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1D modelling of membrane-assisted chemical looping reforming

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Abstract

Membrane-assisted chemical looping reforming (MA-CLR) has been proposed as an alternative to the conventional CLR technology. In this work, a non-isothermal 1D model is used to simulate the MA-CLR fuel reactor. The effect of the resulting axial temperature gradients on the reactor performance is assessed, showing up to 10% declines in reactor performance (hydrogen extraction and fuel slip).The inclusion of the energy balance therefore appears to be important for this application, despite the high degree of mixing achievable in fluidized beds.

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*Keywords:*CCS; Chemical-looping reforming; fluidized bed; membrane; phenomenological model

1. Introduction

The combustion of fossil fuels constitutes the main source for CO_2 emissions to the atmosphere. According to the IPCC fifth assessment report, it corresponds approximately to 78% of the total greenhouse gases emissions[1]. Hence, strategies to reduce this GHG emission are among of the most critical matters in research given the current high concern on climate change. Considering the 2°C scenario (2DS) that foresees a maximum global temperature increase

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of 2°C (limit to avoid catastrophic changes on earth), energy and process-related CO_2 emissions should be cut by almost 60% by 2050 compared to 2012[2, 3].

Hydrogen is considered as a promising carbon-free energy carrier to facilitate a large reduction in energy-related greenhouse gas emissions[4, 5]. Unfortunately, the current hydrogen production at industrial scale is mostly fossil-fuel based by steam methane reforming (SMR) of natural gas and coal gasification that results in about 500 Mt CO_2 per year[2]. To reduce these CO_2-emissions, the integration of hydrogen production from fossil fuels with CO_2 capture and storage (CCS) has been suggested as a key transition technology[2, 6-8].

The current work focusses on the Chemical Looping Reforming (CLR) concept for methane reforming with integrated CO_2 capture. This process is based on the known Chemical Looping Combustion (CLC) technology where an oxygen carrier (usually a metal oxide) circulates between two interconnected reactor units to transfer oxygen for the fuel combustion from the air reactor (AR) to the fuel reactor (FR)[9-11]. Therefore, in the AR the oxygen carrier (OC) is oxidized by a stream of air and in the FR it is reduced converting the fuel to CO_2 and H_2O in conventional CLC technology and syngas in CLR. In CLR, another important role of the oxygen carrier is to transport heat from the air reactor to the fuel reactor where the endothermic reforming reaction takes place.

The syngas produced by the CLR process still requires additional processing to produce a pure H_2 stream. These additional units can be avoided through the use of H_2 perm-selective membranes to extract pure hydrogen directly from the reforming reactor. Thus, a membrane-assisted (MA) design has been presented as an alternative to the conventional CLR[4]. Membrane-assisted chemical looping reforming (MA-CLR) follows the same principles as conventional CLR, but with membranes introduced inside the fuel reactor. Hence, it employs two fluidized beds (FR and AR) with an oxygen carrier circulating between them to supply oxygen for combustion and heat to the endothermic reforming reaction while avoiding fuel/nitrogen mixing. The produced H_2 from the reforming reactions permeates through the membranes, enhancing the CH_4 conversion.

The foundation of this work relies on a previous study by Morgado et al. (2017)[12] where a 1D generic phenomenological model based on the probabilistic approach developed by Thompson et al.[13] has been presented and used to simulate two CLR technologies. In this work, the model presented in[12] has been extended to incorporate membranes. Recently, Spallina et al.[14] conducted studies on the techno-economic assessment of MA fluidized bed reactors (FBRs) for H_2 production with CO_2 capture. Highly favorable economics were presented for the MA-CLR concept (CO_2 avoidance cost of *negative* 30€/ton). In their work, 1D phenomenological modelling is also used to describe the MA-CLR fuel reactor, but the reactor was assumed to be isothermal. The present work includes the energy balance into the 1D model and models the axial dispersion of heat from the heated solids entering from the top of the fuel reactor to the endothermic reaction taking place in the lower regions. Hence, the main objective of the present work is to quantify the effect of non-isothermal conditions (leading to an axial temperature gradient in the bed) on the performance of the MA-CLR fuel reactor.

Nomenclature

E_A	Activation Energy (J/mol)
F_{H_2}	Hydrogen permeation flux (mol/m^{2}s)
LHV	Lower heating value (kJ/mol)
$\dot{n}$	Molar flowrate (mol/s)
P_0	Permeability (mol/m^{2}sPa$^{0.74}$)
P_{H_2}	Hydrogen partial pressure (Pa)
R	Universal gas constant (m^3 Pa/K mol)
S_{fuel}	Fuel slip performance measure (-)
T	Temperature (K)
t_m	Membrane thickness (m)
X_{H_2}	Hydrogen productivity performance measure (-)

Superscripts/subscripts:

ext	Extracted
in	Inlet
out	Outlet
perm	Permeate side
ret	Retentate side

2. Simulation

The MA-CLR reactor was simulated using the developed standalone in-house MATLAB code described in detail in [12]. As aforementioned, the main feature in the present work is the inclusion of the membranes in the code that is described below.

2.1. Model extension: Counter-current configuration

When membranes are added to the CLR fuel reactor, a counter-current configuration enhances the reactor performance. Adding the fresh (oxidized) stream of OC at the top of the FR permits complete utilization of the fuel. The fuel gases that are not reformed and shifted to hydrogen and extracted via the membranes can slip past the membranes to reduce the OC entering from the top of the reactor. This advantage of complete fuel utilization is not possible in a co-current configuration.

2.2. Model assumptions

Important physical properties and simulation parameters are presented in Table 1 and are based on reference [14].

Table 1. Important physical properties and simulation parameters

Particle density	3451 kg/m^3
Particle diameter	250 µm
Particle heat capacity	1200 J/ kg K
Reactor diameter	1.26 m
Reactor height	13 m
Outlet pressure	49.5 bar
Axial resolution	30 volume cells (nodes)
Gas inlet flowrate	7.52 kg/s
Solids inlet flowrate	132.66 kg/s
Gas inlet temperature	454.2 °C
Solids inlet temperature	900°C

Unlike in [14], we assume the reactor to have constant cross section area by assuming the length of the membrane tubes to be equal to the reactor height. Although we retain the assumption that H_2 can only permeate through the membranes up to 10.2 m.

In the present study, Pd-membranes are considered and therefore Sievert´s law is used to model the H_2 permeation [14, 15] . The introduction of membranes has an effect on the hydrodynamics of the reactor (as internals) and mainly restrict bubble growth that consequently reduces the bubble rise velocity and enhances bubble-to-emulsion mass transfer [14, 16]. Although this changes, the same list of closure laws used in [14] was considered. In equation 1, P_0 = 4.24×10^{-10}, E_A = 5.81×10^3 and t_m =5×10^{-6}.

$$F_{H_2} = \frac{P_0}{t_m} e^{\left(\frac{-E_A}{RT}\right)} \left(P_{H_2,ret}^{0.74} - P_{H_2,perm}^{0.74} \right) \tag{1}$$

3. Performance measures

The reactor performance will be quantified via two general performance measures. Firstly, the H_2 productivity that is defined as the ratio of the total hydrogen extracted to the total hydrogen potential.

$$X_{H_2} = \frac{\dot{n}_{H_2}^{ext}}{4\dot{n}_{CH_4}^{in} + \dot{n}_{H_2}^{in}} \tag{2}$$

Secondly, the amount of fuel slip from the reactor is quantified in terms of the lower heating value that is lost with the fuel gases slipping out of the reactor without being extracted as hydrogen or used to reduce the OC.

$$S_{fuel} = \frac{\dot{n}_{CH_4}^{out} LHV_{CH_4} + \dot{n}_{H_2}^{out} LHV_{H_2} + \dot{n}_{CO}^{out} LHV_{CO}}{\dot{n}_{CH_4}^{in} LHV_{CH_4} + \dot{n}_{H_2}^{in} LHV_{H_2}} \tag{3}$$

4. Results and discussion

To gain confidence on the generic 1D phenomenological model used in this work and to ensure that the new features in the model have been correctly implemented, a virtually isothermal case (using high effective thermal conductivity) was conducted to mimic the work by Spallina et al. [14]. The simulation results are presented in Fig. 1 and it is verified that the model results agree with those of Spallina et al.[14].

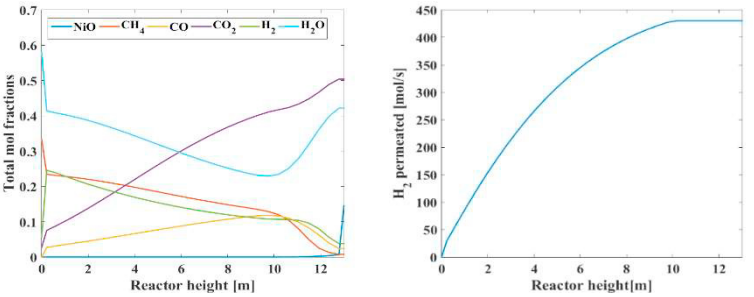

Fig. 1. Species composition profile (left) and permeated H_2 through the membrane (right) along the height of the reactor for the MA-CLR fuel reactor under isothermal conditions

When closure laws from literature are used to define the effective thermal conductivity based on the solids dispersion coefficient[17, 18], temperature gradients are observed along the fluidized bed. It leads to high temperatures in the upper region of the reactor that may compromise the membranes (Fig. 2).

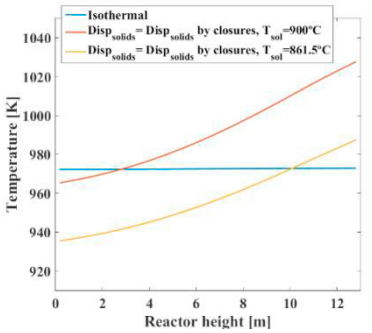

Fig. 2. Temperature profile along the reactor height for the isothermal case and using closures laws to define the effective thermal conductivity

Considering Pd-based membranes, a maximum temperature limit of 700°C is assumed. Fig. 2 shows the temperature profile along the height of the reactor. By comparing the isothermal case given by the blue line against the case using thermal conductivity models for the same inlet OC temperature (red line) it is observed that at 3 m the temperature exceeds the limit given by the membranes. In order to limit the temperature to 700°C where membranes are present (lower 10.2 m of the reactor), the OC inlet temperature has to be reduced. The yellow line represents the temperature profile when this temperature constrain is satisfied by reducing the OC inlet temperature by about 4%.

Given the uncertainty related to the effective thermal conductivity (K_{eff}) model, a sensitivity analysis has been conducted by changing the effective thermal conductivities to double and half the model prediction. In particular, the unknown effect of internal obstructions on axial mixing in such a very tall bed introduces significant uncertainty. These changes where employed in the solids dispersion that is proportional to the effective thermal conductivity. The main results obtained from this analysis are presented in Fig. 3 and Fig. 4.

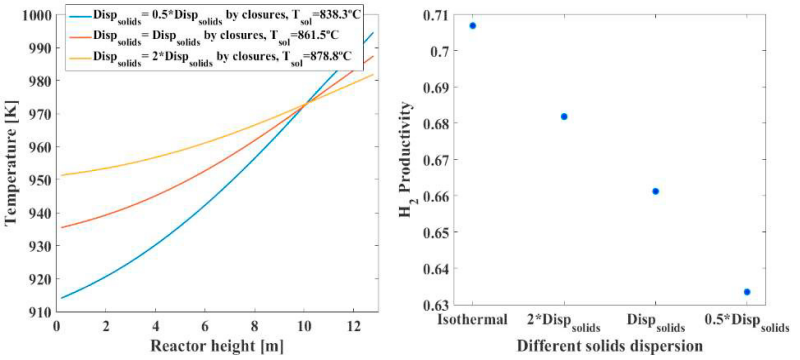

Fig. 3. Left side: Temperature profile along the reactor height for different thermal conductivities; Right side: Hydrogen productivity

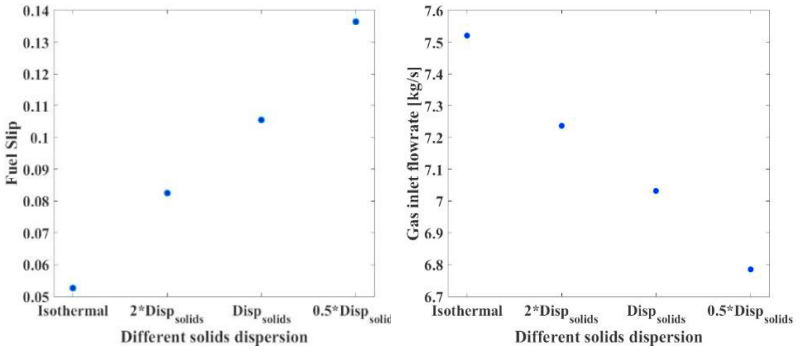

Fig. 4. Fuel slip (left) and Gas flowrate required to meet same H_2 productivity of the isothermal case (right) for different thermal conductivities

Higher effective thermal conductivity results in a lower temperature gradient along the fluidized bed. This relation is clearly observed in Fig. 3 where a lower OC temperature is required for $0.5*K_{eff}$ to satisfy the membrane temperature constraints and vice versa. Fig. 3 (right) shows that the H_2 productivity is higher for higher thermal conductivities. The temperaturein the reactor up to 10.2 m is higher in this case favoring the endothermic reforming reactions and increasing membrane permeability. Neglecting the thermal gradient along the bed would result in an overestimation of the H_2 productivity of about 7%. The reduced hydrogen extraction leaves more fuel to react with the oxygen carrier, causing more unconverted fuel to slip out of the reactor Fig. 4 (left).

In practice, a higher gas residence time will be required to meet the H_2 productivity predicted by isothermal reactor modelling. Fig. 4 (right) shows the required gas flowrates and it is verified that, when using K_{eff} models, the gas flowrate needs to decrease by the considerable amount of 0.3-0.8 kg/s in order to ensure good reactor performance.

5. Summary and conclusions

In this work, the effect of the non-isothermal conditions on the MA-CLR fuel reactor was studied. The in-situ generic 1D model was used to simulate the process and it employs effective thermal conductivity models from literature. Sensitivity studies were carried out by varying the effective thermal conductivity to double and half ($2*K_{eff}$ and $0.5*K_{eff}$) of the predicted value. The results from the study showed that considering temperature gradients is important for the reactor design parameters and has an impact on the reactor performance. In particular, the axial temperature gradient developing inside the reactor can enforce a ~10% lower gas throughput than predicted by isothermal reactor modelling.

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