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Dynamic flowsheet simulation for chemical looping combustion of methane

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ABSTRACT

In a Chemical Looping Combustion system, the fuel and air reactors are strongly coupled because of chemical reactions in both and the circulation of solid oxygen carrier between them. To capture the effects inside the system, a novel dynamic flowsheet simulation environment for solids processes is applied to Chemical Looping Combustion of methane. Flowsheet simulation is a tool for process analysis and optimization covering multiple process units and flows in a system.

An experimental 25 kW_{th} pilot plant is operated, and all of its process units are modeled. The modeling comprises three fluidized bed reactors, two operating in bubbling fluidized bed condition and one as a circulating fluidized bed riser. A cyclone is used for gas-solid separation after the air reactor. The loop seals ensure gas sealing between the reactors. Fluid mechanics inside the systems are modeled with empirical and semi-empirical correlations, to enable fast calculations. This approach becomes handy when long-term dynamic effects like abrasion, start-up, or shut-down procedures as well as load changes are to be modeled.

Chemical reactions for a gaseous fuel and their implications on gas flows were implemented. In addition, oxidation and reduction of the solid oxygen carrier in the three reactors were part of the simulation. To validate the simulation results, the pilot plant was operated with methane as fuel. Gas measurements were taken after both stages of the fuel reactor. Additionally, solid samples were drawn from the hot facility to examine the oxidation state of the carrier, when fuel is introduced.

A transient simulation of plant operation over a total runtime of 40 min reveals that the solids inventories of the fluidized bed reactors in the system need only 30 s in the present case to reach a new steady state after a load change. If the oxidation and reduction reactions of the oxygen carrier are taken into account, however, this response time extends dramatically to several hundreds of seconds, which can also be seen in the experimental campaigns. The simulation of such a system behavior requires a powerful simulation tool for flowsheeting, which has been found here in the dynamic simulation framework.

1. Introduction

The first fluidized bed reactor for Chemical Looping Combustion (CLC) operated in 2001 and was run on methane (Lyngfelt et al., 2001). Since then, various process routes have been proposed for Chemical Looping Conversion processes. Among them, Chemical looping with Oxygen Unclouping (CLOU) and internal Gasification Chemical Looping Combustion (iG-CLC) are considered to be the most promising technologies. (Adanez et al., 2012). In all these processes, a solid oxygen carrier (OC) is used to provide oxygen for the (partial) oxidation of fuel, which can be gaseous, liquid or solid in its state. These processes aim at providing a CO_2 rich flue gas, which is suitable for the later compression and storage. Different from the regular air-fired combustion, the OC plays the role of oxidizing agent in fuel oxidation reaction, which lead to a different process layout. To implement the CLC process, most of the operating laboratory and pilot scale plants use a design of at least two fluidized bed reactors, which are connected by cyclones and loop seals to fulfill gas-solid separation and prevent gas leakage, respectively. A key element for the understanding of the process is modeling work conducted on the reactors' fluid mechanics and the chemical kinetics inside the system.

Process simulation of CLC has been carried out with a variety of methods and approaches. In literature, no sharp separation of process simulation tools exists, but one can make some basic classification among the time and length scales, which the simulations have taken into account. One can, for example, differentiate dynamic and steady state simulations. In dynamic or also called transient simulations, the operation parameters and, hence, the fluid mechanics in the reactors can vary over time, which is closer to reality. Steady state simulations usually find one "steady state" solution for a set of operation conditions and is, therefore, less computationally expensive. Different simulation environments and ideas were used to model the whole process of CLC.

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Nomenclature

Abbreviation description

CLC	Chemical looping combustion
CLOU	Chemical looping with oxygen uncoupling
iG-CLC	Internal gasification chemical looping combustion
FR	Fuel reactor
AR	Air reactor
OC	Oxygen carrier
PFR	Plug flow reactor
CSTR	Continuously stirred tank reactor
CFD	Computational fluid dynamics
CFB	Circulating fluidized bed
TGA	Thermo-gravimetric analysis
AR	Archimedes number

Letter/symbol description

Δp	Pressure drop [mbar]
Δm_{solids}	Mass of solids between a certain height interval [kg]
g	Gravitational acceleration [m/s^2]
ρ_s	Density solid [kg/m^3]
ρ_f	Density fluid [kg/m^3]
A_r	Fluidized bed reactor cross section area [m_2]
$d_{v,0}$	Initial bubble size [m]
d_v	Bubble size [m]
V_{or}	Volumetric flow rate through orifice [m^3/s]
u_b	Bubble rise velocity [m/s]
ε_b	Bubble volume fraction [−]
λ	Bubble lifetime [s]
$\dot{V}_b$	Visible bubble flow [m/s]
θ	Scale dependent geometry parameters [−]
c_v	Solids concentration [−]
c_{v_mf}	Solids concentration at minimum fluidization velocity [−]
$c_{v\_suspension}$	Solids concentration in the dense suspension phase [−]
a	Decay constant [1/m]
H_b	Height above distributor, where the dense bottom zone ends [m]
h	Height inside reactor [m]
$K_{i,\infty}$	Entrainment constant [kg/m2/s] for each particle size interval i
$d_{i,p}$	Average diameter of size interval i
u	Superficial gas velocity [m/s]
$u_{t,i}$	Terminal velocity of particles in size interval i [m/s]
$\dot{m}_{OC}$	Mass flow of oxygen carrier [kg/s]
X_j	Solid conversion of component j [−]
$C_{d,l}$	Gas concentration of gas component l in dense suspsension phase [mol/m^3]
$C_{d,l}$	Gas concentration of gas component l in bubble phase [mol/m^3]
$C_{b,l}$	Gas concentration of gas component l in the freeboard [mol/m^3]
u_d	Velocity in dense suspension phase [m/s]
$r_{s,j,l}$	Solid reaction rate of solid j with gaseous component l [mol/m^3]
$_{m,j}$	Molar density [mol/m^3]
k	Kinetic constant for certain temperature and concentration [1/s]
k_0	Pre-exponential factor [1/s]
E_A	Activation energy [J/mol]
$\dot{j}_{Q,l}$	Convective flow of gas component l [mol/m^3]
K_Q	Convective exchange rate [1/s]
rg,l	Reaction rate of gaseous compound l [mol/m^3]
k_g	Gas diffusion resistance [mol/s]
D	Molar binary diffusion coefficient [m^2/s]
a_t	Exchange area between bubbles and suspension [1/m]

Table 1
List of process modeling approaches by various research groups, (iG = in-situ Gasification).

Process	Fuel	Software	Fluid mechanics	Reaction model	Institution	Researcher	Dynamic
CLC	gas	IPSEpro	0-D	equilibrium reactions	Vienna University of Technology	Bolhàr-Nordenkampf et al. (2009)	no
CLC	gas	Matlab/Simulink	1-D	reaction kinetics	Lappeenranta University of Technology	Peltola et al. (2013), Peltola et al. (2015)	(yes)
CLC	gas	AspenPlus	1-D	reaction kinetics	Heriot-Watt University Edinburgh	Porrazzo et al. (2014)	no
Syngas- CLC	syngas	AspenPlus	0-D	equilibrium reactions	University of Surrey	Mukherjee et al. (2015)	no
Syngas- CLC	syngas	AspenPlus	0-D	equilibrium reactions	Ohio State University	Li et al. (2010)	no
iG-CLC	solid	AspenPlus	0-D	equilibrium reactions	University of Utah	Sahir et al. (2014)	no
iG-CLC	solid	AspenPlus	1-D	reaction kinetics	Technical University of Darmstadt	Ohlemüller et al. (2014)	no
iG-CLC	solid	SolidSim	1-D	reaction kinetics	Hamburg University of Technology	Kramp et al., (2012)	no

Table 1 gives a short overview of flowsheeting software used for CLC process simulation by various research groups.

Process simulations also vary in the depth of phenomena they take into account. When looking at smallest structures of fluid mechanics with CFD methods or analyzing detailed chemical kinetics numerically, then simulations are carried out on micro or even molecular scale. When some phenomena are averaged or closures are used to describe the micro scale behavior, one can speak of meso-scale simulations. In macro-scale simulations, only global mechanisms are resolved. This means that for certain unit operations, mass and energy balances are conducted, whereas in fluidized bed reactors also simplistic models for describing the solids distribution in the reactors can be used. For the different simulation approaches it can be said that the more phenomena included, the more computationally expensive the simulation will be. On the other hand, resolving the micro-scale phenomena accurately gives obviously more comprehensive results.

Flowsheeting is a process simulation tool, which takes into account the predominant macroscopic effects in a complex process network involving multiple process units. For describing these effects, semi-empirical and empirical models are used to characterize the events in each and every process unit in order to keep computational time and effort within manageable limits.

Two main approaches of solving the model equations in a flowsheet simulation environment exist. The first is the equation-oriented approach, in which all equations of the process units are concluded and solved simultaneously. The other is the modular-sequential approach, in which the process units, so called modules, are calculated in series. The big advantage of flowsheeting compared to CFD methods is the short computation time, which makes simulations over a long period of time possible (> 1000s), provided that a dynamic approach is used. With this method, effects over a longer time period can be tracked, like attrition, start-up and shut-down, and load changes, which cannot be