DYNAMIC MODEL OF SINGLE-REACTOR CHEMICAL LOOPING COMBUSTION

K. Bizon, G. Continillo
katarzyna.bizon@unisannio.it
Università degli Studi del Sannio, Piazza Roma 21, 82100, Benevento, Italy

Abstract
The paper presents a simplified model of chemical looping combustion in a fixed bed reactor under isothermal condition. Both reduction and regeneration phases of the oxygen carrier are modeled in the single reactor model under the hypothesis of discontinuous feed and simplified reaction kinetics. This model is meant to be the simplest possible formulation for a description that incorporates all essential aspects of this distributed system. In view of real-time applications, further reduction is sought with POD-Galerkin and optimal sampling, yielding a robust reduced model that can be employed as values of the parameters change.

1. Introduction

In recent years, chemical looping combustion (CLC) has received interest due to its huge potential as a CO_2 separation technology. CLC is an indirect fuel combustion strategy in which metal oxide is used, which is an oxygen carrier and a combustion intermediate between the air and the fuel [1], which never mix in the CLC process. This two-step process usually is performed in a system composed of two reactors: an air reactor and a fuel reactor (Fig.1), and a oxygen carrier (M_yO_x) – typically iron, nickel and copper oxide – circulating between them.

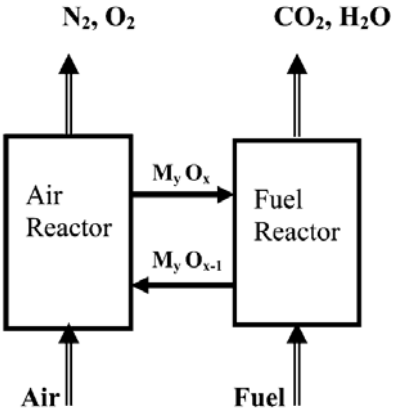

Figure 1. Chemical looping combustion.

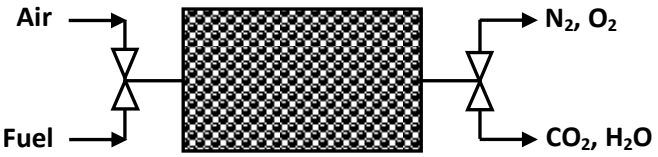

Figure 2. Discontinuous reactor.

A gaseous fuel, usually methane, is introduced into the fuel reactor and is oxidized by the metal oxide according to the global reaction, which can be endothermic as well as exothermic:

$$(2n+m)\,\mathrm{M}_y\mathrm{O}_x + \mathrm{C}_n\mathrm{H}_{2m} \rightarrow (2n+m)\,\mathrm{M}_y\mathrm{O}_{x-1} + n\mathrm{CO}_2 + m\mathrm{H}_2\mathrm{O} \qquad (1)$$

This reaction corresponds to the complete oxidation of the fuel to CO_2 and H_2O. The reduced oxygen carrier is then re-oxidized in the air reactor according to exothermic reaction:

$$\mathrm{M}_y\mathrm{O}_{x-1} + \tfrac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{M}_y\mathrm{O}_x \qquad (2)$$

The CLC process must be well designed to couple the air and fuel reactors efficiently, hence availability of models for improving design and scale up is desirable. Some attempt so modeling of the process on different level of sophistication has been done recently concerning both system based on fixed bed reactors [2] and interconnected fluidized bed reactors [2,3]. Here, on the basis of the model for the reduction phase presented in Reference [2] a simplified model of for reduction and regeneration of the oxygen carrier in the fixed bed reactor under isothermal condition is presented. A single reactor with discontinuous feed is considered (Figure 2). This model represents perhaps the simplest possible formulation for a description that incorporates all essential aspects of the system. Yet, in view of real-time applications, further reduction would be necessary. To this aim, Proper Orthogonal Decomposition with Galerkin projection can be used [4,5], and optimal sampling based in presence of chaotic behavior [6], if any, might be usefully exploited in order to generate a robust reduced model that can be employed as values of the parameters change.

2. Reactor model

Under the assumption of plug flow of the gas in the reactor and isothermal conditions [2], the dynamic balance equations expressed in terms of the conversion degree of the oxidized carrier (X_{MO}) and concentration of oxidized carrier (C_{MO}), reduced carrier (C_M), and gaseous fuel (C_F), respectively, for the reduction phase (oxidation of the fuel) are given as:

$$\begin{aligned}
\frac{dX_{\mathrm{MO}}}{dt} &= \frac{a_0\left(1-X_{\mathrm{MO}}\right)}{C'^{0}_{\mathrm{MO}}} k_1 C_{\mathrm{F}} C_{\mathrm{MO}} \\
\frac{dC_{\mathrm{MO}}}{dt} &= -a_0\left(1-X_{\mathrm{MO}}\right) k_1 C_{\mathrm{F}} C_{\mathrm{MO}} M_{\mathrm{MO}} \\
\frac{dC_{\mathrm{M}}}{dt} &= a_0\left(1-X_{\mathrm{MO}}\right) k_1 C_{\mathrm{F}} C_{\mathrm{MO}} M_{\mathrm{M}} \\
\varepsilon_g \frac{\partial C_{\mathrm{F}}}{\partial t} + u_{GS} \frac{\partial C_{\mathrm{F}}}{\partial z} &= -a_0\left(1-X_{\mathrm{MO}}\right) k_1 C_{\mathrm{F}} C_{\mathrm{MO}} \rho_{\mathrm{MO}}
\end{aligned} \tag{3}$$

In the regeneration phase (oxidation of the carrier) we have:

$$\begin{aligned}
\frac{dX_{\mathrm{MO}}}{dt} &= -\frac{a_0 X_{\mathrm{MO}}}{C'^{0}_{\mathrm{MeO}}} k_2 C_{\mathrm{O_2}} C_{\mathrm{M}} \\
\frac{dC_{\mathrm{MO}}}{dt} &= a_0 X_{\mathrm{MO}} k_2 C_{\mathrm{O_2}} C_{\mathrm{M}} M_{\mathrm{MO}} \\
\frac{dC_{\mathrm{M}}}{dt} &= -a_0 X_{\mathrm{MO}} k_2 C_{\mathrm{O_2}} C_{\mathrm{M}} M_{\mathrm{M}} \\
\varepsilon_g \frac{\partial C_{\mathrm{O_2}}}{\partial t} + u_{GS} \frac{\partial C_{\mathrm{O_2}}}{\partial z} &= -a_0 X_{\mathrm{MO}} k_2 C_{\mathrm{O_2}} C_{\mathrm{M}} \rho_{\mathrm{MO}}
\end{aligned} \tag{3}$$

where $C_{\mathrm{O_2}}$ is the molar concentration of oxygen in the gas stream. It is assumed that the process takes place in a single fixed bed reactor, hence the boundary conditions are cyclically changed when we switch from reduction to regeneration. Moreover, for further simplification, the gas phase is flushed during one residence time between the two phases, using an inert gas. In the simulation model, the values for NiO were assumed [7] with the kinetic parameters for the reactions given by Eqs. (1) and (2) proposed by [7] and reported in Table 1. The gaseous fuel considered was methane (20% in inert gas) and the oxidizer was air.

Table 1. Kinetic parameters for the reduction and oxidation reactions of the $NiO/MgAl_2O_4$ oxygen carrier [5].

	CH_4	O_2
E (kJ/mol)	114	40
k_0 ($(mol^{1-n}m^{3n-2})/s$)	2.75	5.43×10^{-3}
n	0.4	1

3. Results and discussion

The model described by Eqs. (3) and (4) was discretized in space using a method of lines with N=101 nodes and then the resulting set of ODEs was integrated using implicit Gear's method. The model was simulated for a number of reduction (fuel combustion) and regeneration (metal oxidation) cycles.

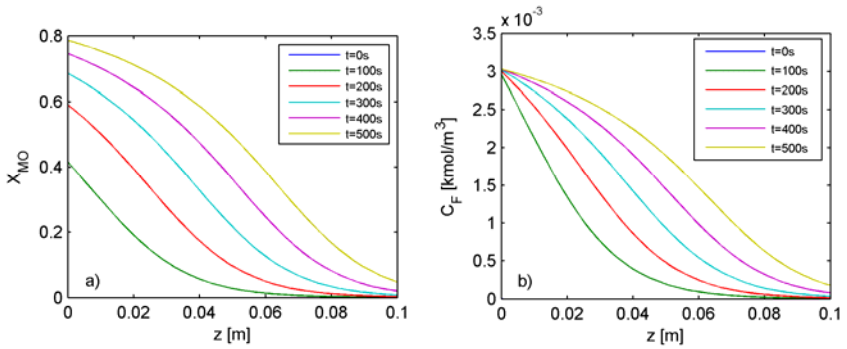

Figure 3. Conversion degree of the oxidized metal (a) and concentration of the fuel along the reactor during reduction (b) @*T*=800K.

Typical spatial profiles – obtained during the reduction phase – of the conversion degree of the oxidized metal and molar concentration in time are reported in Figure 3. Obviously, the conversion degree of the oxidized metal increases in time and space. In the same time, the fuel concentration *z*=0.1m (reactor exit) begins to become non zero, hence the combustion process has to be arrested and the bed has to be regenerated.

Figure 4 reports the molar concentration of the gaseous species – methane during the reduction phase and oxygen during the regeneration phase – at the outlet of the reactor, for a number of reduction and regeneration cycles, and for two values of the temperature: *T*=800K (Fig. 3a) and *T*=600K (Fig. 3b). It can be observed that the increase of the temperature affects significantly reaction rates for both phases of the CLC operation.

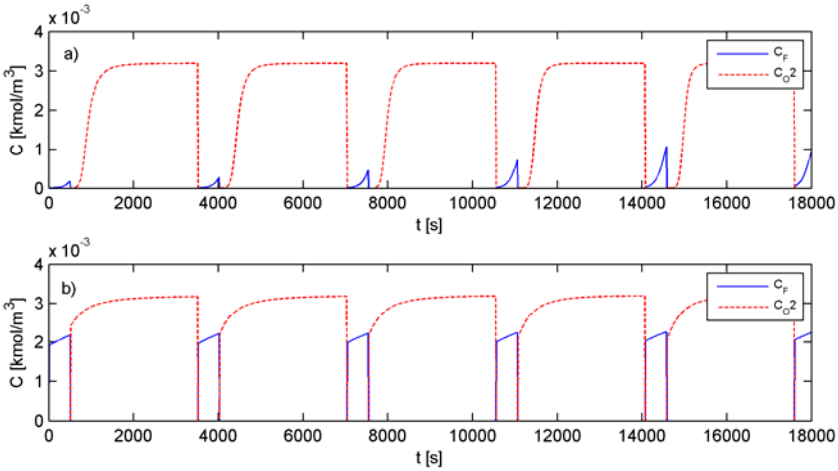

Figure 4. Gaseous species concentration at the outlet for a number of consecutive reduction and regeneration cycles for *T*=800K (a) *T*=600K (b).

4. Conclusions

A distributed model of chemical looping combustion has been presented, featuring a fixed bed reactor under isothermal condition. Reduction and regeneration of the oxygen carrier take place under the assumption of discontinuous feed and modeled with simplified reaction kinetics. This simple model incorporates all essential aspects of the system, and it is amenable of further reduction by means of the efficient POD-Galerkin approach. Optimal solution sampling will yield a robust real-time dynamic model that can be used for various values of the parameters.

5. Acknowledgments

This work benefits of the continuing support of the MISE (Ministero dello Sviluppo Economico) – CNR (Consiglio Nazionale delle Ricerche) Agreement, "Carbone pulito/CO2 capture" Program.

References

[1] Fan, L.-S., *Chemical Looping Systems for Fossil Energy Conversion*, Willey, 2010.

[2] Iliuta, I., Tahoces, R., Patient, S., Rifflart, S., Luck, F., "Chemical-looping combustion process: kinetics and mathematical modeling", *AIChE J.* 5:1063-1079-958 (2010).

[3] Kruggel-Emden, H., Ricklet, S., Stepanek, F., Munjiza, A., "Development and testing of an interconnected multiphase CFD-model for chemical looping combustion"

[4] Holmes, P., Lumley, J.L., Berkooz, G., *Turbulence, Coherent Structures, Dynamical Systems and Symmetry*, Cambridge University Press, 1996.

[5] Bizon, K., Contillo, G., Russo, L., Smuła, J., "On POD reduced models of tubular reactor with periodic regimes", *Comp. Chem. Eng.* 32:1305-1315 (2008).

[6] Bizon, K., Continillo, G., Berezowski, M., Smuła-Ostaszewska, J., "Optimal model reduction by empirical spectral methods via sampling of chaotic orbits", *Physica D* 17:1441-1449 (2012).

[7] Zafar, Q., Abad, A., Mattisson, T., Gevert, B., "Reaction kinetics of freeze-granulated NiO/MgAl2O4 oxygen carrier particles for chemical looping combustion", *Energy Fuels* 21:610-618 (2007).

10.4405/35proci2012.VIII3