) is a novel combustion technology that involves the use of an oxygen-carrier to transfer oxygen from air to the fuel, avoiding the direct contact between the two [1]. The main advantage of CLC is that it allows combustion with inherent CO_2 separation at low cost and with low energy consumption [2]. CLC uses a separate air-reactor and fuel-reactor; see Fig. 1. Interconnected fluidized beds appear to be the preferred configuration for fuel and air-reactors [1,3]. A solid oxygen-carrier, normally a metal oxide (M_xO_y), transports the oxygen between the reactors. Inside the fuel-reactor, the oxygen-carrier is reduced as the fuel is oxidized. Inside the air-reactor, the oxygen-carrier is returned to its original state through oxidization with air. Consequently, direct contact is prevented between the fuel and air, and combustion products are not diluted in N_2 ; however, the net chemical reaction and combustion enthalpy are the same as those found in conventional combustor with air.

Fig. 1. Reactor scheme of the CLC process.

Among the oxygen-carriers used, CaMnO_3 -type oxygen-carriers have been found to be promising materials owing to their oxygen uncoupling capability, or ability to spontaneously release gas-phase O_2 in the fuel-reactor, and the long life-time of their particles [4-7]. The oxygen uncoupling process is particularly beneficial for solid fuels [8], but it can also be favourable for gaseous fuels since the presence of gas phase oxygen could facilitate the full combustion of fuel in a gas-gas reaction without need for the perfect mixing of gases and solids.

The next challenge is to scale up CLC technology to 10 MW_{th} [9]. Considering the experience gained in CLC plants, some questions are still pending to be solved due to the results does not identify the operating conditions mainly affecting to the CH₄ conversion, and therefore the optimization of both the design of the CLC unit and operating conditions cannot be determined. In this context, the availability of theoretical model validated against experimental results is a powerful tool to realize the safe scale-up of CLC. However, few models have been validated against experimental results in continuously operated CLC units [1], and no models have been developed with perovskite-type materials including oxygen uncoupling capability.

In this work, a detailed fluid dynamics and kinetics model was developed for a fuel-reactor in order to obtain a simulation tool for the combustion of methane with a CaMnO₃-type oxygen-carrier. The CLC model was validated against experimental results obtained from the 120 kW_{th} Dual Circulating Fluidised Bed (DCFB) at Vienna University of Technology (TUV) burning natural gas and using CaMg_{0.1}Mn_{0.9}O_{3-δ} as oxygen-carrier. Some insights into the relevance of the oxygen uncoupling process to the complete combustion of natural gas are analysed and discussed.

2. CLC model

The theoretical model for the fuel-reactor considered the main processes affecting the reaction of methane with the oxygen-carrier, such as reactor fluid dynamics, the reactivity of the oxygen-carrier and the reaction mechanism. The model considered the dimensions and operating conditions for the DCFB at TUV [4]; see Fig. 2.

Fig. 2. Schematic diagram of the DCFB at TUV [4].

2.1. Fluid dynamics model

The fuel-reactor was considered to be a fluidized bed working at a high-velocity regime, and it was divided into two vertical zones with respect to axial concentration and back-mixing of solids [10,11]:

1. A bottom or dense bed with a high and roughly constant concentration of solids. Solids in the emulsion were in perfect mixing. In the dense bed, the gas is distributed between the emulsion phase and the visible bubbles and the throughflow phases, with gas exchange by diffusion among them. Gas in the emulsion is always considered at minimum fluidization conditions, and any excess of gas either in the gas fed or generated during the CH_4 conversion (F_{exc}), must move from the emulsion to the visible bubbles and the throughflow.
2. A freeboard or dilute region above the dense bed, where there was a pronounced decay in solids concentration with height. The dilute region is composed of a cluster phase and a transport (dispersed) phase. The cluster phase was in perfect mixing with solids in the dense bed, but the transport phase was characterized by a core/annulus structure with a net flow up of solids in plug flow through the core.

The equations on which the fluid dynamic model is based are compiled in Fig. 3. Most of them are empiric equations compiled by others [12], but no specific fitting of parameters has been done for the CLC model of the 120 kW_{th} unit.

2.2. Mass balances inside the fuel-reactor

Mass balances were developed for each phase in the dense bed and the dilute region. The pathway for methane conversion with the oxygen-carrier in the fuel-reactor is described by the reaction system in Table 1. Following reaction (R1), H_2O was considered a primary product of the methane combustion and CO was considered an intermediate product [13]. The presence of small amounts of CO together unconverted CH_4 justifies the mechanism [4]. Then, CO could be converted to CO_2 by the forward water-gas shift (fWGS) reaction or by reaction with the oxygen-carrier; see reactions (R2) and (R3). Subsequently, the H_2 produced in the fWGS reaction would be able to

react with the oxygen-carrier; see reaction (R4). Also, gaseous oxygen was evolved from the solid oxygen-carrier –reaction (R5)– which would be able to react with gaseous fuels (CH_4 , CO or H_2) in a homogeneous reaction; see reactions (R6)-(R8).

FLUID DYNAMICS			
Dense bed			
Porosity	at minimum fluidization	$\epsilon_{mf} = 0.586 \text{Ar}^{-0.029} \left(\frac{\rho_s}{\rho_g} \right)^{0.021}$	
	in the bed	$\epsilon_{bs} = (1 - \delta_s) \epsilon_{mf} + \delta_s$	
Solids	concentration	$C_{bs} = \rho_s (1 - \epsilon_{bs})$	
Gas	distribution	$u_0 = (1 - \delta_s) u_{mf} + u_{in} + u_f$	
	minimum fluidization	$u_{mf} = \frac{\mu_g}{\rho_g d_p} \left[\sqrt{27.2^2 + 0.0408 \text{Ar}} - 27.2 \right]$	
	visible bubbles	$u_{in} = \psi (u_0 - u_{mf} (1 - \delta_s))$	
	throughflow	$u_f = (1 - \psi) (u_0 - u_{mf} (1 - \delta_s))$	
fraction of visible bubbles		$\psi = \frac{0.26 + 0.70 e^{-3300 d_p}}{(0.15 + u_g - u_{mf})^{1/3}} (z + 4 \sqrt{A_0})^{0.4}$	
Bubbles	diameter	$d_b = 0.54 (u_0 - u_{mf})^{0.4} (z + 4 \sqrt{A_0})^{0.3} g^{-0.2}$	
	volumetric fraction	$\delta_s = \frac{u_{in}}{u_{in} + 0.71 \sqrt{g d_b}}$	
	mass transfer coefficient	Bottom: $k_{bw} = 4.5 \left(\frac{u_{mf}}{d_p} \right) + 5.85 \left(\frac{D^{1/2} g^{1/4}}{d_p^{3/4}} \right)$ Freeboard: $k_{bw} = 1.631 u_{mf} \text{Sc}^{0.77}$	
Diluted region			
Gas	Terminal velocity	$u_t = \left(\frac{18}{\text{Ar}^{0.75}} + \frac{0.59}{\text{Ar}^{0.75}} \right)^{-1} \left(\frac{\rho_s}{\mu_g (\rho_s - \rho_g) g} \right)^{-0.13}$	
Solids distribution	splash	$\frac{dC_{sp}}{dz} = - \left[\frac{4}{u_g} \right] C_{sp}$	
	transport	$\frac{dC_{tr}}{dz} = - \left[\frac{0.23}{u_g - u_{mf}} \right] C_{tr}$ $C_{tr,bs} = \left[\frac{131.1}{\epsilon_{bs}} \rho_g \left(\frac{\text{Re}_0}{\text{Ar}} \right)^{0.31} \right] u_{in}$ $C_{bs,bs} = C_{sp,bs} + C_{tr,bs}$	
Core diameter	$z < \{H_r - 6D_r\}$	$D_c = 0.87 D_r$	
	$z > \{H_r - 6D_r\}$	$D_c = D_r - 0.0217 (H_r - z)$	
Solids flow		$F_v = C_{bs} A_c (u_g - u_{mf})$	
Gas-solid contact	efficiency	$\xi_{f-v} = 1 - 0.75 \left(\frac{C_{sp} + C_{tr}}{C_{bs,bs}} \right)^{0.4}$	

MASS BALANCES	
Dense bed	
$\frac{dF_{s,i}}{dV} = \frac{d}{dz} \left[(1 - \delta_s) u_{sf} C_{s,i} \right] = -(1 - \delta_s) \sum_k (-\bar{r}_{s,i})_{s,k} - \delta_s k_{so} (C_{s,i} - C_{so,i}) - y_{s,i} \frac{dF_{sm}}{dV}$	
$\frac{dF_{s,i}}{dV} = \frac{d}{dz} \left[(u_{so} + u_{sf}) C_{s,i} \right] = -\delta_s \sum_k (-\bar{r}_{s,i})_{s,k} + \delta_s k_{so} (C_{s,i} - C_{so,i}) + y_{s,i} \frac{dF_{sm}}{dV}$	
Diluted region	
$\frac{dF_{s,i}}{dV} = \frac{d}{dz} \left[u C_{s,i} \right] = -\epsilon_{mf} \left[\sum_k (-\bar{r}_{s,i})_{s,k} + \sum_k (-\bar{r}_{s,i})_{p,k} \right]$	
REACTION RATE	
Reaction kinetics:	
$t = \tau_{ch} X'_{OC,k} + \tau_{pl} \left(1 - 3 \left(1 - X'_{OC,k} \right)^{2/3} + 2 \left(1 - X'_{OC,k} \right) \right)$ with $X'_{OC} = (X_{OC} - \bar{X}_{OC,in})$	
$\tau_{ch} = \frac{1}{k_s \left(\left(C_i^m - C_{i,eq}^m \right) \right)}$	and $\tau_{pl} = \frac{1}{D_{pl} \left(C_i^m - C_{i,eq}^m \right)}$
The reaction rate of the oxygen carrier, defined as dX_{OC}/dt , was obtained by	
$-\bar{r}_{OC,i,j,k} = \frac{dX_{OC}}{dt}$	
Reaction considering external mass transfer in the particle:	
$(-\bar{r}_{s,i})_p = \frac{\rho_{OC} R_{OC}}{2 d_p M_O} \left(\frac{4}{3} \pi r_p^3 \right) \left[\frac{d(X_{OC}(t) - \bar{X}_{OC,in})}{dt} \right] = k_{s,i} (4 \pi r_p^2) (C_{s,i} - C_{p,i})$	
Dense bed:	$\text{Sh} = \frac{k_{s,i} d_p}{D_{s,i}} = 2 \epsilon_{mf} + 0.117 \text{Ar}^{0.39} \text{Sc}^{1/3}$
Diluted region:	$\text{Sh} = \frac{k_{s,i} d_p}{D_{s,i}} = 2 \epsilon_z + 0.69 \text{Re}_p^{1/2} \text{Sc}^{1/3}$
Solids conversion distribution as a function of RTD curve $E(t) = \frac{1}{t_{mr}} e^{-t/t_{mr}}$:	
$(1 - \bar{X}_{OC,out}) = \int_0^{t_{in}} (1 - X_{OC}(t)) E(t) dt$ with $X_{OC}(t) = \bar{X}_{OC,in} + \frac{t}{\tau_m}$	
Reaction rate at position z in the reactor:	
$(-\bar{r}_{OC,i})_{j,k} = \frac{C_i}{b_i} \frac{\rho_{OC} R_{OC,k}}{M_O} (1 - \epsilon_i) \int_0^{t_{r,i}} \frac{d(X_{OC,k} - \bar{X}_{OC,k}^{in})}{dt} E(t) dt$	
being $t_{r,i}$ defined as the reacting time to achieve a conversion value of $X'_{OC} = (1 - \bar{X}_{OC}^{in})$	

Fig. 3. Compilation of equations used in the fluid dynamic and mass balances sections of the model [11,14].

Table 1. Reaction scheme of methane with the $\text{CaMg}_{0.1}\text{Mn}_{0.9}\text{O}_{3.8}$ material.

$3 \text{M}_x\text{O}_y (\text{s}) + \text{CH}_4 (\text{g}) \rightarrow 3 \text{M}_x\text{O}_{y-1} (\text{s}) + \text{CO} (\text{g}) + 2 \text{H}_2\text{O} (\text{g})$	(R1)
$\text{CO} (\text{g}) + \text{H}_2\text{O} (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + \text{H}_2 (\text{g})$	(R2)
$\text{M}_x\text{O}_y (\text{s}) + \text{CO} (\text{g}) \rightarrow \text{M}_x\text{O}_{y-1} (\text{s}) + \text{CO}_2 (\text{g})$	(R3)
$\text{M}_x\text{O}_y (\text{s}) + \text{H}_2 (\text{g}) \rightarrow \text{M}_x\text{O}_{y-1} (\text{s}) + \text{H}_2\text{O} (\text{g})$	(R4)
$2 \text{M}_x\text{O}_y (\text{s}) \rightarrow 2 \text{M}_x\text{O}_{y-1} (\text{s}) + \text{O}_2 (\text{g})$	(R5)
$\text{CH}_4 (\text{g}) + 1.5 \text{O}_2 (\text{g}) \rightarrow \text{CO} (\text{g}) + 2 \text{H}_2\text{O} (\text{g})$	(R6)
$\text{CO} (\text{g}) + 0.5 \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g})$	(R7)
$\text{H}_2 (\text{g}) + 0.5 \text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{g})$	(R8)

The variation of the flow of every compound, i.e. CH₄, CO, H₂, CO₂, H₂O and O₂, in each phase described in the fluid dynamics model is given by the differential equations compiled in Fig. 3. They include the main processes by which a compound can appear or disappear in a phase: chemical reaction, diffusion, and bulk gas transfer, F_{exc} , due to volumetric expansion during methane conversion. The reaction rate was obtained considering the residence time distribution of the solids. In addition, the oxygen transport capacity and conversion of oxygen-carrier were defined considering the possible mass loss of a reaction k . Two oxygen transport capacity parameters were differentiated: (1) the total oxygen transport capacity of the solids with a gas fuel, $R_{OC,t}$, about 10 wt%; and (2) the oxygen transport capacity in oxygen uncoupling, $R_{OC,ou}$, about 1 wt%. More details regarding the kinetics and thermodynamics of the CaMg_{0.1}Mn_{0.9}O_{3-δ} material are found elsewhere [14]. Kinetics parameters for fresh CaMg_{0.1}Mn_{0.9}O_{3-δ} particles were considered as no variation in reactivity was observed in a CLC unit [15].

Kinetics of the fWGS reaction -reaction (R2)- and homogeneous combustion of fuel gases (CH₄, H₂ and CO) -reactions (R6-R8)- were taken from [16] and [17]. It was assumed that H₂ combustion would only occur in the emulsion phase in the bottom bed [18].

3. Model results

The theoretical model was developed in Fortran Code ® and solved following the method described by Abad et al. [10]. The main outputs of the model were the axial profiles of gas and solids. From these outputs, the performance of the DFBC system was assessed by calculating methane conversion and combustion efficiency.

$$X_{CH_4} = \frac{F_{in,CH_4} - F_{out,CH_4}}{F_{in,CH_4}} \quad (1)$$

$$\eta_{comb} = 1 - \frac{(4F_{CH_4} + F_{CO} + F_{H_2})_{out}}{(4F_{CH_4})_{in}} \quad (2)$$

The relevance of possible amounts of CO or H₂ was also evaluated with these parameters. Consequently, the amounts of CO and H₂ at the fuel-reactor outlet were lower the closer η_{comb} was to X_{CH_4} .

The theoretical model focused on the processes occurring in the fuel-reactor of the DCFB at TUV when methane was burnt with CaMn_{0.9}Mg_{0.1}O_{3- δ} particles as oxygen-carrier (ρ_{OC} =3330 kg/m³, d_p =130 μ m). Table 2 shows the 29 experimental conditions in the fuel-reactor, in addition to the methane conversion obtained, which was used for model validation. Steady state conditions are used to evaluate the experiments [4]. The reactor temperature, pressure drop, solids circulation rate and fuel power were varied in these experiments. The solids circulation rate was calculated by measuring the difference in the oxygen-carrier conversion entering and leaving the air-reactor, following the procedure described elsewhere [19].

Table 2. Operating conditions in experiments during methane combustion with $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ oxygen-carrier in the DCFB at TUV [4].

Test	T_{FR} (°C)	ΔP_{FR} (kPa)	Q_{CH_4} (Nm ³ /h)	$Q_{H_2O,ILS}$ (Nm ³ /h)	$Q_{H_2O,ULS}$ (Nm ³ /h)	$R_{OC,t}$ (%)	$R_{OC,ou}$ (%)	$\dot{m}_{OC}$ (kg/h)	$X_{OC,in}$ (%)	ϕ	m_{FR} (kg/MW)	X_{CH_4} (%)
1	949	7.5	11.2	2.5	3.7	9.8	1.2	4138	3.6	12.8	138	82.7
2	948	7.4	11	2.5	3.7	9.8	1.2	4063	3.7	12.8	139	82.2
3	951	7.5	11.7	2.5	3.7	9.8	1.2	4675	2.9	13.8	133	84.2
4	951	6.6	8	2.5	3.7	9.8	1.3	3588	3.4	15.7	172	88
5	946	8	7.6	2.5	3.7	9.9	1.3	4506	3.2	20.8	220	92.1
6	950	7.8	7.9	2.5	3.7	9.9	1.3	5474	3.1	24.2	204	92.7
7	949	6.6	7.5	2.5	3.7	9.8	1.2	2746	3.6	12.7	180	85.4
8	898	6.9	7.9	2.5	3.7	10.1	1.5	3726	3.4	16.9	182	74.8
9	950	7.6	7.8	2.5	3.7	9.8	1.3	3844	3.7	17.2	203	89.2
10	950	8.8	7.9	2.5	3.7	9.8	1.3	4731	3.5	20.9	230	91.1
11	947	9.6	7.7	2.5	3.7	9.8	1.3	4550	3	20.5	257	92.1
12	950	9.7	6	2.5	5	9.9	1.3	4983	3.1	29.2	337	99.1
13	948	9.6	6	2.5	3.7	9.9	1.3	5471	3.4	31.8	333	97.9
14	948	9.8	5.4	2.5	5	9.9	1.3	5910	3.2	38	369	99.7
15	947	10.5	7.9	2.5	3.7	9.8	1.3	5671	3.2	25	275	91.4
16	946	19.3	6.8	2.5	3.7	9.9	1.3	6317	3.2	32.6	589	95
17	948	10.3	6	2.5	3.7	9.9	1.3	5825	2.9	34	355	97.9
18	947	31.4	6	2.5	5	9.9	1.3	6058	3.1	35.6	1104	98.6
19	924	7.9	5.9	2.5	3.7	10	1.4	3960	3.3	23.8	279	87.8
20	923	7.1	5.9	2.5	3.7	10	1.4	3032	3.6	18.2	251	81.1
21	963	7.1	5.9	2.5	3.7	9.8	1.2	2982	3.8	17.6	248	90.1
22	962	7.6	5.8	2.5	3.7	9.8	1.3	4471	3.5	26.7	272	94.6
23	922	9.1	5.7	2.5	3.7	10	1.4	3211	3.3	20	332	85.3
24	922	10	5.9	2.5	3.7	10	1.4	4872	3.1	29.1	352	90.2
25	948	11.9	6.1	2.5	3.7	9.9	1.3	5522	3.4	31.8	404	92.7
26	950	8.1	8.4	2.5	3.7	9.9	1.3	5570	3.6	23.3	203	83
27	948	10.2	6.1	2.5	3.7	9.9	1.3	4926	2.8	28.4	349	93.4
28	950	10.3	5.5	2.5	4.9	9.9	1.3	5143	3.2	33.1	392	97.1
29	949	10.1	5.6	2.5	3.7	9.9	1.3	5527	3.1	34.3	374	95.9

The solids circulation flow rate affected the variation of solids conversion in the reactor [20]. The conversion of solids for the global mass balance to the system was calculated with $R_{OC,t}$. However, $R_{OC,ou}$ was used to obtain the conversion of solids for the oxygen uncoupling reaction. The values of both $R_{OC,t}$ and $R_{OC,ou}$ depended on temperature, and were calculated following the procedure presented by de Diego et al. [14].

At that point, the oxygen-carrier-to-fuel ratio, ϕ , and the solids inventory per thermal power in the fuel-reactor, m_{FR} , were introduced to better analyse the interrelation between fuel flow, pressure drop –i.e. the amount of solids in the reactors– and solids circulation flow rate [20]; see Table 2. ϕ was defined as the availability of oxygen in the flow of oxygen-carrier divided by the oxygen required to fully convert the fuel to CO_2 and H_2O .

3.1. Fluid dynamics and fuel conversion inside the fuel-reactor

By way of example, the axial profile of solids concentration and gas velocity predicted in the fuel-reactor for the test 10 are depicted in Fig. 4(a). The dense bed, characterized by a roughly constant porosity, was stretched out to a height of 0.4 m. Above the dense bed, the solids concentration decreased with the reactor height. This finding agrees with results previously found in the DCFB [21]. Solids concentration subsequently increased at the entrance from the upper loop seal ($z = 2$ m).

Gas velocity increased through the reactor because of gas expansion during methane conversion. Abrupt changes in gas velocity were found at the position where steam entered from the internal and upper loop seals. Gas flow increased throughout the entire reactor; but a decrease in gas velocity was observed in the upper part of the reactor resulting from the core section increase above the saturation height.

Fig. 4. Axial profiles in the fuel-reactor for test 10 of (a) solids fraction and gas velocity, and (b) gas concentration.

Fig. 4(b) shows the axial profiles of the concentration of gases. The methane inlet point corresponds to $z = 0$, while the inlet of solids from the upper loop seal, which is fluidized by steam, is at $z = 2$ m. In the dense bed, methane was slowly converted because the chemical reaction was restricted by the slower diffusion of methane from the bubbles to the emulsion phase, where reaction with the oxygen-carrier takes place. Methane conversion at the top of the dense bed was $X_{CH_4} = 14\%$. Faster conversion had been predicted in the dilute region because the contact between gas and solids was improved in this region. Furthermore, a relevant improvement in methane conversion can be observed above $z = 2$ m, caused by solids coming from the upper loop seal, which reached $X_{CH_4} = 91\%$ at the reactor exit.

3.2. Validation of the CLC model

Fig. 5 compares the experimental and predicted values of methane conversion and combustion efficiency for the operating conditions shown in Table 2. In general, good agreement was found between the experimental and model predictions, with a deviation lower than $\pm 5\%$ in most cases.

Moreover, combustion efficiency values were close to those of methane combustion, indicating that the model also predicted very low H_2 and CO concentration values, similar to those found during the tests [4]. Nevertheless, non-negligible deviations were found in some specific cases. These deviations are probably due to lack of reproducibility and associated uncertainty inherently associated to experimental data, as it will be discussed below.

Fig. 5. Comparison between experimental and predicted values of methane conversion ($\square$) and combustion efficiency ($\diamond$).

In test 16, methane conversion was 95%, whereas complete combustion had been predicted by the model. This test can be included together with tests 17 and 18 in an experimental series where solids inventory increased but the rest of operating conditions were maintained roughly constant; see Fig. 6(a). Methane conversion slightly increased with the solids inventory when tests 17 and 18 are considered. But, methane conversion in test 16 fell to 95%, which is not a logical trend, probably due to the inherent uncertainty of experimental data. Of course, this illogical trend cannot be captured by the model.

This case is similar to that of test 24, where the analysis can be performed with the effect of fuel-reactor temperature; see Fig. 6(b). The tendency of methane conversion with temperature is perfectly demonstrated in series 24-12 and 20-4-21, where an increase in the temperature resulted in higher methane conversion. However, the importance of the temperature increase is higher in tests 24-12 than in tests 20-4-21. Theoretical results showed a similar trend for both series 24-12

and 20-4-21, which resulted in a disagreement between the experimental methane conversion and the conversion predicted for test 24.

Fig. 6. Methane conversion in series varying: (a) solids inventory (tests 16-18); (b) temperature (tests 20-4-21 and 24-12); (c) operating time (tests 12-14-25-28-29). Experimental ($\diamond$) and predicted (—) values. Fig. (a) also shows the simulation with the inlet of solids in the dense bed (---).

Finally, methane conversion values for similar conditions (series 12-14-25-28-29) are plotted in Fig. 6(c). Obviously, the methane conversion predicted by the model is similar in all cases. However, the experimental methane conversion was lower for tests 25, 28 and 29. The difference could be found in a possible decrease in the oxygen uncoupling capacity of $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material with the operating time, as observed in a 500 W_{th} CLC unit [15].

Here, it is important to note that if the model had been modified for a better fit of results in tests 12, 24, 25, 28 and 29, agreement for the other tests would have been worse. Therefore, the model was considered to be validated, as good agreement between predicted and experimental values for methane conversion in the fuel-reactor was observed in most of the cases; see Fig. 5. This fact demonstrates that the fuel-reactor model adequately describes the processes taking place during the fuel conversion, as well as the effect of operating conditions on methane conversion.

4. Discussion

The $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material is able to transfer oxygen to the fuel by gas-solid reaction and oxygen uncoupling mechanism, which is known as Chemical-Looping *assisted* by Oxygen Uncoupling (CLaOU) [22]. From results obtained with the CLC model it was possible to calculate the flow of oxygen being transferred inside the fuel-reactor *via* oxygen uncoupling by accounting for the oxygen reacted by reaction (R5) in the mass balances. As the total flow of oxygen transferred in the fuel-reactor was also known, the relative amount of oxygen transferred to the fuel *via* oxygen uncoupling could be calculated. Fig. 7(a) shows these values in regard to those of methane conversion. A clear relationship can be observed between the increase in the oxygen transferred *via* oxygen uncoupling and the increase in methane conversion. Moreover, the fraction of oxygen *via* oxygen uncoupling is more relevant at the lowest temperatures due to the low reactivity of the $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material with CH_4 at these temperatures [14].

Fig. 7. Relevance to methane conversion of oxygen transferred to fuel *via* oxygen uncoupling.

It should be noted that the oxygen transport capacity for oxygen uncoupling, $R_{\text{OC},ou}$, is lower than the total oxygen transport capacity, $R_{\text{OC},t}$. Thus, very high solids circulation rates are necessary to increase the relevance of the oxygen uncoupling mechanism to oxygen transfer; see Fig. 7(b). Therefore, high temperature and oxygen-carrier-to-fuel ratio values are advisable in order to achieve complete fuel combustion in a CLC unit with the $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-\delta}$ material. But the required temperature depends on other operating conditions. Fig. 6(b) shows that a temperature

above 950 °C is required for high values of oxygen-carrier to fuel ratio ($\phi \approx 29$) and solids inventory in the fuel-reactor ($m_{FR} \approx 340$ kg/MW). At these high ϕ values, the oxygen transference through the oxygen uncoupling mechanism is promoted, which clearly improves methane conversion; see Fig. 7. But the required temperature is higher (≈ 1000 °C) when lower values of ϕ (~ 17) and m_{FR} (~ 250 kg/MW) are used. In this case, most of oxygen is transferred via gas-solid reaction between methane and the oxygen-carrier. This reaction is relatively slow at temperatures below 1000 °C [14], which justify the high temperature required at lower ϕ values.

Considering conditions existing in tests 16-18, i.e. $T_{FR} \approx 950$ °C and $\phi \approx 34$, a minimum solids inventory to achieve complete methane conversion in the fuel-reactor of $m_{FR} = 320$ kg/MW is deduced from results presented in Fig. 6(a).

In addition, it is also of interest to mention that the entry point for the solids in the fuel-reactor is highly relevant if good use is to be made of their oxygen uncoupling capability. Oxidized particles enter into the dilute region of the DCFB, where a relatively low concentration of methane is to be found. To evaluate the relevance of the entry point of solids in the fuel-reactor, Fig. 6(a) shows predictions obtained assuming that solids enter in the dense bed, where they would be quickly mixed with existing solids in the reactor. In this case, methane conversion values are lower than those predicted when solids enter in the dilute region and a minimum solids inventory of $m_{FR} = 500$ kg/MW would be required to achieve complete methane combustion. Therefore, the oxygen uncoupling mechanism gains in relevance when solids enter in the dilute region, compared to the direct gas-solid reaction between the methane and the oxygen-carrier [23].

5. Conclusions

A theoretical model for Chemical-Looping Combustion (CLC) was developed for the combustion of methane with $\text{CaMn}_{0.9}\text{Mg}_{0.1}\text{O}_{3-8}$ material. This model properly predicted the fuel conversion in 29 tests conducted at the DCFB built at TUV. Thus, the effect of pressure drop, gas flow and

temperature inside the fuel-reactor was properly described. In addition, it was determined that methane conversion could be highly improved by using an oxygen-carrier with oxygen uncoupling properties and that there was a window in operating conditions where this mechanism became prevalent. Therefore, the validated model is a powerful tool for simulating and optimizing the methane combustion in the fuel-reactor of a CLC system.

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Figure captions

Fig. 1. Reactor scheme of the CLC process.

Fig. 2. Schematic diagram of the DCFB at TUV [4].

Fig. 3. Compilation of equations used in the fluid dynamic and mass balances sections of the model [11,14].

Fig. 4. Axial profiles in the fuel-reactor for test 10 of (a) solids fraction and gas velocity, and (b) gas concentration.

Fig. 5. Comparison between experimental and predicted values of methane conversion ($\square$) and combustion efficiency ($\diamond$).

Fig. 6. Methane conversion in series varying: (a) solids inventory (tests 16-18); (b) temperature (tests 20-4-21 and 24-12); (c) operating time (tests 12-14-25-28-29). Experimental ($\diamond$) and predicted (——) values.

Fig. 7. Relevance to methane conversion of oxygen transferred to fuel via oxygen uncoupling.