Optimisation of hydrogen production with CO₂ capture by methane steam reforming integrated with a chemical-looping combustion system

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Abstract

Methane steam reforming (SR) integrated with a chemical-looping combustion (CLC) system is a new process for producing hydrogen from natural gas, allowing carbon dioxide capture with a low energy penalty. In this study, mass and enthalpy balances of a SR-CLC system were carried out to determine the autothermal operating conditions for optimal H₂ production. The evaluation was conducted using iron-based oxygen carriers. Two configurations were analysed, firstly with the reformer tubes inside the fuel reactor and, secondly, with the reformer tubes inside the air reactor. This paper analyses the effect of two parameters affecting the SR process, namely the conversion of methane in the reformer (X_{CH_4}) and the efficiency of the hydrogen separation of a pressure swing adsorption (PSA) unit (η_{PSA}), as well as two parameters affecting the CLC system, namely the Fe₂O₃ content in the oxygen carrier and its conversion variation (ΔX_{OC}), on the H₂ yields. Moreover, it also analyses the reduction of Fe₂O₃ to Fe₃O₄ or to FeAl₂O₄. The results shown that a H₂ yield value of 2.45 mol H₂ per mol of CH₄ can be obtained with the reformer tubes located inside the air reactor and with

Fe_2O_3 being reduced to Fe_3O_4 . This corresponds to a CH_4 to H_2 conversion of 74.2%, which is similar to state-of-the-art H_2 production technologies, but with inherent CO_2 capture in the SR-CLC process.

Keywords: hydrogen (H_2) production; chemical looping combustion; carbon dioxide (CO_2) capture; oxygen carrier; iron oxide.

1. Introduction

Carbon dioxide emissions are the main cause of the increase in the greenhouse effect, leading to global warming. One of the options available to combat this problem is that of CO_2 capture and storage, a medium-term solution to stabilise atmospheric CO_2 concentrations [1]. These technologies are currently being developed to be implemented in the industrial and energy generation sectors. However, CO_2 capture technology applied to transport sector is less straightforward, with the use of hydrogen as a fuel being an option to reduce CO_2 emissions. However, H_2 is an energy carrier that must be produced from a primary energy source and is often obtained by steam reforming (SR) methane (CH_4) [2]. In this process, the reforming reactions take place in reformer tubes packed with a nickel catalyst. Fuel combustion is needed outside the reformer tubes to supply the energy required for the endothermic SR. In a low carbon emission scenario, the CO_2 generated in this process should be captured in order to use H_2 as a fuel in vehicles as a carbon-free energy vector.

One possible alternative to conventional SR is autothermal reforming (ATR) whereby the exothermic partial oxidation of CH_4 is used as a heat source for the reforming reactions [2]. In this process, CH_4 , H_2O and O_2 (or air) are fed into an adiabatic reactor where both partial oxidation and CH_4 reforming take place. The main drawback of this

process is the need for an air separation unit (ASU) to produce the oxygen needed for partial oxidation, which involves high energy consumption and costs. Otherwise, a CO₂ capture step would be needed if air was used instead of O₂.

Different chemical-looping technologies for H₂ production integrated with CO₂ capture have been proposed [3-4]. In general, chemical-looping technologies are viewed as highly promising fuel conversion technologies for CO₂ capture [5], providing a CO₂ stream ready for sequestration without the need for costly gas separation techniques. Chemical-looping involves fuel conversion by means of a solid oxygen carrier which transfers oxygen from the air to the fuel. Chemical-looping systems are generally composed of two interconnected fluidised bed reactors, one air reactor and one fuel reactor, with the oxygen carrier material circulating between them; see Fig. 1 (a). In the fuel reactor, the fuel is partially or fully oxidised by the oxygen carrier. It is referred to as chemical-looping combustion (CLC) if the fuel is fully combusted. In chemical-looping reforming (CLR), however, H₂ is produced by means of a partial oxidation of the fuel. The spent oxygen carrier is then transferred to the air reactor where it is oxidised with air. The regenerated material is then ready to start a new cycle. Thus, direct contact between the fuel and air is avoided. The flue gas leaving the air reactor contains N₂ and unreacted O₂. Thus, exiting gas from the fuel reactor does not contain N₂ from the air. In CLC, a pure CO₂ stream is produced after steam condensation. In CLR, a H₂ separation step is required to obtain a very pure stream of H₂. Moreover, the net chemical reaction and energy release is the same as conventional combustion or when the fuel is partially oxidised.

In autothermal chemical-looping reforming (CLRa) technology, the autothermal reforming of CH₄ is carried out in a chemical-looping system [3]. From several options analysed by Rydén and Lyngfelt, a maximum hydrogen yield of 2.68 mol H₂ per mol of

CH₄ was obtained with a CLR system operating at atmospheric pressure [3]. Through optimising the system, a H₂ yield of 2.75 mol H₂ per mol of CH₄ was reached [6].

Another option for H₂ production using chemical-looping technologies is the SR-CLC process, which integrates a chemical-looping combustion process into the conventional SR process. The SR-CLC process was proposed by Rydén and Lyngfelt [4] and it uses the benefits of CLC in terms of CO₂ capture in an inexpensive way. In this process, steam and hydrocarbons are converted into syngas using reformer tubes packed with a catalyst, just as in a conventional tubular steam reforming unit. The main difference with respect to conventional steam reforming is that the heat required for endothermic reforming reactions is provided by the solids circulating in the CLC system. The reformer tubes may be located either in the fuel reactor; see Fig. 1 (b), or in the air reactor; see Fig. 1 (c). Both reactors are fluidised beds, providing highly favourable conditions for heat transference. For H₂ production, water-gas shift (WGS) and pressure swing adsorption (PSA) units are integrated into the SR-CLC unit. In the WGS reactor, H₂ production is maximised by the conversion of CO by the WGS reaction. Next, H₂ is separated from the other components in a PSA unit. The PSA tail gas is used as a fuel gas in the fuel reactor of the CLC system. To increase the heating value of the PSA tail gas, a portion of the CH₄ fed to the reformer tubes can be diverted to the fuel reactor. Thus, the CLC system is used both to provide heat for reforming and to capture CO₂.

Rydén and Lyngfelt [4] proposed a preliminary reactor design in order to demonstrate the feasibility of the SR-CLC process. They concluded that reactor dimensions seem to be reasonable, and that the SR-CLC process has potential to achieve better selectivity towards H₂ than conventional SR plants owing to low reactor temperatures and favourable heat transfer conditions. The H₂ yield in the SR-CLC process depends on the integration of SR with a CLC system. CH₄ conversion in SR and H₂ separation

efficiency in the PSA unit affect the enthalpy balance in the CLC system because PSA tail gas is the fuel used in the CLC system.

Choosing a suitable oxygen carrier is key for the development of SR-CLC technology. An oxygen carrier usually consists of a metal oxide supported on an inert material [7]. Because of their low cost and environmental compatibility, iron-based oxygen carriers are considered an attractive option for SR-CLC application [8-9]. Continuous operation in a CLC system was performed using simulated PSA tail gas as fuel with an iron enriched waste from aluminium manufacture [8] or an impregnated $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ material [9] as an oxygen carrier. Both materials performed well and are promising materials for use as an oxygen carrier in SR-CLC.

The aim of this study is to determine the optimum operating conditions for the SR-CLC system in order to maximise H_2 production. For this purpose, mass and enthalpy balances in a SR-CLC system are analysed. The study was carried out varying two main operating parameters: the conversion of CH_4 in the reforming process (X_{CH_4}) and the PSA separation unit efficiency (η_{PSA}). The X_{CH_4} - η_{PSA} pairs of values that allow operation in autothermal conditions are determined. The effect of different design and operating conditions in the CLC system –such as the SR-CLC arrangement (i.e. SR tubes inside the fuel reactor or the air reactor), the solids circulation flow rate or the characteristics of the iron-based oxygen carrier– on the H_2 production per mole of CH_4 was evaluated for autothermal operating conditions. Through analysing the results, the operating conditions to maximise H_2 production are determined.

2. Procedure

To determine the autothermal operating conditions to maximise H₂ production in a SR-CLC system, mass and enthalpy balances were carried out. This study was carried out using iron-based oxygen carriers.

The mass balance formulation was made for the global process, integrating the SR-CLC system with a water gas shift reactor, and a pressure swing adsorption (PSA) unit downstream to produce a highly concentrated H₂ stream, as shown in Figs. 1 (b) and 1 (c). The mass balance was calculated varying the conversion of CH₄ in the reforming process (X_{CH_4}) and the PSA separation unit efficiency (η_{PSA}). Regarding the mass balance, the following reactions may occur in the reformer:

The CH₄ conversion in the reformer, X_{CH_4} , is calculated as:

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

Then, the gas is introduced in the WGS reactor, where H₂ is increased by decreasing the CO amount. The gas composition exiting the WGS reactor is considered to have a thermodynamic equilibrium, and it depends on the CH₄ conversion in the SR process and the WGS temperature. Thus, for a given X_{CH_4} - η_{PSA} pair, the flow of every compound (CH₄, CO₂, CO, H₂) exiting the WGS reactor is calculated using the following equations:

$$F_{CH_4, out WGS} = F_{CH_4, in SR} (1 - X_{CH_4}) \quad (2)$$

$$F_{CO_2, out WGS} + F_{CO, out WGS} = F_{CH_4, in SR} \cdot X_{CH_4} \quad (3)$$

$$F_{H_2, out WGS} + F_{H_2O, out WGS} = F_{H_2O, in SR} + 2F_{CH_4, in SR}(X_{CH_4}) \quad (4)$$

$$2F_{CO_2, out WGS} + F_{CO, out WGS} + F_{H_2O, out WGS} = F_{H_2O, in SR} \quad (5)$$

$$\frac{F_{CO_2, out WGS} \cdot F_{H_2, out WGS}}{F_{CO, out WGS} \cdot F_{H_2O, out WGS}} = K_{WGS}; \quad \ln K_{WGS} = -3.147 + \frac{2815.6}{T} + \frac{670976}{T^2} \quad (6)$$

Then the gas is dried and introduced into the PSA unit. The H₂ separation efficiency in the PSA is obtained as:

$$\eta_{PSA} = \frac{F_{H_2, in PSA} - F_{H_2, tail PSA}}{F_{H_2, in PSA}} \quad (7)$$

The flow of H₂ obtained from the SR-CLC system in the highly concentrated stream is calculated as:

$$F_{H_2, SR-CLC} = \eta_{PSA} \cdot F_{H_2, in PSA} \quad (8)$$

The flow of CH₄, CO and CO₂ in the tail gas is the same as that exiting the WGS. The flow of H₂ in the tail gas depends on the η_{PSA} , given by Eq. (7). In some cases, a fraction of the CH₄ must be diverted and fed directly into the fuel reactor; see Figs. 1(b) and 1(c). Thus, the total flow of CH₄ is shared in:

$$F_{CH_4, T} = F_{CH_4, in SR} + F_{CH_4, div CLC} \quad (9)$$

The flow of CH₄ entering the CLC system is:

$$F_{CH_4, in CLC} = F_{CH_4, tail PSA} + F_{CH_4, div CLC} \quad (10)$$

The mass balance in the fuel reactor of the CLC system is:

$$\frac{1}{M_O} \cdot \dot{m}_{OC} \cdot R_{OC} \cdot \Delta X_{OC} = (4F_{CH_4} + F_{H_2} + F_{CO})_{tail PSA} + (4F_{CH_4})_{div CLC} \quad (11)$$

With R_{OC} being the oxygen transport capacity of the oxygen carrier, obtained as:

$$R_{OC} = \frac{(m_{ox} - m_{red})}{m_{ox}} \quad (12)$$

Iron compounds need special attention owing to their different oxidation states (Fe_2O_3 - Fe_3O_4 - FeO - Fe). Reduction to Fe_3O_4 allows the fuel to be fully converted into CO_2 and H_2O [7] and avoids the agglomeration problems associated with the phase change from magnetite to wustite [10]. When alumina is present in the particles, the mixed oxide $\text{FeO} \cdot \text{Al}_2\text{O}_3$ can be formed as a reduced compound whereas complete combustion can be reached using thermodynamic calculations [7,11]. Later, experimental evidence of complete combustion and $\text{FeO} \cdot \text{Al}_2\text{O}_3$ formation was found both in a batch reactor and a continuously operated CLC unit [9]. Thus, the oxygen transport capacity corresponds to the $\text{Fe}_2\text{O}_3/\text{FeO}$ pair, which is increased with respect to the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system.

When the Fe_2O_3 is reduced to Fe_3O_4 , the main reactions happening in the fuel reactor are:

The main reaction happening in the air reactor is:

When the reduction of the Fe_2O_3 proceeds to the form $\text{FeO} \cdot \text{Al}_2\text{O}_3$, the main reactions occurring with different contribution in the fuel reactor are:

And the main reaction occurring in the air reactor is:

Assuming complete conversion to CO_2 and H_2O , the flows of gases exiting the fuel reactor are:

$$F_{\text{CO}_2, \text{out FR}} = (F_{\text{CH}_4} + F_{\text{CO}} + F_{\text{CO}_2})_{\text{tail PSA}} + (F_{\text{CH}_4})_{\text{divCLC}} \quad (13)$$

$$F_{\text{H}_2\text{O}, \text{out FR}} = (2F_{\text{CH}_4} + F_{\text{H}_2})_{\text{tail PSA}} + (2F_{\text{CH}_4})_{\text{divCLC}} \quad (14)$$

Assuming the complete oxidation of the oxygen carrier in air reactor, the solids flow into the fuel reactor is:

$$F_{\text{Fe}_2\text{O}_3} = \dot{m}_{\text{OC}} \cdot x_{\text{Fe}_2\text{O}_3} \cdot \frac{1}{M_{\text{Fe}_2\text{O}_3}} \quad (15)$$

$$F_{\text{Al}_2\text{O}_3} = \dot{m}_{\text{OC}} \cdot (1 - x_{\text{Fe}_2\text{O}_3}) \cdot \frac{1}{M_{\text{Al}_2\text{O}_3}} \quad (16)$$

The flow of solids into the air reactor is:

Reduction to Fe_3O_4

$$F_{\text{Fe}_2\text{O}_3, \text{in AR}} = F_{\text{Fe}_2\text{O}_3, \text{in FR}} \cdot (1 - \Delta X_{\text{OC}}) \quad (17)$$

$$F_{\text{Fe}_3\text{O}_4, \text{in AR}} = \frac{2}{3} F_{\text{Fe}_2\text{O}_3, \text{in FR}} \cdot \Delta X_{\text{OC}} \quad (18)$$

$$F_{\text{Al}_2\text{O}_3, \text{in AR}} = F_{\text{Al}_2\text{O}_3, \text{in FR}} \quad (19)$$

Reduction to $\text{FeO} \cdot \text{Al}_2\text{O}_3$

$$F_{\text{Fe}_2\text{O}_3, \text{in AR}} = F_{\text{Fe}_2\text{O}_3, \text{in FR}} \cdot (1 - \Delta X_{\text{OC}}) \quad (20)$$

$$F_{\text{FeO} \cdot \text{Al}_2\text{O}_3, \text{in AR}} = 2F_{\text{Fe}_2\text{O}_3, \text{in FR}} \cdot \Delta X_{\text{OC}} \quad (21)$$

$$F_{\text{Al}_2\text{O}_3, \text{in AR}} = F_{\text{Al}_2\text{O}_3, \text{in FR}} - F_{\text{FeO} \cdot \text{Al}_2\text{O}_3, \text{in AR}} \quad (22)$$

The flow of air to the air reactor is defined assuming an air excess ratio of $\lambda = 1.2$, with λ being:

$$\lambda = \frac{2F_{\text{O}_2, \text{in AR}}}{(4F_{\text{CH}_4} + F_{\text{CO}} + F_{\text{H}_2})_{\text{tail PSA}} + (4F_{\text{CH}_4})_{\text{divCLC}}} \quad (23)$$

The corresponding flow of N_2 in air is:

$$F_{N_2, in AR} = \frac{0.79}{0.21} F_{O_2, in AR} \quad (24)$$

At the air reactor exit, the gaseous flows are calculated assuming the complete combustion of gases to CO_2 and H_2O :

$$F_{N_2, out AR} = F_{N_2, in AR} \quad (25)$$

$$F_{O_2, out AR} = F_{O_2, in AR} \frac{\lambda - 1}{\lambda} \quad (26)$$

The enthalpy balance over fuel and air reactors is calculated taking into account the enthalpy of the incoming and exiting solid and gaseous compounds to every reactor in the system, i.e. the fuel reactor, the air reactor, the steam reformer and the WGS reactor.

The enthalpy balance for every reactor can be expressed as:

$$H_{reac} = H_{prod} - \Delta H_i \quad (27)$$

The enthalpy of reactants and products is calculated as:

$$H_{reac} = \sum F_{reac, i} h_{reac, i} \quad (28)$$

$$H_{prod} = \sum F_{prod, i} h_{prod, i} \quad (29)$$

Where the enthalpy of component i is calculated from:

$$h_i = h_i^o + \int_{T_o}^T C_{p, i}(T) dT \quad (30)$$

The enthalpy difference between products and reactants (ΔH_i) in every reactor is calculated depending on the location of the reformer tubes. In a previous study, it was determined that in a CLC system some heat flux should be extracted from the air or fuel reactor to maintain the enthalpy balance in the system [12]. In the case of the SR-CLC system, some enthalpy is transferred to the reformer. However, only in specific cases the required enthalpy extracted from the system would be equal to the required enthalpy in the reformer. So, it was assumed that some enthalpy should be extracted or supplied

to the CLC system through Q_{ext_8} in the air reactor. With this in mind, the enthalpy balance in the reactors is:

SR in the fuel reactor

$$\Delta H_{AR} = +Q_{ext_8} \quad (31)$$

$$\Delta H_{FR} = -\Delta H_{SR} \quad (32)$$

SR in the air reactor

$$\Delta H_{AR} = +Q_{ext_8} - \Delta H_{SR} \quad (33)$$

$$\Delta H_{FR} = 0 \quad (34)$$

The temperature in the reactor where SR is located is set at 900°C. The temperature of the other reactor is calculated from the enthalpy balance. Once the temperature of the air reactor is determined, Q_{ext_8} is calculated from the enthalpy balance. All thermochemical data are adopted from Barin [13]. All gases (CH_4 , CO , CO_2 , H_2 , H_2O , O_2 , N_2) and solids present in the reactors (Fe_2O_3 , Fe_3O_4 , Al_2O_3 and $\text{FeO} \cdot \text{Al}_2\text{O}_3$) are considered to be reactants and products. When Q_{ext_8} is equal to 0, the system is autothermic. $Q_{ext_8} < 0$ means that there is excess of energy in the CLC system. However, when $Q_{ext_8} > 0$ the heat generated in the air reactor is not enough to fulfil the heat balance and an external heat supply is needed. Note that the air reactor is usually the hottest part of the SR-CLC system, and heat cannot be transferred to the air reactor from any stream in the SR-CLC system.

Once the autothermal operating conditions for the SR-CLC system are determined, an enthalpy balance for the overall system is created by integrating pre-heaters and a water gas shift reactor into the SR-CLC system; see Figs. 1 (b) and 1(c). This enthalpy balance takes into account the energy that can be extracted from the gas outlet streams at high temperature to preheat the gas inlet streams to the reactors and to evaporate and

heat the water fed to the water gas shift reactor. The heat flux extracted or supplied to every stream is calculated as:

$$Q_i = \Sigma [F_i C_{p,i} (T_{out_i} - T_{in_i})] \quad (35)$$

The excess of enthalpy recovered from the SR-CLC process can be obtained as the sum of all inputs and outputs of enthalpy to the system less the enthalpy obtained from condensing steam, an enthalpy assumed to be unusable in the system:

$$Q_{rec} = \Sigma Q_{ext_i} + \Sigma Q_{in_i} - (Q_{ext_2} + Q_{ext_6}) \quad (36)$$

The mass and enthalpy balances are calculated considering the following assumptions:

- 1 MW energy in CH₄ is taken as a reference, considering both the CH₄ introduced into the SR and the CH₄ diverted from the main stream, i.e. CH₄(T) = CH₄(SR) + CH₄(CLC) in Figs. 1 (b) and 1 (c).
- Gases are fed to the SR-CLC system at 400 °C. It is assumed that these gases are heated with the energy extracted from the gas outlet streams of both reactors.
- The temperature inside the reformer tubes is kept constant at 800 °C.
- The temperature outside the reformer tubes is kept constant at 900 °C.
- The initial and final temperatures of all gases and H₂O (l) is 25 °C.
- There are no heat losses in the system.
- There is full conversion of the fuel in the fuel reactor to CO₂ and H₂O.
- The temperature of the water gas shift reactor is kept constant at 237 °C.
- The ratio of H₂O flow to CH₄ flow to the SR is 4.
- There is complete oxidation of the oxygen carrier in the air reactor.
- The air excess ratio λ is 1.2
- The CLC operates at atmospheric pressure.

Firstly, an analysis is done about the effect of methane conversion and PSA separation efficiency on the enthalpy balance of the SR-CLC system. The reforming pressure is not

defined at this point because methane conversion at thermodynamic equilibrium is dependent on total pressure. This involves the assumption that in many cases there is a low pressure inside the reformer tubes, which is not realistic for the global process. The reforming temperature can lie within the range of 700-950°C, depending on the application [2]. A relatively low temperature (800°C) was chosen here in order to increase the H₂ yield since it is well known that in chemical-looping processes H₂ production is higher with lower reactor temperatures [6].

3. Results and discussion

3.1. Analysis of the global SR-CLC process: the effect of X_{CH_4} - η_{PSA} values

The SR-CLC process was analysed by changing two main variables in the system: the CH₄ conversion in the reforming process (X_{CH_4}) and the PSA unit efficiency (η_{PSA}). For this purpose, a sweep of CH₄ conversions in SR from 10% to 100% was firstly carried out. The assumptions mentioned above were taken into account. Furthermore, to avoid the influence of parameters affecting the CLC system, ΔX_{OC} was set at 0.5 and the Fe₂O₃ content in the oxygen carrier was 20 wt.%. A preliminary analysis is presented assuming a reduction of Fe₂O₃ to Fe₃O₄ with the reformer tubes placed inside the fuel reactor. Fig. 2 shows the effect of several pairs of values (X_{CH_4} - η_{PSA}) on the overall SR-CLC enthalpy balance (Q_{ext_g}). This figure shows the pairs of X_{CH_4} - η_{PSA} values which allow the air reactor to work under autothermal conditions, with an excess of energy ($Q_{ext_g} < 0$) or with an energy deficit ($Q_{ext_g} > 0$). As the X_{CH_4} and/or η_{PSA} value increases, the system moves towards the area with energy deficit as a result of the decrease in the calorific value of the PSA-offgas. Fig. 3 shows the X_{CH_4} - η_{PSA} pairs of values which define the autothermal operating zone. Energy excess conditions are

located in the region below the autothermal conditions. In these cases, a heat flux should be extracted from the air reactor ($Q_{ext_8} < 0$). The energy deficit conditions zone is located above these values, and it defines the pairs which would require an external power supply ($Q_{ext_8} > 0$). Under energy deficit conditions, it is impossible to achieve the temperature required outside the reformer tubes (900°C), one of the initial requirements. This is because some heat has to be supplied to the air reactor. This condition should be avoided in a SR-CLC system to prevent the use of an external energy source. Thus, a percentage of the initial quantity of CH₄ fed could be diverted directly to the fuel reactor in order to increase the calorific value of the PSA tail gas, thus avoiding the need for an external energy source. The amount of CH₄ needed to be diverted to maintain the system within autothermal conditions increases with X_{CH_4} or η_{PSA} ; see Fig. 4.

To calculate the H₂ flow obtained in the concentrated stream from the PSA, $F_{H_2, SR-CLC}$, a mass balance to the SR-CLC global process was done. Fig. 5 presents the effect of X_{CH_4} and η_{PSA} over the H₂ production per mole of total methane fed, i.e. the sum of the methane flow to SR and CLC. Two regions can be identified in this figure. When there is an excess of energy, i.e., low values of X_{CH_4} or η_{PSA} , there is a significant increase in H₂ production when X_{CH_4} increases. However, at autothermal conditions, i.e. when diverting a certain amount of CH₄ directly to the fuel reactor, the curves incline slightly upwards. Diverting a part of the initial methane fed in involves decreasing the amount of methane fed into the tubes. Thus, the water flow required by the reformer is lower since the H₂O/CH₄ ratio to the reformer is maintained constant at 4. As a result, less energy losses from Q_{ext_2} during steam condensation are predicted and more hydrogen will be produced.

Fig. 6 shows the effect of the X_{CH_4} on the oxygen carrier circulation flow rate, $\dot{m}_{OC}$, at different η_{PSA} values. The increase in the X_{CH_4} and/or η_{PSA} values involves a decrease in the oxygen carrier circulation rate due to the lower amount of CH_4 and/or H_2 fed into the fuel reactor, and therefore a lower amount of oxygen needed to burn the fuel gases fed into the fuel reactor. The relationship between the oxygen carrier circulation rate and X_{CH_4} and η_{PSA} follows a reverse trend to the H_2 production shown in Fig. 5, since a higher H_2 yield means that a lower flow of oxygen is demanded by the gases fed into the fuel reactor. Similar to the effect of X_{CH_4} and η_{PSA} on the H_2 production shown in Fig. 5, two different slopes are observed in the curves obtained in Fig. 6, corresponding to the excess energy conditions (slope with high inclination) and the autothermal conditions, diverting the necessary amount of methane to the fuel reactor (slope with low inclination).

The oxygen carrier circulation rate affects the enthalpy balance between the air reactor and the fuel reactor, meaning that a lower circulation rate requires a higher temperature in the air reactor [14]. Fig. 7 (a) shows the effect of X_{CH_4} on the temperature difference between the air and fuel reactors at different values of η_{PSA} when the reformer tubes are placed inside the fuel reactor. The global process occurring in the fuel reactor is endothermic, i.e. Fe_2O_3 is reduced to Fe_3O_4 and SR inside the tubes; thus, the air reactor temperature is higher than fuel reactor temperature. Again two different slopes are obtained. The zone with the higher slope corresponds to the energy excess area. The zone with no slope corresponds to the autothermal conditions area. In the energy excess area, it can be seen that as X_{CH_4} and/or η_{PSA} increases, the temperature difference between both reactors also increases. As can be seen in Fig. 6, when X_{CH_4} and/or η_{PSA} increases, a lower amount of oxygen needs to be carried to the fuel reactor through the

solids and therefore a lower solids circulation rate would be required. If the solids circulation rate decreases, in order to fulfil the enthalpy balance and to reach the temperature required outside the reformer tubes (900°C) the solids must leave the air reactor at a higher temperature and therefore a higher temperature difference between both reactors must be achieved. At autothermal conditions, the solids circulation flow is less affected by X_{CH_4} and η_{PSA} . Therefore, the temperature difference barely changes with X_{CH_4} and η_{PSA} .

In the case of Fe_2O_3 reduction to Fe_3O_4 with the reformer tubes inside the fuel reactor, the maximum temperature difference between the air reactor and fuel reactor is 34°C. This means that if the fuel reactor temperature must be 900°C, the air reactor temperature must be 934°C. Moreover, the minimum temperature difference obtained is 14°C. This means that the air reactor temperature must be 914°C. Therefore operational problems in this range of temperatures are not expected.

When Al_2O_3 is used as support, $FeO \cdot Al_2O_3$ can appear as product of reduction. This changes the thermochemistry of the process. The study of the SR-CLC process in this case is carried out in a similar way to the balances done for the Fe_2O_3/Fe_3O_4 system, i.e. by analysing the effect of the conversion of CH_4 in the reforming process (X_{CH_4}) and the PSA separation unit efficiency (η_{PSA}) on the SR-CLC system. With respect to the autothermal conditions, similar results are obtained in the CH_4 diverted and H_2 yield (Figs. 2-5). In Fig. 6, the oxygen carrier circulation flow rate when Fe_2O_3 is reduced to $FeO \cdot Al_2O_3$ is also included at different values of X_{CH_4} or η_{PSA} . When comparing the results when reducing to Fe_3O_4 or $FeO \cdot Al_2O_3$, it can be observed that the oxygen carrier circulation rate is three times lower when reduced to $FeO \cdot Al_2O_3$ than to Fe_3O_4 . This is owing to differences in the R_{OC} in each system ($R_{OC} = 0.034$ for Fe_2O_3/Fe_3O_4 system

and $R_{OC} = 0.1$ for $\text{Fe}_2\text{O}_3/\text{FeO}$ system). A lower value in the oxygen carrier circulation flow rate means a higher variation of the temperature between both reactors in order to fulfil the heat balance. This is particularly true at high values of X_{CH_4} ; see Fig 7 (a). A value of $\Delta T = 56^\circ\text{C}$ is reached at autothermal conditions, higher than the 34°C reached for the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system. The opposite occurs with low X_{CH_4} values. In this case, the exothermic reduction of the oxygen carrier (see reactions R8-R10) is more relevant than the heat transferred to SR. Thus, the temperature in the fuel reactor increases as X_{CH_4} decreases, and it can be even higher than the temperature in the air reactor ($\Delta T < 0$).

As mentioned earlier, the reformer tubes may also be placed inside the air reactor. In this case, the temperature of the air reactor was set at 900°C . The overall SR-CLC heat balance, the percentage of CH_4 diverted to the fuel reactor to reach autothermal conditions, the H_2 production and the solids circulation flow rate obtained for different pairs of X_{CH_4} - η_{PSA} values were similar to the results achieved by placing the tubes inside the fuel reactor (Figs. 2-6). The only difference found in the results relates to the temperature difference between air reactor and fuel reactor. Fig. 7 (b) shows the effect of X_{CH_4} on the temperature difference between the air and fuel reactors at different η_{PSA} values with the reformer tubes placed inside the air reactor, reducing the oxygen carrier to Fe_3O_4 or to $\text{FeO}\cdot\text{Al}_2\text{O}_3$. The opposite X_{CH_4} trend is obtained in comparison to that found when locating the reformer tubes inside the fuel reactor. The heat flux to the SR process is directly transferred into the air reactor when the tubes are placed inside the air reactor. Therefore the energy required in the fuel reactor is lower and the sensible heat transferred from the air reactor to the fuel reactor by means of circulating solids is lower. As a consequence, as X_{CH_4} increases, ΔT decreases. In fact, temperature is

higher in the fuel reactor than in the air reactor for $X_{CH_4} > 0.6$ when $FeO \cdot Al_2O_3$ is formed because of the exothermicity reaction (R8) occurring in the fuel reactor. Regarding the effect of η_{PSA} , the decrease of η_{PSA} in the excess energy zone means a decrease in the oxygen carrier circulation rate, meaning that ΔT increases. In this case, the fuel reactor temperature decreases since the air reactor temperature was set at 900°C. In the autothermal zone, the flow of CH_4 diverted to the fuel reactor increases as η_{PSA} increases. Therefore, the reaction in the fuel reactor becomes more endothermic if the reduced product is Fe_3O_4 (see R4-R6). Therefore, ΔT increases because the fuel reactor temperature decreases as η_{PSA} increases. If Fe_2O_3 is reduced to $FeO \cdot Al_2O_3$, the fuel reactor temperature is higher than the air reactor temperature ($\Delta T < 0$) and the reaction is less exothermic as more CH_4 is diverted (see R8-R10). As a consequence, the temperature in the fuel reactor decreases as η_{PSA} increases, i.e. the absolute value of ΔT decreases, although always at $\Delta T < 0$.

A decrease in the fuel reactor temperature means that the reaction rate of the oxygen carrier is also decreased. Gayan et al. [9] shown the strong influence of the fuel reactor temperature on the combustion efficiency working with an iron-based oxygen carrier in a CLC system, using PSA tail gas as fuel. It was concluded that full conversion of the PSA tail gas can be reached working at 880°C and with oxygen carrier-to-fuel ratio values higher than 1.5. Thus, a lower limit of 880°C in the fuel reactor must be considered to reach complete combustion of gases in the fuel reactor. This condition is limited by a maximum value of $\Delta T = +20^\circ C$ when the reformer tubes are located inside the air reactor. Remember that if tubes are placed in the fuel reactor, the fuel reactor temperature is fixed to 900°C. The zone with ΔT values under this limit is considered to have unsuitable conditions and it has therefore been shaded in grey in Fig. 7 (b). This

lower limit for the fuel reactor temperature could disappear if complete conversion of the fuel could be reached at temperatures below 880°C.

3.2. Analysis of factors affecting the CLC system: Fe_2O_3 content and ΔX_{OC}

In section 3.1 it was concluded that H_2 production increases as X_{CH_4} and η_{PSA} increase. Autothermal conditions in the CLC system can be easily reached. However, factors affecting the CLC system, such as the metal content or the variation in solids conversion, ΔX_{OC} , can affect the H_2 yield. Thus, enthalpy and mass balances are calculated, setting the methane conversion in the reformer and H_2 separation efficiency in the PSA unit at the typical values of $X_{\text{CH}_4} = 80\%$ and $\eta_{\text{PSA}} = 90\%$ [4]. This value for CH_4 conversion corresponds to equilibrium conditions for methane SR at 800°C and 2 MPa, which are suitable conditions to perform SR [2, 4]. In all cases, autothermal conditions are considered, i.e., diverting the necessary amount of CH_4 to the fuel reactor when required.

3.2.1 Reformer tubes inside the fuel reactor

The analysis was initially carried out with the reformer tubes located inside fuel reactor. Fig. 8 (a) shows the effect of the oxygen carrier conversion on the oxygen carrier circulation flow rate at autothermal conditions, i.e., diverting the necessary amount of CH_4 to the fuel reactor for the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system. A higher conversion of the oxygen carrier and/or higher metal content in the solid means that a lower solids circulation rate is needed. The same trend is observed when Fe_2O_3 is reduced to $\text{FeO}\cdot\text{Al}_2\text{O}_3$; see Fig. 8 (b). In this case, the stoichiometric amounts of Al_2O_3 and Fe_2O_3 required to fully form $\text{FeO}\cdot\text{Al}_2\text{O}_3$ are 57 wt.% and 43 wt.%, respectively. Higher Fe_2O_3 fraction means that some FeO cannot form $\text{FeO}\cdot\text{Al}_2\text{O}_3$ because of a deficit of Al_2O_3 . In this case, a scale of

0-40 was therefore used to study of the effect of the percentage of Fe_2O_3 on the oxygen carrier. Solids circulation flow rate values are almost three times lower than when reducing to $\text{FeO}\cdot\text{Al}_2\text{O}_3$ because the oxygen transport capacity of the solid for the $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$ reaction is three times higher than for the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ reaction.

Fig. 9 (a) shows the effect of the oxygen carrier conversion on the temperature difference between the air and fuel reactors at different Fe_2O_3 contents, with the reformer tubes placed in the fuel reactor at autothermal conditions for the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system. An increase in any of those variables (ΔX_{OC} and Fe_2O_3 content) means an increase of the temperature difference between both reactors because the solids circulation rate decreases. Therefore, the solids must leave the air reactor at a higher temperature. The same trend is obtained when Fe_2O_3 is reduced to $\text{FeO}\cdot\text{Al}_2\text{O}_3$, as shown in Fig. 9 (b). However, higher temperature differences are obtained for the $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$ system at similar levels of Fe_2O_3 content because of the lower solids circulation flow required, in spite of the exothermic nature of reducing Fe_2O_3 to $\text{FeO}\cdot\text{Al}_2\text{O}_3$ with CH_4 (R8).

Fig. 10 (a) shows the effect of the oxygen carrier circulation flow rate on the percentage of CH_4 diverted to the fuel reactor required for it to operate at autothermal conditions, for different Fe_2O_3 contents, with the reformer tubes placed in the fuel reactor and a $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system. When the solids circulation rate increases, the fraction of CH_4 required to be diverted to the fuel reactor is lower. This is a direct consequence of the lower temperature in the air reactor as the solids circulation increases. Thus, a lower flow of Fe_3O_4 or $\text{FeO}\cdot\text{Al}_2\text{O}_3$ is required to be oxidised in the air reactor to maintain the temperature in this reactor. As a consequence, the flow of CH_4 fed to the fuel reactor decreases with the solids circulation flow rate. Slight differences are found for different Fe_2O_3 contents when the solids circulation rate is maintained. These differences are due

to the different thermal capacity of metal oxide and support material. The lower end of the m_{OC} curves for each Fe_2O_3 content is determined by the condition $\Delta X_{OC} = 1$. Thus, lower circulation rates are not permitted. The same trend was observed for the $Fe_2O_3/FeO \cdot Al_2O_3$ system; see Fig. 10 (b).

H_2 production is affected by the flow of CH_4 diverted to the fuel reactor, which depends on the ΔX_{OC} and Fe_2O_3 contents. Fig. 11 (a) shows the effect of the oxygen carrier conversion ΔX_{OC} on the H_2 production per mol of CH_4 fed at different Fe_2O_3 contents, with the reformer tubes located inside the fuel reactor and for the Fe_2O_3/Fe_3O_4 system. A decrease in ΔX_{OC} s and/or Fe_2O_3 content means an increase in H_2 production. This result is related to the effect of ΔX_{OC} and Fe_2O_3 content on ΔT . A decrease in the ΔX_{OC} and/or the Fe_2O_3 content means that the temperature of the air reactor must decrease, as shown in Fig. 9 (a). Consequently, the heat extracted from the air reactor gases, Q_{ext_7} in Fig. 1 (b), is lower. As the sum of all the inputs and outputs of thermal and chemical enthalpies of the system must be 1 MW, a lower amount of heat extracted from the air reactor means a higher amount of chemical energy in form of H_2 , i.e., the H_2 yield is increased. The same trend is observed for the $Fe_2O_3/FeO \cdot Al_2O_3$ system; see Fig. 11 (b). A comparison between Figs. 11 (a) and (b) shows that less hydrogen is produced with the $Fe_2O_3/FeO \cdot Al_2O_3$ system than with Fe_2O_3/Fe_3O_4 using the same Fe_2O_3 content. In each case, this result is directly related to the temperature increase in the air reactor, which is higher for the $Fe_2O_3/FeO \cdot Al_2O_3$ system. In these cases, higher ΔT means a lower H_2 production.

In a CLC system, the circulation of the oxygen carrier is determined by the velocity of the gas in the air reactor, which is usually designed as a high-velocity fluidised bed reactor [15]. An upper limit of $m_{OC}=16 \text{ kg s}^{-1}$ per MW of fuel converted to CO_2 and H_2O has been proposed [14]. In SR-CLC, not all CH_4 fed into the system is converted to

CO₂ and H₂O, since the production of H₂ is the purpose of this process. The fraction of CH₄ burnt to CO₂ and H₂O depends on the H₂ yield as:

$$F_{CH_4, burn} = F_{CH_4, T} \left(1 - \frac{F_{H_2, out}}{4} \right) \quad (37)$$

Therefore, the upper limit for solids circulation per MW of CH₄ depends on the H₂ yield:

$$\dot{m}_{OC, up} = 16 \left(\frac{kg}{s MW_{CLC}} \right) \times \frac{F_{CH_4, burn}}{F_{CH_4, T}} = 16 \times \left(1 - \frac{F_{H_2, SR-CLC}}{4} \right) \quad (38)$$

As a first approximation, a value for the H₂ yield of 2.4 mol H₂ per CH₄ mol is considered in all cases. This means that the upper limit for the solids circulation is $\dot{m}_{OC, up} = 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$. Circulation rates above this value are unsuitable and the zone that contains them is marked in grey in Fig. 8. Low oxygen carrier conversion values and/or low Fe₂O₃ contents in the solids result in unsuitable conditions. For the Fe₂O₃/FeO·Al₂O₃ system, the unsuitable conditions appear in a lower area than for Fe₂O₃/Fe₃O₄ due to the $\dot{m}_{OC}$ values being three-times lower. If higher solids circulation is required, the velocity of the gas in the air reactor should be increased, which means that λ must be increased. This would cause a loss in the energetic efficiency of the process. Conditions that are unsuitable owing to the solids circulation flow rate higher than $\dot{m}_{OC, up}$ are also marked in Figs. 9, 10 and 11.

Another limitation could come from the maximum temperature allowed in the CLC reactors. Using iron-based materials, good performance has been reported at temperatures above 1000°C [16,17]. In this case, a maximum temperature in the air reactor of 1100°C is assumed. The maximum temperature difference reached with the reformer tubes located in fuel reactor and Fe₂O₃/Fe₃O₄ system, for $\Delta X_{OC} = 1$ and Fe₂O₃ content = 100%, is 350°C. This would lead to an air reactor temperature of 1250°C. The

restriction of the air reactor temperature of 1100°C means that $\Delta T_{\max} = 200^\circ\text{C}$. Thus, the permitted Fe_2O_3 content and ΔX_{OC} pairs are restricted, as shown in Fig. 9 (a). Limitations for the solids circulation flow rate, the CH_4 diverted to the fuel reactor, and in H_2 production are shown in Figs. 9, 10, and 11. Thus for the reduction of Fe_2O_3 to Fe_3O_4 , a maximum H_2 yield of 2.37 H_2 mol per CH_4 mol can be obtained with a 20 wt.% of Fe_2O_3 and $\Delta X_{\text{OC}} = 0.8$. On the contrary, only low values of ΔX_{OC} are unsuitable for the $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$ system, and the maximum H_2 production obtained in this case is 2.39 mol H_2 per mol of CH_4 with a 10 wt.% of Fe_2O_3 and $\Delta X_{\text{OC}} = 0.5$.

3.2.2. Reformer tubes inside the air reactor

A similar analysis is carried out assuming that the reformer tubes are located in the air reactor. On the one hand, with regards the solids circulation flow rate at autothermal conditions, i.e., diverting the necessary amount of CH_4 to the fuel reactor, the same results are achieved as when placing the reformer tubes in the fuel reactor. So the results shown in Fig. 8 (a) and (b) are also valid for SR tubes placed inside the air reactor. On the other hand, differences are observed in the effects of the oxygen carrier conversion and Fe_2O_3 content on the temperature difference between the air and fuel reactors. The results obtained when placing the reformer tubes inside the air reactor are shown in Fig. 12. As when placing the reformer tubes in the fuel reactor, when the ΔX_{OC} and/or the Fe_2O_3 content is higher, the solids circulation rate is lower and therefore there is a higher temperature difference between the air reactor and the fuel reactor.

In the case of the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system, reduction with CH_4 (R4) means that the reactions taking place inside the fuel reactor are endothermic. Therefore, an increase in ΔT means the fuel reactor temperature falling below the air reactor temperature, which was established at 900°C. As discussed above, iron-based materials tested with PSA-tail gas

cannot completely convert fuel gases to CO_2 and H_2O at temperatures below 880°C [9]. This means that there is an upper limit of $\Delta T = 20^\circ\text{C}$ in order for the fuel reactor temperature to be higher than 880°C . If the lower limit is considered due to the maximum circulation flow rate of $6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$, the permitted conditions are restricted to a narrow region defined by $\Delta X_{\text{OC-Fe}_2\text{O}_3}$ content pairs, as shown in Fig. 12 (a).

The same trend was observed for the $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$ system; see Fig. 12 (b). However, in this case, the temperature in the fuel reactor is higher than in the air reactor, due to the exothermic nature of the reduction of the Fe_2O_3 to $\text{FeO}\cdot\text{Al}_2\text{O}_3$ with CH_4 (R8). Due to this fact, the ΔT parameter is negative. Here there is not an upper limit for ΔT , and only the lower limit defined by the maximum solids circulation rate allowed should be considered; see Fig. 12 (b).

Fig. 13 (a) shows the effect of the oxygen carrier circulation flow rate on the percentage of CH_4 diverted to the fuel reactor to enable it to operate in autothermal conditions, with different Fe_2O_3 contents, for the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system. The results are the opposite of those found observed when the SR tubes were placed in the fuel reactor. A decrease of $\dot{m}_{\text{OC}}$ involves lowering the fuel reactor temperature below the temperature in the air reactor. Therefore, less CH_4 is diverted to the fuel reactor in order to maintain the temperature required in the air and fuel reactors under autothermal conditions.

Fig. 13 (b) shows the effect of the solids circulation flow rate on the percentage of CH_4 diverted to the fuel reactor in order for it to work in autothermal conditions, at different Fe_2O_3 contents and with reduction to $\text{FeO}\cdot\text{Al}_2\text{O}_3$. In this case, a similar trend is observed as when the reformer tubes are placed in the fuel reactor: a lower solids circulation rate means a higher temperature difference between reactors. Here, the fuel

reactor temperature rises above the air reactor temperature and therefore more CH_4 must be fed directly into fuel reactor to enable this temperature increase.

The limits for the upper circulation flow rate and the lower circulation flow rate (presented here only in the case of the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system) are also shown in Figs. 13 (a) and (b). These limits are related to the restrictions imposed on the CLC system in terms of the solids circulation and the fuel reactor temperature, respectively, as commented in the discussion of Figs. 8 and 12.

Fig. 14 (a) shows the effect of the oxygen carrier conversion X_{CH_4} on the H_2 production per mol of CH_4 fed with the reformer tubes placed inside the air reactor with different Fe_2O_3 contents when reducing to Fe_3O_4 . An increase in ΔX_{OC} and/or the Fe_2O_3 content involves an increase in the H_2 production. As seen in Fig. 12 (a), an increase in the ΔX_{OC} and/or the Fe_2O_3 content means a decrease in the fuel reactor temperature as a result of the increase of the endothermic nature of (R4). Consequently, the gas coming from the fuel reactor will have a lower temperature, and therefore the heat extracted from this stream, Q_{ext_5} in Fig. 1 (c), is lower. Eventually the H_2 yield increases with ΔX_{OC} or the Fe_2O_3 content to remain steady at 1 MW, the sum of thermal and chemical power.

The reverse trend, and therefore lower H_2 production with the ΔX_{OC} value, is found for the $\text{Fe}_2\text{O}_3/\text{FeO} \cdot \text{Al}_2\text{O}_3$ system; see Fig. 14 (b). An increase in the ΔX_{OC} and/or the Fe_2O_3 content means an increase in the fuel reactor temperature as a result of the enhancement of the exothermic nature of (R8). Consequently, the gas extracted from the fuel reactor is at higher temperature, and therefore the heat extracted from this stream, Q_{ext_5} in Fig. 1 (c), will be higher, resulting in a lower amount of H_2 produced.

Restrictions with respect to the oxygen carrier circulation flow rate and the fuel reactor temperature are shown in Figs 14 (a) and (b). The operational conditions permitted for the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system are highly restrictive and correspond to a $\dot{m}_{\text{OC}}$ value of around $6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$. This zone could be expanded if a higher oxygen carrier circulation flow and/or a lower temperature in fuel reactor could be used. Nevertheless, a maximum H_2 yield of 2.41 mol of H_2 per mol of CH_4 can be obtained with a 20 wt.% of Fe_2O_3 and $\Delta X_{\text{OC}} = 1$. A higher Fe_2O_3 content means that the fuel reactor temperature is below 880°C and unconverted products could appear from the fuel reactor [9]. This limitation would be overcome if complete combustion was reached at lower temperatures, either by increasing the oxygen carrier reactivity or increasing the solids inventory in the fuel reactor. Nevertheless, no major restrictions were found for the $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$ system.

4. Discussion

Table 1 shows the main results obtained from the two possible configurations of the SR-CLC process, i.e., with the reformer tubes placed in the fuel reactor or in the air reactor, using the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ or $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$ systems. The table shows the best results obtained in accordance with the restrictions imposed, except in the case of reduction to Fe_3O_4 and with the reformer tubes inside the air reactor. In this particular case, the H_2 production was the highest and the results obtained in the unsuitable and suitable conditions with two extreme Fe_2O_3 contents are shown.

These results show that the best configuration is with the reformer tubes inside the air reactor. This is because in this case the heat needed for the reforming reaction is generated inside the air reactor itself and it is therefore not necessary to transport the heat through the solids, which is the case when the reformer tubes are placed in the fuel reactor. However, in the latter configuration higher erosion of the reformer tubes is

expected owing to the higher fluidisation velocities used. Furthermore, with the tubes placed in the air reactor, a slightly higher H_2 production is expected and it is necessary to divert less CH_4 to the fuel reactor. However, with higher values of ΔX_{OCs} and Fe_2O_3 content, the fuel reactor temperature drop means it is necessary to use a highly reactive oxygen carrier for lower temperatures.

A higher H_2 production is obtained when placing the reformer tubes in air reactor and with the Fe_2O_3/Fe_3O_4 system. This is the only case where, in order to fulfil the heat balance, the temperature of the fuel reactor decreases owing to the global endothermic nature of the reduction of Fe_2O_3 or Fe_3O_4 with CH_4 , and, therefore, the gases leave the fuel reactor at a temperature below the fixed temperature outside the reformer tubes ($900^\circ C$). Then H_2 production is higher. The best H_2 production obtained using this method is 2.45 mol per mol of CH_4 , using an oxygen carrier with a Fe_2O_3 content of 100 wt.% and with $\Delta X_{OC} = 1$. This is the limit value. However, in more realistic conditions, with a Fe_2O_3 content of 60 wt.% and $\Delta X_{OC} = 0.5$, a value of 2.43 mol H_2 per mol of CH_4 can be obtained. Conversion to H_2 is defined as the fraction of the chemical power present in H_2 produced compared to chemical power of the total CH_4 fed into the system. Chemical power means the thermal power when the fuel is burnt in air. A 100% value for conversion to H_2 corresponds to 3.3 H_2 mol per mol of CH_4 . The conversion to H_2 is 74.2% in this case, with 100% CO_2 capture. However, to reach this H_2 production, a value of $\Delta T = 115^\circ C$ is needed, see Fig. 12 (a), i.e. a fuel reactor temperature of $785^\circ C$. As the lowest temperature in the fuel reactor was set at $880^\circ C$, in order to obtain a complete combustion of the fuel gases [9], the maximum production should be obtained with an oxygen carrier with a Fe_2O_3 content of 20 wt.% and $\Delta X_{OC} = 100$; see Fig. 12 (a). The conversion to H_2 is 73.0% in this case, with 100% CO_2 capture. Autothermal chemical looping reforming (CLRa) has the capacity to produce around 2.7 mol H_2 per

mol of CH_4 [3.6] at atmospheric pressure, which is an 81.8% of conversion to H_2 . This value is higher than the one obtained for the SR-CLC process. However, at 15 bar this value is reduced to 2.5 [18].

The optimum conversion to H_2 obtained in this experiment was similar to that obtained with state-of-the-art SR technologies with MDEA [19], but in this case the carbon capture rate was 83%. Advanced ATR technologies are able to produce 74% of conversion efficiencies with a carbon capture of 90% [19]. Thus, SR-CLC seems to be a competitive technology for H_2 production under conditions where there are restrictions on CO_2 emissions. Furthermore, SR-CLC produces surplus energy, which could be used for electricity production or to supply heat to another adjacent process.

5. Conclusions

Mass and enthalpy balances were carried out to determine the autothermal operating conditions that maximise H_2 production in a SR-CLC system operating with iron-based oxygen carriers. The reduction of Fe_2O_3 to Fe_3O_4 or FeO was analysed. Two different configurations –the reformer tubes placed inside the fuel reactor or inside the air reactor– were also studied. The study was conducted varying two main operating parameters affecting the H_2 yields, namely the conversion of CH_4 in the reforming process (X_{CH_4}) and the efficiency of the PSA separation unit (η_{PSA}), as well the effect of CLC system parameters on the H_2 yield of the SR-CLC system, namely the conversion variation of the oxygen carrier (ΔX_{OC}) and its Fe_2O_3 content.

It is concluded that H_2 production increases as X_{CH_4} and η_{PSA} increases. Moreover, autothermal conditions are favourable for maximising H_2 production. Under these conditions, heat is not extracted from the CLC system itself, but some CH_4 from the fuel stream must be diverted to the fuel reactor to fulfil the enthalpy balance.

The H_2 production depends on the operating temperature of the fuel and/or air reactors.

Lower reactors temperatures yield a higher H_2 production. H_2 production is maximised when the reformer tubes are placed in the air reactor and Fe_2O_3 is reduced to Fe_3O_4 . At the values of $X_{CH_4} = 80 \%$ and $\eta_{PSA} = 90 \%$, a maximum hydrogen yield of 2.45 mol H_2 per mol of CH_4 can be reached with inherent CO_2 capture in the SR-CLC process.

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Nomenclatures

$C_{p,i}$ heat capacity of the compound i , $\text{kJ mol}^{-1} \text{K}^{-1}$

F_i molar flow of compound i , mol s^{-1}

h_i enthalpy of component i , kJ mol^{-1}

H_{reac} enthalpy flow of the reactants (solids and gases), kJ s^{-1}

H_{prod} enthalpy flow of the products (solids and gases), kJ s^{-1}

K_{WGS} equilibrium constant of the WGS reaction

m_{ox} mass of the oxidised oxygen carrier, kg

m_{red} mass of the reduced oxygen carrier, kg

$\dot{m}_{\text{OC}}$ solids circulation flow rate, kg s^{-1}

$\dot{m}_{\text{OC},\text{up}}$ upper limit for solids circulation flow rate, $\text{kg s}^{-1} \text{MW}^{-1}$

M_i atomic or molecular mass of compound i , kg mol^{-1}

Q_{in_i} heat flux supplied to the point i , kJ s^{-1}

Q_{ext_i} heat flux extracted from the point i , kJ s^{-1}

Q_{rec} flux of enthalpy recovered from the SR-CLC system (kJ s^{-1})

R_{OC} oxygen transport capacity of the oxygen carrier

T temperature, K

X_{CH_4} methane conversion in the reformer tubes

Greek symbols

ΔH_i variation of enthalpy, kJ s^{-1}

ΔH_r^o standard reaction enthalpy, kJ s^{-1}

ΔT temperature difference between fuel and air reactors, K

ΔX_{OC} conversion variation of the oxygen carrier

λ air excess ratio

η_{PSA} hydrogen separation efficiency in the PSA unit

Abbreviations

AR air reactor

CLC chemical looping combustion system

div diverted flow

FR fuel reactor

in inlet stream

OC oxygen carrier

out outlet stream

prod product

PSA pressure swing adsorption unit

reac reactant

SR steam reforming reactor

SR-CLC steam reforming integrated in the chemical looping combustion system

T total flow

tail tail stream from the PSA unit

WGS water gas shift reactor

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Captions for tables and figures

Table 1. Summary of results obtained from the evaluation of the SR-CLC system.

Fig. 1. Diagram of: (a) CLC system; (b) SR-CLC system with the reformer tubes inside the fuel reactor with the energy inputs and outputs; (c) SR-CLC system with the reformer tubes inside the air reactor with the energy inputs and outputs.

Fig. 2. Effect of X_{CH_4} on the required enthalpy flux extracted from or supplied to the air reactor of a SR-CLC, i.e. Q_{ext_8} , at different values of η_{PSA} . -●- autothermal conditions. Fe_2O_3/Fe_3O_4 system. $\Delta X_{OC}=0.5$. $Fe_2O_3 = 20$ wt%. SR tubes inside the fuel reactor.

Fig. 3. Regions defined by X_{CH_4} - η_{PSA} pairs where the air reactor of a SR-CLC system operates with excess of energy ($Q_{ext_8} < 0$) or deficit of energy ($Q_{ext_8} > 0$). Autothermal conditions ($Q_{ext_8} = 0$): - - - - - Fe_2O_3/Fe_3O_4 system. $\Delta X_{OC}=0.5$. $Fe_2O_3 = 20$ wt%. SR tubes inside the fuel reactor.

Fig. 4. Effect of X_{CH_4} on the necessary percentage of diverted CH_4 flow to the fuel reactor to operate in autothermal conditions at different values of η_{PSA} . Fe_2O_3/Fe_3O_4 system. $\Delta X_{OC}=0.5$. $Fe_2O_3 = 20$ wt.%. SR tubes inside the fuel reactor.

Fig. 5. Effect of X_{CH_4} on the H_2 production per mol of total CH_4 fed to the SR-CLC system at different values of η_{PSA} . Fe_2O_3/Fe_3O_4 system. $\Delta X_{OC}=0.5$. $Fe_2O_3 = 20$ wt%. SR tubes inside the fuel reactor.

Fig. 6. Effect of X_{CH_4} on the oxygen carrier circulation flow rate at different values of η_{PSA} when reduction of Fe_2O_3 to Fe_3O_4 or $FeO \cdot Al_2O_3$ is considered. $\Delta X_{OC}=0.5$. $Fe_2O_3 = 20$ wt.%. SR tubes inside the fuel reactor.

Fig. 7. Effect of X_{CH_4} on the temperature difference between the air and fuel reactors at different values of η_{PSA} : (a) reformer tubes inside the fuel reactor; (b) reformer tubes inside the air reactor. $\Delta X_{OC}=0.5$. $Fe_2O_3 = 20$ wt%. Unsuitable conditions due to $T_{FR} < 880^\circ C$: (only for the Fe_2O_3/Fe_3O_4 system).

Fig. 8. Effect of the oxygen carrier conversion and the Fe_2O_3 content in the oxygen carrier on the oxygen carrier circulation flow rate at autothermal conditions. (a) Fe_2O_3/Fe_3O_4 system; (b) $Fe_2O_3/FeO \cdot Al_2O_3$ system. $X_{CH_4} = 80\%$, $\eta_{PSA} = 90\%$. SR tubes inside the fuel reactor. Unsuitable conditions due to $\dot{m}_{OC} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: .

Fig. 9. Effect of the oxygen carrier conversion on the temperature difference between the air and fuel reactors with different Fe_2O_3 contents at autothermal conditions. (a) Fe_2O_3/Fe_3O_4 system; (b) $Fe_2O_3/FeO \cdot Al_2O_3$ system. Tubes inside the fuel reactor. $X_{CH_4} = 80\%$, $\eta_{PSA} = 90\%$. SR tubes inside the fuel reactor. Unsuitable conditions due to $\dot{m}_{OC} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: ; unsuitable conditions due to $\Delta T > 200^\circ C$, i.e. $T_{AR} > 1100^\circ C$: .

Fig. 10. Effect of the oxygen carrier circulation flow rate on the percentage of CH_4 diverted to the fuel reactor needed to operate at autothermal conditions for different Fe_2O_3 contents. (a) $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system; (b) $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$. Reformer tubes inside the fuel reactor. $X_{\text{CH}_4} = 80\%$, $\eta_{\text{PSA}} = 90\%$. Unsuitable conditions due to $\dot{m}_{\text{OC}} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: . Unsuitable conditions due to $\Delta T > 200^\circ\text{C}$, i.e. $T_{\text{AR}} > 1100^\circ\text{C}$: .

Fig. 11. Effect of the oxygen carrier conversion on H_2 production per mol of CH_4 fed at different Fe_2O_3 contents at autothermal conditions. (a) $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system; (b) $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$. Reformer tubes inside fuel reactor. $X_{\text{CH}_4} = 80\%$, $\eta_{\text{PSA}} = 90\%$. Unsuitable conditions due to $\dot{m}_{\text{OC}} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: . Unsuitable conditions due to $\Delta T > 200^\circ\text{C}$, i.e. $T_{\text{AR}} > 1100^\circ\text{C}$: .

Fig. 12. Effect of the oxygen carrier conversion on the temperature difference between the air and fuel reactors at different Fe_2O_3 contents, at autothermal conditions. (a) $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system; (b) $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$ system. Reformer tubes inside the air reactor. $X_{\text{CH}_4} = 80\%$, $\eta_{\text{PSA}} = 90\%$. Unsuitable conditions due to $\dot{m}_{\text{OC}} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: . Unsuitable conditions due to $T_{\text{FR}} < 880^\circ\text{C}$: .

Fig. 13. Effect of the oxygen carrier circulation flow rate on the percentage of CH_4 diverted to the fuel reactor required for it to operate in autothermal conditions at different Fe_2O_3 contents: (a) $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system; (b) $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$ system. Reformer tubes inside the air reactor. $X_{\text{CH}_4} = 80\%$, $\eta_{\text{PSA}} = 90\%$. Unsuitable conditions due to $\dot{m}_{\text{OC}} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: . Unsuitable conditions due to $T_{\text{FR}} < 880^\circ\text{C}$: .

Fig. 14. Effect of the oxygen carrier conversion on H_2 production per mol of CH_4 fed at different Fe_2O_3 contents: (a) Fe_2O_3/Fe_3O_4 system, (b) $Fe_2O_3/FeO \cdot Al_2O_3$ system.

Reformer tubes inside the air reactor. $X_{CH_4} = 80\%$, $\eta_{PSA} = 90\%$. Unsuitable conditions

due to $\dot{m}_{OC} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: . Unsuitable conditions due to $T_{FR} < 880^\circ\text{C}$:

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Table 1. Summary of results obtained from the evaluation of the SR-CLC system.

	Reformer tubes in fuel reactor		Reformer tubes in air reactor		
	Fe ₂ O ₃ /Fe ₃ O ₄	Fe ₂ O ₃ /FeO·Al ₂ O ₃	Fe ₂ O ₃ /Fe ₃ O ₄	Fe ₂ O ₃ /FeO·Al ₂ O ₃	
Fe ₂ O ₃ (wt %)	20	10	100	20	10
ΔX_{OC} (%)	0.8	0.5	1	1	0.5
$\dot{m}_{OC}$ (kg s ⁻¹ MW ⁻¹)	6.1	6.4	0.9	4.8	6.4
ΔT (°C)	54	28	115	19	-8
CH ₄ to fuel reactor (%)	17.5	17.0	14.9	16.2	16.6
H ₂ (mol/mol CH ₄)	2.37	2.39	2.45	2.41	2.40
Conversion to H ₂ (%)	71.8	72.4	74.2	73.0	72.7
Q_{rec} (MW/MW _{th} CH ₄)	0.136	0.132	0.113	0.125	0.128

Fig. 1. Diagram of (a) CLC system; (b) SR-CLC system with the reformer tubes inside the fuel reactor with energy inputs and outputs & (c) SR-CLC system with the reformer tubes inside the air reactor with the energy inputs and outputs.

Fig. 2. Effect of X_{CH_4} on the required enthalpy flux extracted or supplied to the air reactor of a SR-CLC, i.e. Q_{ext_g} , at different values of η_{PSA} . -●- autothermal conditions.

Fe_2O_3/Fe_3O_4 system. $\Delta X_{OC}=0.5$. $Fe_2O_3 = 20$ wt.%. SR tubes inside the fuel reactor.

Fig. 3. Regions defined by X_{CH_4} - η_{PSA} pairs where the air reactor of a SR-CLC system operates with an excess of energy ($Q_{ext_8} < 0$) or deficit of energy ($Q_{ext_8} > 0$). Autothermal conditions ($Q_{ext_8} = 0$): ----- Fe_2O_3/Fe_3O_4 system. $\Delta X_{OC} = 0.5$. $Fe_2O_3 = 20$ wt.%. SR tubes inside fuel the reactor.

Fig. 4. Effect of X_{CH_4} on the percentage of CH₄ flow diverted to the fuel reactor required to operate in autothermal conditions at different values of η_{PSA} . Fe₂O₃/Fe₃O₄ system. $\Delta X_{OC}=0.5$. Fe₂O₃ = 20 wt %. SR tubes inside the fuel reactor.

Fig. 5. Effect of X_{CH_4} on the H_2 production per mol of total CH_4 fed to the SR-CLC system at different values of η_{PSA} . Fe_2O_3/Fe_3O_4 system. $\Delta X_{OC}=0.5$. $Fe_2O_3 = 20$ wt %. SR tubes inside the fuel reactor.

Fig. 6. Effect of X_{CH_4} on the oxygen carrier circulation flow rate at different values of η_{PSA} with the reduction of Fe_2O_3 to Fe_3O_4 or $FeO \cdot Al_2O_3$. $\Delta X_{OC}=0.5$. $Fe_2O_3 = 20$ wt %. SR tubes inside the fuel reactor.

Fig. 7. Effect of X_{CH_4} on the temperature difference between the air and fuel reactors at different values of η_{PSA} : (a) reformer tubes in the fuel reactor; (b) reformer tubes inside the air reactor. $\Delta X_{OC}=0.5$. $Fe_2O_3 = 20$ wt %. Unsuitable conditions due to $T_{FR} < 880^\circ C$: (only for the Fe_2O_3/Fe_3O_4 system).

Fig. 8. Effect of the oxygen carrier conversion and the Fe_2O_3 content in the oxygen carrier on the oxygen carrier circulation flow rate at autothermal conditions. (a) $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system; (b) $\text{Fe}_2\text{O}_3/\text{FeO} \cdot \text{Al}_2\text{O}_3$ system. $X_{\text{CH}_4} = 80\%$, $\eta_{\text{PSA}} = 90\%$. SR tubes inside the fuel reactor. Unsuitable conditions due to $\dot{m}_{\text{OC}} > 6.4 \text{ kg s}^{-1} \text{MW}^{-1}$: .

Fig. 9. Effect of the oxygen carrier conversion on the temperature difference between the air and fuel reactors at different Fe_2O_3 contents at autothermal conditions. (a) $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system; (b) $\text{Fe}_2\text{O}_3/\text{FeO} \cdot \text{Al}_2\text{O}_3$ system. SR tubes inside the fuel reactor. $X_{\text{CH}_4} = 80\%$, $\eta_{\text{PSA}} = 90\%$. SR tubes inside the fuel reactor. Unsuitable conditions due to $\dot{m}_{\text{OC}} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: ; unsuitable conditions due to $\Delta T > 200^\circ\text{C}$, i.e. $T_{\text{AR}} > 1100^\circ\text{C}$: .

Fig. 10. Effect of the oxygen carrier circulation flow rate on the percentage of CH_4 diverted to the fuel reactor required to operate at autothermal conditions for different Fe_2O_3 contents (wt %). (a) Fe_2O_3/Fe_3O_4 system; (b) $Fe_2O_3/FeO \cdot Al_2O_3$. Reformer tubes inside the fuel reactor. $X_{CH_4} = 80\%$, $\eta_{PSA} = 90\%$. Unsuitable conditions due to $\dot{m}_{OC} > 6.4$ kg s⁻¹ MW⁻¹: . Unsuitable conditions due to $\Delta T > 200^\circ C$, i.e. $T_{AR} > 1100^\circ C$: .

Fig. 11. Effect of the oxygen carrier conversion on H_2 production per mol of CH_4 fed at different Fe_2O_3 contents (wt %) at autothermal conditions. (a) Fe_2O_3/Fe_3O_4 system; (b) $Fe_2O_3/FeO \cdot Al_2O_3$ system. Reformer tubes inside the fuel reactor. $X_{CH_4} = 80\%$, $\eta_{PSA} = 90\%$. Unsuitable conditions due to $\dot{m}_{OC} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: . Unsuitable conditions due to $\Delta T > 200^\circ\text{C}$, i.e. $T_{AR} > 1100^\circ\text{C}$: .

Fig. 12. Effect of the oxygen carrier conversion on the temperature difference between the air and fuel reactors at different Fe_2O_3 contents, at autothermal conditions. (a) $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system; (b) $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$ system. Reformer tubes inside the air reactor. $X_{\text{CH}_4} = 80\%$, $\eta_{\text{PSA}} = 90\%$. Unsuitable conditions due to $\dot{m}_{\text{OC}} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$:

■. Unsuitable conditions due to $T_{\text{FR}} < 880^\circ\text{C}$: ▨.

Fig. 13. Effect of the oxygen carrier circulation flow rate on the percentage of CH_4 diverted to the fuel reactor required to operate in autothermal conditions at different Fe_2O_3 contents (wt %). (a) $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ system; (b) $\text{Fe}_2\text{O}_3/\text{FeO}\cdot\text{Al}_2\text{O}_3$. Reformer tubes inside the air reactor. $X_{\text{CH}_4} = 80\%$, $\eta_{\text{PSA}} = 90\%$. Unsuitable conditions due to $\dot{m}_{\text{OC}} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: . Unsuitable conditions due to $T_{\text{FR}} < 880^\circ\text{C}$: .

Fig. 14. Effect of the oxygen carrier conversion on H_2 production per mol of CH_4 fed at different Fe_2O_3 contents (wt %). (a) Fe_2O_3/Fe_3O_4 system; (b) $Fe_2O_3/FeO \cdot Al_2O_3$ system. Reformer tubes inside the air reactor. $X_{CH_4} = 80\%$, $\eta_{PSA} = 90\%$. Unsuitable conditions due to $\dot{m}_{OC} > 6.4 \text{ kg s}^{-1} \text{ MW}^{-1}$: [shaded area]. Unsuitable conditions due to $T_{FR} < 880^\circ\text{C}$: [hatched area].