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ScienceDirect

Energy Procedia 114 (2017) 429 – 435

Energy Procedia

13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

Simplified model description of a CLOP reactor for system simulation and analysis.

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Abstract

In order to perform overall system simulations and optimization at the flowsheet level, simplified models of process units are required. We present a simplified model of the CLOP reactor (chemical looping for oxygen production) and compare it against a rigorous dynamic fixed bed model, which uses a 1D phenomenological approach. The model is validated towards the detailed model to verify that the performance is captured correctly. In this way, after model validation, system simulations can be performed and optimized both based on process flow configuration, and temperature/pressure ranges. When combined in a process simulation, the model can give an understanding of the potential of a given oxygen carrier material (OCM) for usage in power plants utilizing the novel COMPOSITE concept, which is a concept for energy production with CO_2 capture. Both the rigorous and the simplified models are based on using fuel burning to maintain the desired operating reactor temperature. The model can be used for finding equilibrium points in the air and fuel reactors, and thus identify what is the limiting factor for the reactor performance.

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: CO_2 capture, process modelling, chemical looping oxygen production, process optimization

1. Introduction

The COMPOSITE concept is a novel, efficient process for solid fuel combustion with CO_2 capture. The process is a combination of two looping capture technologies, Chemical Looping Oxygen Production (CLOP) and Chemical Looping Combustion (CLC). Details are described in Larring et al[1]. In the CLOP process, compressed air is used to oxidize the bed material while a small hot gas stream of combustibles mixed with a stream of syngas is used as a sweep to produce oxygen into a stream of combusted gas for the gasification of coal. The aim is to create a gas stream with sufficient energy needed for the (endothermic) gasification of solid fuel. A sufficiently high temperature

Peer-review under responsibility of the organizing committee of GHGT-13.
doi:10.1016/j.egypro.2017.03.1185

for efficient gasification can be obtained by high thermal energy (combusted gas at high temperature) or with a mixture of less thermal energy with more O_2 in the sweep gases. A useful way of understanding how this integration of power production with the CO_2 capture process in the concept is to perform system modelling in a way such that the overall process potential can be assessed. Preliminary work shows that the potential of this concept for power production is high[1].

This paper describes a simplified model of the CLOP unit. This is the least mature unit in the COMPOSITE concept and also the unit that is associated with most uncertainties. Thus, the main objective of this work is to set up a model that reproduces to an acceptable accuracy the most important characteristics of the CLOP model for use in a future overall system analysis framework.

A subsequent paper will present an efficiency analysis of the overall COMPOSITE process by use of simplified models. The CLOP model is tested against a rigorous model, which utilizes a novel oxygen carrier material (OCM), based on $Ca_2AlMnO5.5$, abbreviated as CAM[1]. Further details about the experimental work as well as description of the OCM is also be found here.

For the given CAM material under investigation, sufficient oxygen uncoupling is not possible without the aid of additional fuel. To reach the desired temperature for the CAM for sufficient cyclic O_2 oxidation/reduction capacity, a portion of the produced fuel from the gasification process is used. In the simplified model, it is assumed that the fuel is combusted prior to reaching the CLOP unit. The combusted fuel is then mixed with the sweep gas stream from the CLC prior to the CLOP inlet, and combusted in the CLOP unit.

1.1. Model description

Figure 11a shows the actual fixed-bed CLOP reactor, which extracts oxygen from air by means of a metal oxide. The feed F alternately cycles between an oxidation stage using air and a reduction stage using a mixture of fuel gas and combustion products. During the reduction, fuel gas reacts with CuO to provide the heat necessary to maintain the reactor temperature. Oxygen is released from the oxide during reduction, so that the reduction outlet stream contains ~17% oxygen.

Figure 1b shows the simplified steady state model for flowsheet simulation. The switching between oxidation and reduction in the CLOP is modelled as a recycle of solid between two reactors. Thus, there is a feed F_1 and F_2 [kmol/s] during oxidation and reduction; outflows G_1 and G_2 [kmol/s]; and transport of oxygen R_1 and R_2 [kmol/s] through the solid recycle. The fuel burning is represented by the combustion heat that it provides.

The model is based on an energy balance, a mass balance of oxygen and an expression for solid-gas equilibrium for oxygen. The equilibrium expression is based on the van't Hoff equation based on a heat of combustion of ~91 kJ/mol O_2.

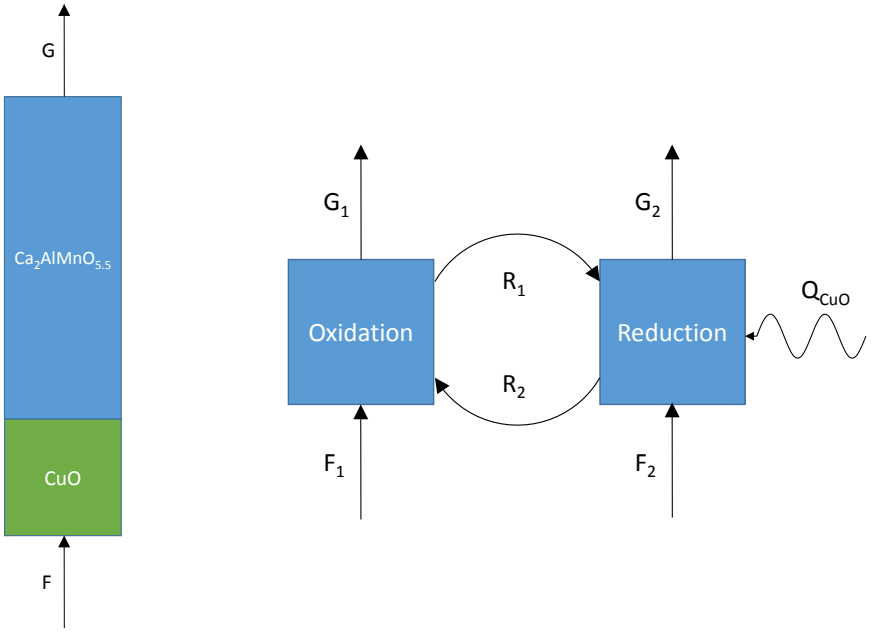

Figure 1: Illustration of the simplified CLOP model. a) Fixed bed, b) Flowsheet representation

A mass balance for oxygen for oxidation and reduction yields

$$F_1 x_{1,in} + R_2 - R_1 - G_1 x_1 = 0$$
$$F_2 x_{2,in} + R_1 - R_2 - G_2 x_2 - S_{CuO} = 0 \quad (1)$$

where x_1 and x_2 are the mole fraction of O_2 in the oxidation and reduction respectively and S_{CuO} [kmol/s] is the amount of O_2 that is consumed by fuel burning.

Simplified energy balances are:

$$F_1 C_{p,1} T_{1,i} + R_2 C_{p,2} T_2 - R_1 C_{p,1} T_1 - G_1 C_{p,1} T_1 + R\left(-\Delta H_{rx}\right) + \dot{m}_{solid} C_{p,solid}\left(T_2 - T_1\right) = 0$$
$$F_2 C_{p,2} T_{2,i} + R_1 C_{p,1} T_1 - R_2 C_{p,2} T_2 - G_2 C_{p,2} T_2 - R\left(-\Delta H_{rx}\right) + \dot{m}_{solid} C_{p,solid}\left(T_1 - T_2\right) + Q_{CuO} = 0 \quad (2)$$

where $R=R_1-R_2$ [kmol/s] is the net oxygen transport from oxidation to reduction, $\dot{m}_{solid}$ [kg/s] is the circulation rate of solid, Q_{CuO} [W] is the heat input by fuel burning, $-\Delta Hrx$ [J/kmol] is the oxidation heat of reaction and the Cp's are heat capacities.

In normal operation there is excess air during oxidation and equilibrium during reduction. The equilibrium mole fraction O_2 in reduction, x_2, is described by a modified van't Hoff equation:

$$x_2 = x_{2,eq} = k_2(T)\frac{p_{O2,ref}}{p} e^{-\frac{\Delta Hrx}{R}\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)} \quad (3)$$

where $pO_{2,ref}$ [Pa] is the equilibrium O_2 pressure at a reference temperature T_{ref} [K] and p [Pa] is the operating pressure.

In general, if there is too little air feed to the oxidation or if the oxidation temperature becomes too high, the

equilibrium will be in the oxidation instead of in reduction. Also, oxidation is not possible if the temperature during oxidation is higher than corresponding to equilibrium with the air feed.

The simplified CLOP model consists of solving the mass and energy balances together with the appropriate equilibrium relation (in reduction in case of air excess, in oxidation otherwise). The degrees of freedom are selected as the inlet streams together with a specified outlet temperature in the reduction stage. The latter specification is achieved by adjusting the amount of fuel burnt. In general, the reduction temperature can be increased until the point where an equilibrium limitation occurs in the oxidation stage. Beyond this, the oxidation reactor is too hot, and further increase reduces the CLOP performance.

1.2. Description of the benchmark simulations

The CLOP model as described in Larring et al[1] is used for the benchmark simulations. A set of 12 simulations were used which represents different operational ranges; varying input flow rates, temperatures and OCM bed size. As the rigorous model includes dynamic operation of a fixed bed, the input flow rates, fuel duty, OCM "circulation rate" were converted to continuous flows. A steady state unit operation like this can then be readily implemented into a process simulator. The input data are shown in Table 1.

Table 1: Input data to the model.

	Average reactor Temperature	Fuel Time	Air Time	Fuel	O_2 in sweep	O_2 in depleted air	Specified Sweep Temperature
Run	°C	s	s	kg/m2s	molfrac	molfrac	°C
1	780	60	360	2.96	0.16	0.17	804.5
2	790	60	360	3.07	0.16	0.17	807.4
3	800	60	360	3.18	0.17	0.17	813.1
4	810	60	360	3.29	0.18	0.16	818.0
5	820	60	360	3.39	0.18	0.16	816.7
6	830	60	360	3.50	0.15	0.16	798.2
7	800	30	180	3.18	0.16	0.17	803.6
8	800	90	540	3.18	0.18	0.16	816.9
9	800	120	720	3.18	0.13	0.18	781.1
10	800	60	360	3.18	0.18	0.16	815.6
11	800	60	360	3.18	0.18	0.16	819.0
12	800	60	360	3.18	0.19	0.16	822.7

Other data: Oxidation flow rate: 5.5 kg/m2s, Sweep flow rate: 3.54 kg/m2s, Oxidation temperature: 404.4°C, Fuel temperature: 432.2°C, Combustion gasses Temperature: 1200°C. The specified sweep temperature is internally calculated in the model, based on the sweep outlet O_2 molar fraction.

1.3. Model assumptions

It is assumed that either the oxidation or the reduction reactors may go to equilibrium depending on the limiting side. Equilibrium at the reactor outlet requires that the size of the reactor is large enough for this to occur.

1.4. Model comparison.

Key process variables to monitor are the output temperatures of the air and fuel reactor, output sweep O_2 concentrations, and the O_2 contents of the depleted air stream. The fuel requirement for reaching the target reduction temperature is calculated. To compare the simplified model with the rigorous model we perform the following:

- Calculate the equilibrium temperature corresponding to the sweep outlet O_2 concentration of the rigorous model. Adjust the fuel amount in the simple model required to achieve this. If no equilibrium

limitations occur in the oxidation reactor, the sweep outlet O_2 concentration will match the rigorous ones exactly. Verify that the fuel amount corresponds to the fuel amount in the rigorous model.

- Verify that the O_2 concentration at the air side matches the rigorous model

In Figure 2 is shown the outlet O_2 sweep stage molar fractions for the test set between the rigorous CFD model and the simplified model (see Table 1). Where the limiting side is on reduction, an exact match is possible by adjusting the fuel consumption. Figure 3 shows the corresponding O_2 mole fractions at the air stage outlet. Except case 4 and 5, the test runs are limited by equilibrium in the reduction stage. Figure 4 shows the oxidation temperature of the stages.

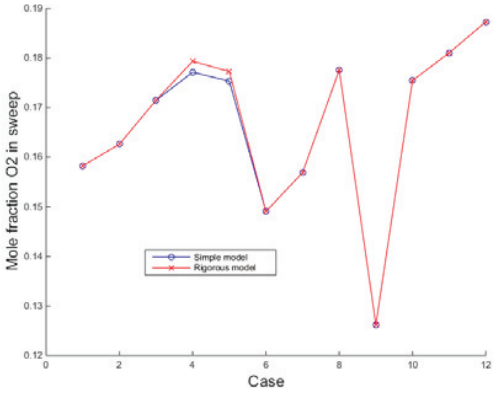

Figure 2: Matched O_2 fraction in sweep gas based on an equilibrium temperature.

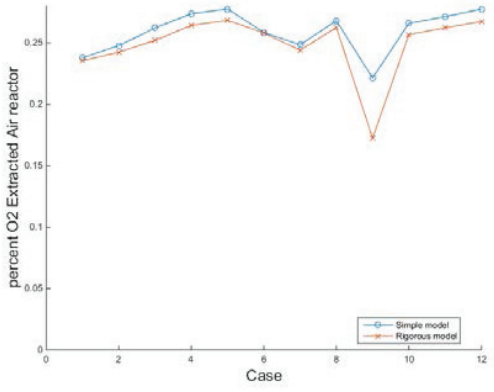

Figure 3: Percent oxygen extracted in the air stage.

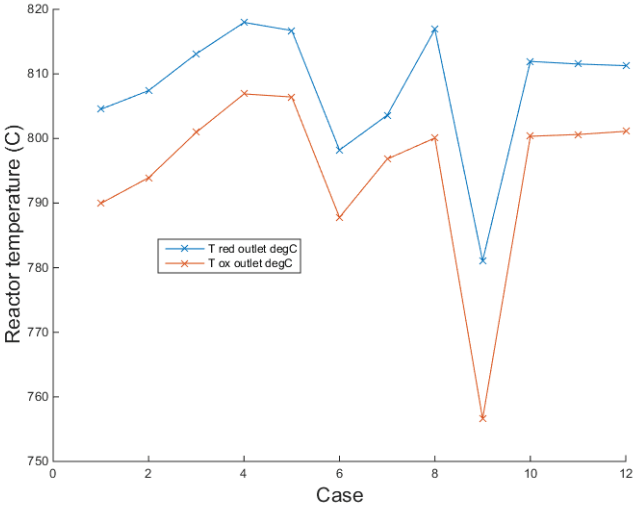

Figure 4: Top: Outlet temperatures from air and sweep stages for the cases.

1.5. Sensitivity analysis

In order to achieve the oxygen concentrations needed for efficient gasification, the CLOP reactors are efficient when operated at a temperature yielding a high equilibrium oxygen partial pressure, thus, providing maximum driving force at the sweep stage. This operating point is close to the O_2 concentration in air, implying that only a relatively small fraction of O_2 in the incoming air stream can be consumed in the oxidation stage of the CLOP process. However, in the COMPOSITE process the resulting large depleted air stream can be efficiently utilized in the CLC unit to combust syngas from the gasification unit with inherent CO_2 separation.

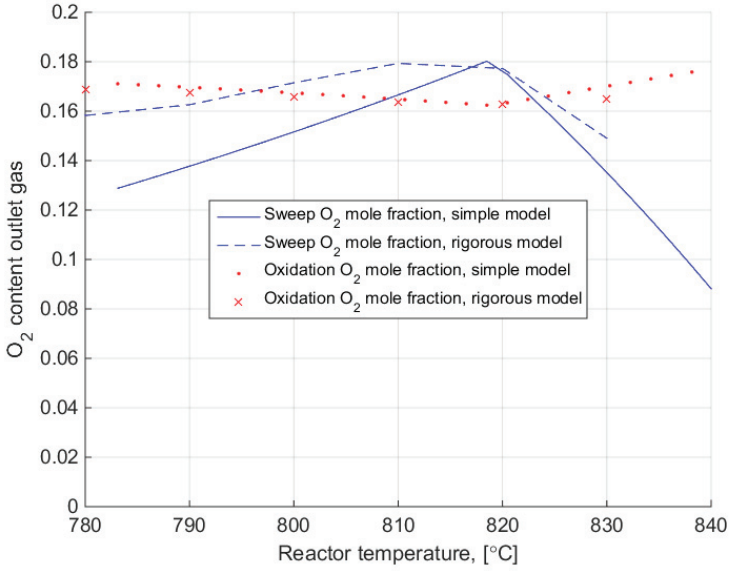

Figure 5: Comparison between the simple model and the rigorous model. Outlet O_2 molar fractions vs sweep reactor temperature. Red indicating air stage, blue indicating sweep stage

In Figure 5 results from running a sensitivity test on Case nr. 3 w.r.t. sweep reactor temperature. The result is compared to the rigorous model. As the temperature rises in the sweep stage by the increased fuel usage, increased efficiency is seen to the point where excessive heat results in an equilibrium limitation in oxidation. When the equilibrium O_2 pressure in oxidation becomes too high, the driving force for oxidation is lost, thus, an optimum is found.

Minimum loss of thermodynamic availability, i.e. maximum oxygen extraction, is thus found at a close to equilibrium condition at both the air and sweep stages, indicated by appropriate oxygen feed to the reactor during air stage for oxidation and equilibrium in the reduction reactor, as shown as the optimums in the figures. This optimum can be very informative in process simulation as long as the base assumptions for the model is valid. For validation, the optimum performance requires specific knowledge of the given reactor configuration and OCM under investigation. Detailed regulation is also necessary to maintain close to constant maximum temperature at the sweep outlet. Reactor optimization based on laboratory OCM tests should therefore be first performed, which accounts for the dynamics involved in the fixed bed.

1.6. Summary and conclusion

A simplified model of the CLOP unit appropriate for flowsheet simulation and optimization has been developed. We have applied it to analyse and understand the novel COMPOSITE concept, which is a concept for energy production with CO_2 capture. When combined in a process simulation, the model can give an understanding of the potential of a given oxygen carrier material (OCM). Both the rigorous and the simplified models are based on using fuel burning to maintain the desired operating reactor temperature. The model can be used for finding equilibrium points in the air and fuel reactors, and thus identify what is the limiting factor for the reactor performance.

Acknowledgements

The COMPOSITE project is funded by the Research Council of Norway under the CLIMIT call for promising new concepts for CO_2 capture.

References

[1] Yngve Larring, Schalk Cloete, Antonio Giuffrid, Matteo C. Romano, Paolo Chiesa, John Morud, Mehdi Pishahang, Actor Chikukwa, Shahriar Amini, Andrew Tobiesen., 2016, COMPOSITE: A concept for high efficiency power production with integrated CO2 capture from solid fuels, The 13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland.