INTERNATIONAL JOURNAL OF
ENERGY AND ENVIRONMENT

Volume 5, Issue 1, 2014 pp.53-58
Journal homepage: www.IJEE.IEEFoundation.org

Simulation and validation of chemical-looping combustion using ASPEN plus

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Abstract
Laboratory-scale experimental studies have demonstrated that Chemical-Looping Combustion (CLC) is an advanced technology which holds great potential for high-efficiency low-cost carbon capture. The generated syngas in CLC is subsequently oxidized to CO_2 and H_2O by reaction with an oxygen carrier. In this paper, process-level models of CLC are established in ASPEN Plus code for detailed simulations. The entire CLC process, from the beginning of coal gasification to reduction and oxidation of the oxygen carrier is modeled. The heat content of each major component such as fuel and air reactors and air/flue gas heat exchangers is carefully examined. Large amount of energy is produced in the fuel reactor, but energy needs to be supplied to the air reactor. The overall performance and efficiency of the modeled CLC systems are also evaluated.

Keywords: Carbon capture; Simulation; Chemical-looping combustion; Coal; Solid fuel.

1. Introduction
In recent years, there has been considerable effort devoted towards the development of Carbon Capture and Sequestration (CCS) technology to prevent or significantly reduce the CO_2 emissions in the atmosphere resulting from the combustion of fossil fuels in electricity generation power plants and other industrial manufacturing processes such as cement etc. In contrast to other methods for CO_2 separation from flue gas such as oxy-combustion, chemical absorption and physical adsorption, the Chemical-Looping Combustion (CLC) is an advanced technology that creates and captures a concentrated CO_2 stream [1, 2] with relatively less energy requirement. Several theoretical and experimental studies have demonstrated the potential of CLC to capture almost pure CO_2 very efficiently [3-6]. A typical CLC system consists of two fluidized bed reactors, namely a fuel reactor and an air reactor. Although not restricted to a solid fossil fuel such as coal, in a CLC plant usually coal is used as fuel which is devolatilized and gasified to the syngas consisting of CO and H_2. Thus in the CLC process, the combustion of solid carbonaceous fuels like coal and petcoke requires that the fuel is initially gasified, then the products of the gasification reaction directly react with the oxygen carrier in the fuel reactor. The exhaust stream of the fuel reactor is CO_2 and H_2O. After separating and pressurizing H_2O, pure CO_2 is captured. The reduced oxygen carrier is transported to the air reactor by reaction with the atmospheric air [7-9].

ASPEN Plus is a process simulation software which uses basic engineering relationships such as mass and energy balances and multi-phase and chemical reaction models in modeling a process at system level. It consists of flow sheet simulations that calculate stream flow rates, compositions, properties and operating conditions. In this paper, two cases of CLC process simulation are conducted in ASPEN Plus to analyze the performance and energy requirements. For both the cases, the entire CLC process is developed and analyzed including the coal devolatilization, gasification, combustion in air reactor, and reaction in fuel reactor, etc.

2. Validation test case of CLC process simulation in ASPEN plus

A CLC process simulation in ASPEN Plus is conducted to validate the code following the experimental work of Sahir et al. [10]. The Colombian coal is used as the solid fuel, the physical and chemical properties are summarized in Table1.

The schematic of the flow sheet for this simulation is shown in Figure1. First, the coal is pulverized and dried, and then it is pressurized and introduced into a shell gasifier to be oxidized partially. For the gasification process, a RYIELD reactor in combination with a RGIBBS equilibrium reactor is employed and modeled. The mole ratio of steam/carbon is maintained at unity for the process model. The syngas composition at the gasifier outlet is 34.5% CO, 50.3%H_2, 12.3% H_2O and 2.4% CO_2. Then the syngas is converted completely to CO_2 and H_2O in the fuel reactor. Calculation models used in ASPEN Plus are summarized in Table 2.

Table 1. Physical and chemical properties of Colombian coal

Colombian coal	Parameter	Value
Proximate Analysis (wt.%)	Moisture	3.3
	Fixed carbon	54.5
	Volatiles	37
	Ash	5.2
Ultimate Analysis	Carbon	80.7
(wt% d.a.f)	Hydrogen	5.5
	Oxygen	11.5
	Nitrogen	1.7
	Sulfur	0.6
Heating Value (MJ/kg)		29.1

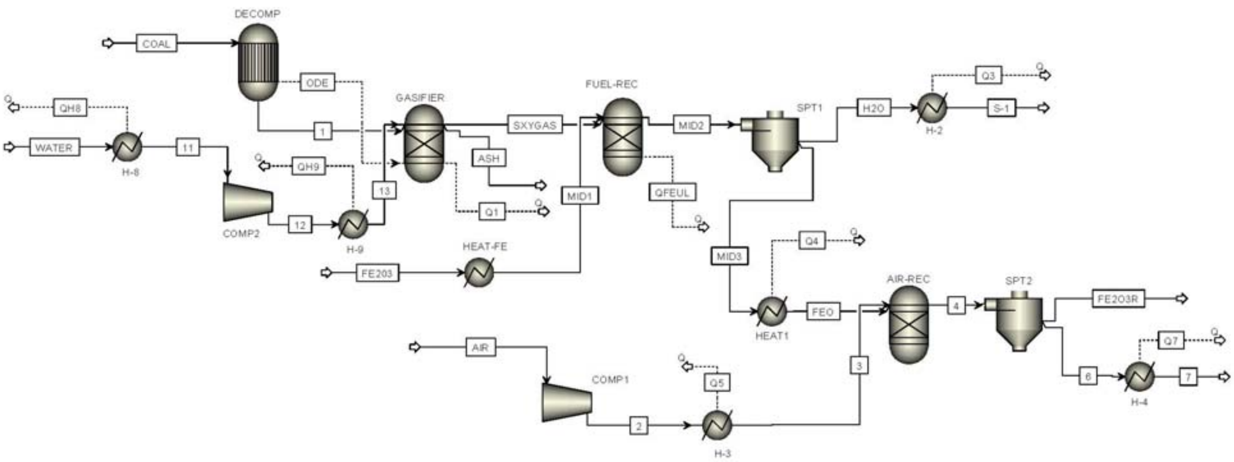

Figure 1. Schematic of the process model in ASPEN plus

In the fuel reactor, the mixture of 60% Fe_2O_3 and 40% Al_2O_3 is used as the oxygen carrier. A concentrated H_2O/CO_2 stream flows out from the fuel reactor. After condensing the stream, high purity CO_2 is obtained. RSTOIC reactor is used to simulate this process. There are two reactions that occur in the fuel reactor:

$3Fe_2O_3(s)+CO(g)\rightarrow 2Fe_3O_4(s)+CO_2(g)$ (1)

$3Fe_2O_3(s)+H_2(g)\rightarrow 2Fe_3O_4(s)+H_2O(g)$ (2)

In the air reactor, the reaction is calculated by a RSTOIC reactor with an 80% conversion of Fe_3O_4 to Fe_2O_3. The oxidation reaction takes place as follows:

$4Fe_3O_4(s)+O_2(g)\rightarrow 6Fe_2O_3(s)$ (3)

Table 2. Process models used in different parts of CLC process

Coal Devolatilization	RYIELD
Coal Gasification	RGIBBS
Fuel Reactor	RGIBBS
Air Reactor	RGIBBS
Cyclone Separator	SPLT

Two cases with different initial values of various input parameters are considered to analyze the differences in the energy balance. Energy requirements for various units and streams in Figure 1 are summarized in Table 3. Energy is mainly consumed by the compressor for the purpose of heating the air, for Fe_3O_4 oxidation, product gas compression, and other uses. Compressed air is required in the combustor to regenerate Fe_2O_3 from Fe_3O_4. The air compressor for the combustor compresses air to 18 atm. Another compressor is used to compress the water stream.
There is large amount of energy produced in the air reactor, but the fuel reactor needs to be supplied with energy. From the ASPEN Plus simulation of a 100 kg/h of coal feed to the CLC system, 161 kW of energy is obtained from the fuel reactor, however 688 kW of energy is consumed by the air reactor. Additionally, since the metal oxide works as an oxygen transporter and heat carrier for the tar oxidation reactions in the fuel reactor, the amount of the metal oxide has an obvious effect on the overall energy balance as seen in Table 3.

Table 3. Initial values used in the two simulations and energy balance

		Case 1	**Case 2**
Initial values	Coal	100 kg/h	150 kg/h
	Water	140 kg/h	210 kg/h
	Air Flow Rate	713kg/h	1470 kg/h
	Temperature of Fuel Reactor	950 ºC	950 ºC
	Temperature of Air Reactor	935 ºC	935 ºC
	Fe_2O_3 flow in Fuel Reactor	5921kg/h	9000 kg/h
	Al_2O_3 in the System	3951kg/h	6000 kg/h
	Particle Density	$3200kg/m^3$	$3200kg/m^3$
Energy Balance (kW)	Fuel Reactor	-161.8	-222.6
	Air Reactor	688.0	1401.2
	Cool Air Reactor exhaust	135.4	280.2
	Cool flue gas	148.3	229.5
	Cool OC for Air Reactor	40.9	65.6
	Reheat OC for Fuel Reactor	-42.7	-68.5
	Heat steam	-69.8	-104.7
	Heat air	-184.1	-379.6
	Net	472.4	1200.9

The results shown in Table 3 for case 1 of coal with stream of 100 kg/h are in excellent agreement with those reported in Reference [10]. These calculations validate our use of ASPEN Plus. The results for case 2 of coal with stream of 150 kg/h have never been reported before; they provide some estimate of the scalability of the CLC process in terms of energy balance and overall performance.

3. CLC process simulation and comparison with experiment

A CLC laboratory scale plant for solid fuel CLC with a rated power of 25kW has been built at the Hamburg University of Technology [11, 12] in Germany. The schematic of the test rig of this plant is shown in Figure 2. The solid fuel is introduced in the lower stage of the fuel reactor and the oxidized oxygen carrier coming from the air reactor is added in the upper stage of the fuel reactor. This type of design improves the conversion of volatiles and the products of char gasification. Between the fuel and the air reactor, siphons are located which separate the respective gaseous environments in the two reactors from each other. Each siphon is connected to a steam generator. Coal is pneumatically conveyed by flow of CO_2 into the lower stage of the fuel reactor. The experiments were carried out at Hamburg University of Technology using German brown coal at 900 ºC in both the air and fuel reactor [11]. The physical and chemical properties of German brown coal are summarized in Table.4.

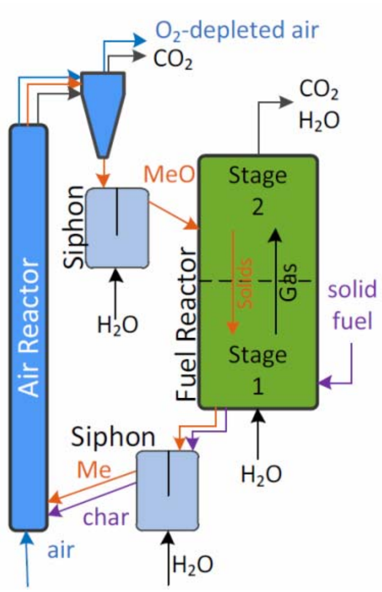

Figure 2. Schematic of the CLC plant in Ref. [11]

Table 4. Physical and chemical properties of German brown coal

German brown coal	Parameter	Value
Proximate Analysis (wt.%)	Moisture	11
	Fixed carbon	40
	Volatiles	45
	Ash	4
Ultimate Analysis (wt% d.a.f)	Carbon	59.5
	Hydrogen	4.3
	Oxygen	20.3
	Nitrogen	0.7
	Sulfur	0.35
Heating Value (MJ/kg)		22.2

In References [11, 12], the experimental results are summarized employing the two performance indicators: the carbon capture ratio η_{CC} which indicates the fraction of CO_2 produced in the air reactor; it is defined as follows:

$$\eta_{cc} = \frac{\left[\dot{n}_{CO_2} + \dot{n}_{CO} + \dot{n}_{CH_4}\right]_{FR\,out} - \left[\dot{n}_{CO_2}\right]_{FR\,in}}{\left[\dot{n}_{CO_2} + \dot{n}_{CO} + \dot{n}_{CH_4}\right]_{FR\,out} - \left[\dot{n}_{CO_2}\right]_{FR\,in} + \left[\dot{n}_{CO_2}\right]_{AR,out}} \tag{4}$$

Another performance indicator is the oxygen demand of the gaseous products Ω_{OD} leaving the fuel reactor. It describes to what extent the products of char gasification and fuel devolatilization are oxidized in the fuel reactor by the oxygen carrier particles.

$$\Omega_{OD} = \frac{O_2\text{-demand of FR off-gas}}{O_2\text{-demand of coal}} = \frac{\left[0.5 \cdot \dot{n}_{CO} + 2 \cdot \dot{n}_{CH_4} + 0.5 \cdot \dot{n}_{H_2}\right]_{FR\ out}}{O_2\text{-demand of coal}} \tag{5}$$

The process simulation for the CLC plant whose schematic is shown in Figure 2 has been carried out with ASPEN Plus; the experimental data for this case is available from References [11, 12]. The schematic of the flow sheet of simulation is shown in Figure 3.

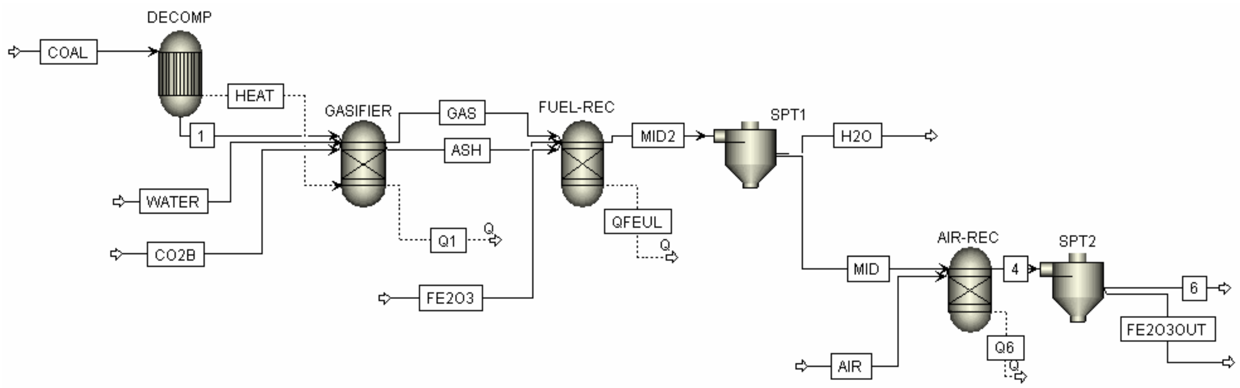

Figure 3. Schematic of the process model in ASPEN Plus for CLC plant of Figure 2

The results of the process simulation are compared with the experimental performance data in Table 5. Considering some uncertainties in the measurements, there is good agreement between experiment and simulation for the two performance indicators. In the experiment, char transported from the fuel reactor to the air reactor combusts to a great extent and the carbon dioxide produced is lost to the atmosphere. Hence the carbon capture ratio should be as close to unity as possible.

Table 5. Performance data comparison

Performance data	Experiment	Simulation
η_{CC}	0.99	1.00
Ω_{OD}	0.24	0.238

4. Conclusions

Two sets of steady-state flow sheet simulations of the CLC process using the ASPEN Plus software have been carried out. In the simulations the entire CLC process, from the beginning of coal gasification to reduction and oxidation of the oxygen carrier, is modeled. Heterogeneous reactions in different reactors are simulated and analyzed. Results from process modeling suggest that both circulation rate of oxygen carrier and supply rate of water for coal gasification play a crucial role in the overall heat output of the system. The overall performance and efficiency of the modeled CLC systems is evaluated. For one of the cases where experimental data is available, good agreement between the experimental results and the simulation calculations is obtained. The current focus of our simulation work is directed towards additional considerations needed for design improvement and optimization of energy balance in the CLC system.

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