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Validation of chemical-looping with oxygen uncoupling (CLOU) using Cu-based oxygen carrier and comparative study of Cu, Mn and Co based oxygen carriers using ASPEN plus

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Abstract

The chemical-looping with oxygen uncoupling (CLOU) has been demonstrated to be an effective technological pathway for high-efficiency low-cost carbon dioxide capture when particulate coal serves as the fuel. In this paper, complete process-level modeling of CLOU process conducted in ASPEN Plus is presented. The heat content of fuel and air reactors and air/flue gas heat exchangers is carefully examined. It is shown that the established model provides results which are in excellent agreement with the experiments for the overall power output of the CLOU process. Finally the effect of varying the air flow rate and three different types of coal as the solid fuel on energy output is investigated, and the performance of three – Copper (Cu), Manganese (Mn) and Cobalt (Co) based oxygen carriers in CLOU process is compared. It is shown that there exists an optimal air flow rate to obtain the maximum power output for a given coal feeding rate and coal type. The effect of three different oxygen carriers on energy output is also investigated using the optimal air flow rate. Among the three oxygen carriers - CuO, Mn_2O_3, and Co_3O_4; Mn_2O_3 shows the best performance on power output. The results presented in this paper can be used to estimate the amount of various quantities such as the air flow rate and oxygen carrier (and its type) required to achieve near optimal energy output from a CLOU process based power plant.

Keywords: Carbon-dioxide capture; Chemical-looping combustion; Oxygen decoupling; Process simulation.

1. Introduction

Chemical-lopping combustion (CLC) is an emerging and highly promising technology that can produce a pure stream of CO_2 [1, 2]; it requires much less energy for CO_2 capture compared to other CO_2 capture processes [3]. Chemical-looping with oxygen uncoupling (CLOU) was recently proposed to be an alternative CLC process for the combustion of solid fuels with low-energy-consumption CO_2 capture. The CLOU process is based on a special material as oxygen carrier (OC) which can release gaseous oxygen at suitable temperatures in the fuel-reactor [4-7]. In the fuel-reactor of CLOU, the fuel conversion is processed by different reactions. Since the fuel-reactor is a high-temperature and oxygen-deficient environment, the oxidized OC first decomposes to reduced OC and gaseous O_2:

$$2MeO_x \rightleftarrows 2MeO_{x-1} + O_2(g) \quad (1)$$

The coal fed into the fuel reactor undergoes a two stage process. It first devolatilizes, producing a solid residue char and volatile matter as gas product:

$$Coal \rightarrow char + volatiles(g) + H_2O(g) \quad (2)$$

Then these combustibles are burnt immediately as in normal combustion. The reduced OC is then transported to the air-reactor to be regenerated by absorbing oxygen from air, and being ready for a new cycle. It is worth noting that in the CLOU system coal does not have to be gasified first in the fuel-reactor since the oxygen release of OC and the combustion of char are usually far faster than the gasification of char. Thereby, a higher overall reaction rate in the fuel-reactor is attained, leading to much less OC inventory and lower circulation rate, and much higher carbon conversion, CO_2 capture efficiency and combustion efficiency.

In previous study Zhou et al. [8] successfully modeled the complete CLOU process in ASPEN Plus based on a series of detailed experiments. The results from their model were in excellent agreement with the experiments for the flue stream contents of the reactors, oxygen carrier conversion kinetics, and the overall performance of the CLOU process. Scaled-up cases were also carried out to investigate the influence of increase in the coal and oxygen carriers feeding rates. Different types of coals were also investigated to determine their effect on the CO_2 concentration in the flue stream and on the overall energy. This previous work of Zhou et al. [8] has formed the basis for modeling of the CLOU process in this paper.

In this paper, we first present the model of CLOU process in ASPEN Plus and compare the simulation results with the data in the recent experiments on CLOU process. After the validation, additional simulations are performed using ASPEN Plus. These include the use of three different types of coal to determine their effect on the overall energy output, and the effect of varying the air flow rate on energy output and the performance of three – Copper (Cu), Manganese (Mn) and Cobalt (Co) based oxygen carriers in the CLOU process.

2. Process simulations in ASPEN plus

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. For the study of CLOU process, ASPEN Plus can be employed for designing and sizing the reactors, for predicting the reaction conversion efficiency, and for understanding the reaction equilibrium behavior. For validation of CLOU process using ASPEN Plus, we simulate the experiment conducted by Abad et al. [9]. The ASPEN Plus flow sheet model corresponding to the experiment of Abad et al. [9] is shown in Figure 1.

As shown in Figure 1 and summarized in Table 1, in ASPEN Plus coal devolatilization is defined by the RYIELD reactor, followed by the gasification of coal represented by the RGIBBS reactor. The RSTOIC reactor defines the actual fuel combustion. It should be noted here that these three reactor blocks together represent the fuel reactor in Abad et al.'s experiments [9]. The flow sheet within the ASPEN Plus simulation package cannot model this entire reaction with one reactor. As a result, the fuel reactor is divided into several different reactor simulations. The air reactor is modeled as a RSTOIC reactor. The molar flow rates of CuO exiting and Cu_2O feeding in the RSTOIC reactor is defined in two separate blocks in the flow sheet in Figure 1; these rates are identical and represent the circulation of oxygen Carrier (OC) within the system. It should be noted that the circulation of OC cannot be defined explicitly in the ASPEN Plus model.

3. Validation of ASPEN plus

ASPEN Plus model for CLOU process is validated against the experimental data of Abad et al. [9]. Since the focus of this paper is primarily on energy output from various types of coals using varying air flow rates and different oxygen carriers, only a few CLOU process validation results against the experiment of Abad et al. [9] are presented; in particular the comparison of overall power output between the simulation and the experiment is given. Additional validation results (flue gas concentration, oxygen carrier efficiency etc.) can be found in the paper by Zhou et al. [8]. Figure 2 compares the thermal power output of CLOU process employed in the experiment in Reference [9] with the simulations reported in Reference [8]. It can be seen from this figure that the overall power output determined by the ASPEN Plus model is in reasonably good agreement with the experimental values for different coal feeding rates. The small differences between the simulations and the experimental results can be attributed to the inability of ASPEN Plus to account for the inevitable losses that occur at multiple locations in the experimental apparatus; the ASPEN Plus system modeling software neglects miscellaneous energy losses in the system due to changes in the hydrodynamic characteristics. To account for the changes in the hydrodynamics characteristics, detailed hydrodynamic simulations are needed using the computational fluid dynamics software.

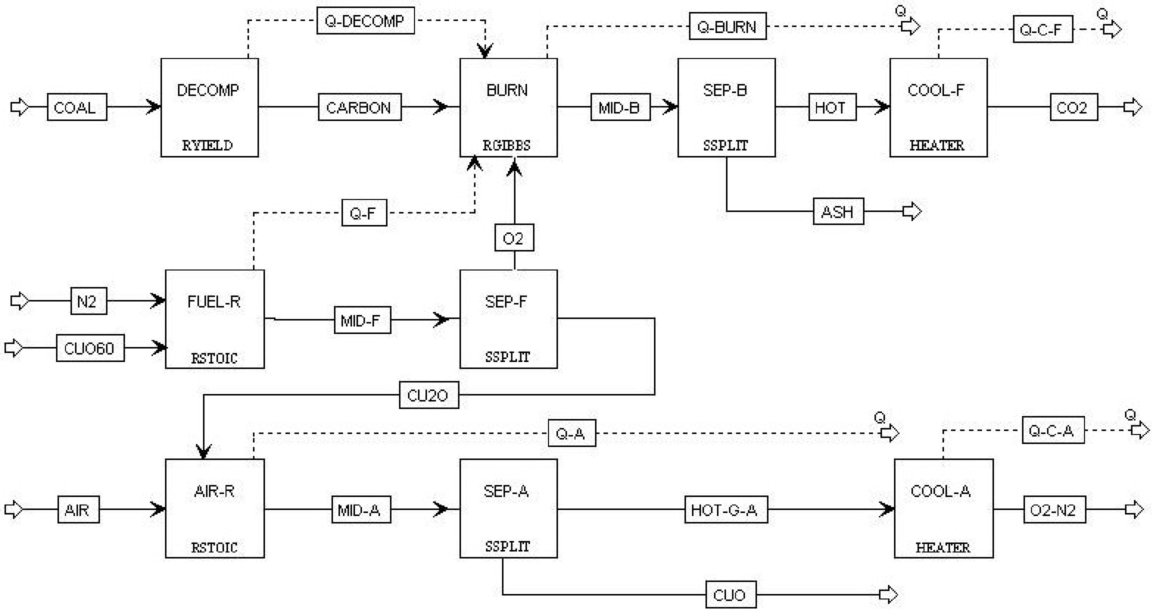

Figure 1. The flow sheet model of CLOU process in ASPEN Plus

Table 1. Process models used in different parts of CLOU process in ASPEN Plus

Name	Model	Function	Reaction formula
DECOMP	RYIELD	coal devolatilization and gasification	coal → volatile matter + char
BURN	RGIBBS	syngas and char burn with O_2	char +volatile matter + O_2 → CO_2+ H_2O
FUEL-R	RSTOIC	carrier reduction reaction	$4CuO \rightarrow 2Cu_2O+O_2$
AIR-R	RSTOIC	carrier oxidation reaction	$2Cu_2O+O_2 \rightarrow 4CuO$
SEP-F	SSPLIT	O_2 and Cu_2O separation	~
SEP-A	SSPLIT	CuO and air separation	
SEP-B	SSPLIT	separation - ash and flue gas	
COOL-F	HEATER	flue gas cooler, fuel reactor	H_2O(gas) →H_2O(liquid)
COOL-A	HEATER	flue gas cooler, air reactor	~

Table 2 summarizes the breakdown of power output for various components of the modeled CLOU system in ASPEN Plus. Energy is consumed mainly in the compressor processes. Compressed air is required in the air reactor to regenerate CuO from Cu_2O. Another compressor is used to compress the steam for the gasifier. There is large amount of energy produced in the air reactor, but the fuel reactor needs to be supplied with energy. This is because the net heat work in the fuel reactor is the summation of the heat work from the DECOMP, BURN, and FUEL-R blocks in Figure 1. Although BURN produces energy because of the combustion of syngas, the energy requirement of FUEL-R is more than the energy produced in DECOMP and BURN.

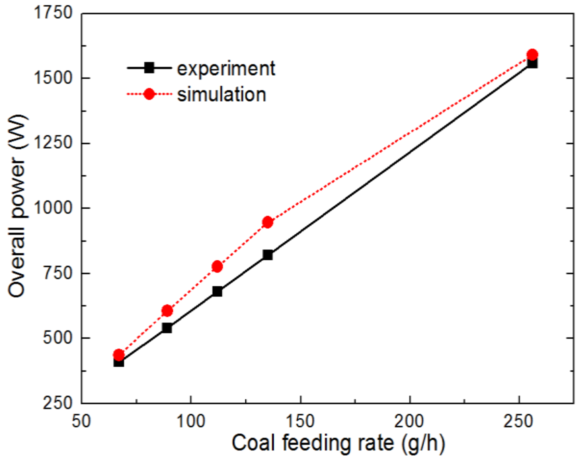

Figure 2. Comparison of overall power output between the simulation and the experiment

Table 2. Thermal analysis at various locations of the modeled CLOU system in ASPEN Plus (Figure 1)

Test No.	Total power (W)	Q-A (W)	Q-Burn (W)	Q-C-A (W)	Q-C-F (W)	Q-Decomp (W)	Q-F (W)
CLOU1	436.6	-175.1	116.4	380	115.3	31.6	-380.1
CLOU2	606.4	-79.9	181.9	370.1	134.3	41.7	-477.6
CLOU3	777.6	-30.5	296.1	361.1	150.8	53.5	-534.5
CLOU4	946.5	51.5	372.7	352.3	170	64.2	-628.8
CLOU5	1591.4	180.3	803.6	338.2	269.3	120.7	-1094

4. Effect of varying the air flow rate on energy output using different types of coal and oxygen carriers

The recent paper of Mukherjee et al. [10] suggests that it is favorable to operate the air reactor of the chemical looping combustion (CLC) process at higher temperatures with excess air supply in order to achieve greater power efficiency. Since CLC and CLOU are very similar processes, therefore it is of interest to investigate the effect of air flow rate in the air reactor on the energy output in the CLOU process. In addition it is also of interest to investigate the influence of different OCs on energy output. We consider three types of OCs namely the CuO/Cu_2O, Mn_2O_3/Mn_3O_4, and Co_3O_4/CoO in the simulations. In case of Mn_2O_3/Mn_3O_4 and Co_3O_4/CoO, the oxygen is released according to the following reversible reactions:

$$6Mn_2O_3 \rightleftarrows 4Mn_3O_4 + O_2 \quad (3)$$

$$2Co_3O_4 \rightleftarrows 6CoO + O_2 \quad (4)$$

We also consider three different types of coals, namely the Bituminous, Anthracitic, and Lignite. The detailed properties of these three types of coals are summarized in Table 3.

Table 3. Properties of three types of coals

Coal name	Proximate Analysis (wt. %)				Ultimate Analysis (wt. %)						Energy
	Moisture	Volatile matter	Fixed carbon	Ash	C	H	N	S	O	Ash	LHV (kJ/kg)
Bituminous	2.3	33.0	55.9	8.8	65.8	3.3	1.6	0.6	17.6	11.1	21899
Anthracite	1.0	7.5	59.9	31.6	60.7	2.1	0.9	1.3	2.4	32.6	21900
Lignite	12.6	28.6	33.6	25.2	45.4	2.5	0.6	5.2	8.5	37.8	16250

4.1 Effect of air flow rate on energy output using three different types of coals with CuO/Cu_2O as OC
In order to evaluate the effect of air flow rate, we keep the amount of coal feeding rate and OC fixed. CuO/Cu_2O is employed as OC for the three types of coals in Table 3. Figure 3 shows the trend in power output with increasing air flow rate. Table 4 summarizes the power output using three types of coals with CuO/Cu_2O as OC. It can be noted form Figure 3 that power increases rapidly and linearly with increase in air flow rate until the air flow rate reaches an almost optimal value of nearly 1500 l/h for 256 g/h of coal feeding rate, beyond which the increase in power output is very gradual. When the air flow rate is less than 1500 l/h, there is not enough air in the air reactor to re-oxidize the Cu_2O which comes from the fuel reactor. 1500 l/h of air is the exact stoichiometric amount to re-oxidize the Cu_2O completely, which is responsible for releasing the total amount of heat. The reason that the overall power continues to increase albeit very gradually for air flow rate greater than 1500 l/h is that the temperature of air reactor is slightly higher than that of the following heat exchanger (which cools the gas out of the air reactor). Therefore with additional air input, slightly additional energy benefit is obtained. However, it is important to note that in the ASPEN Plus model the focus is entirely on heat energy; it does not take into account the mechanical energy consumed by each block of flow sheet in Figure 1, for instance the energy required for blowing the air into the air reactor which may consume a significant amount of mechanical energy. Therefore there is lesser benefit of adding more air in the system beyond the stoichiometric amount of 1600 l/h to re-oxidize the Cu_2O. The result of Figure 3 is nevertheless important in estimating the amount of nearly optimal air flow rate and expected near optimal energy output for a given type of coal and OC. It should also be mentioned that these results scale linearly for higher coal feeding rates because of the assumptions made in ASPEN Plus modeling.

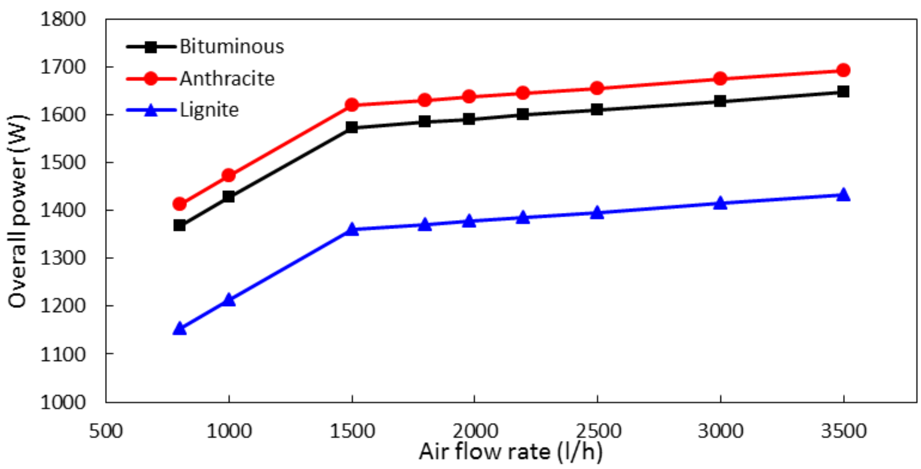

Figure 3. Overall energy output with increasing air flow rate using CuO as OC for 256 g/h of coal feeding rate

Table 4. Power output from three types of coal with increasing air flow rate using CuO as OC with coal feeding rate of 256 g/h

Coal name	Air flow rate (l/h)								
	800	1000	1500	1800	1980	2200	2500	3000	3500
	Energy output (W)								
Bituminous	1367.6	1428.2	1573.7	1584.7	1591.3	1599.5	1610.5	1628.9	1647.3
Anthracite	1413.3	1473.8	1619.4	1630.4	1637.0	1645.1	1656.2	1674.6	1693.0
Lignite	1153.4	1214.0	1359.5	1370.6	1377.2	1385.3	1396.3	1414.7	1433.1

4.2 Effect of air flow rate on energy output using three different coals with different OCs
Using different OCs, namely the Co_3O_4/CoO and Mn_2O_3/Mn_3O_4, the effect of varying the air flow rate is similar to that shown in Figure 3 using CuO/Cu_2O as an OC as shown in Figures 4 and 5 respectively. The optimal air flow rates are however 1500 l/h and 1800 l/h with Co_3O_4/CoO and Mn_2O_3/Mn_3O_4 as OC respectively. Tables 5 and 6 summarize the power output for three types of coal using Co_3O_4/CoO and Mn_2O_3/Mn_3O_4 as OC respectively.

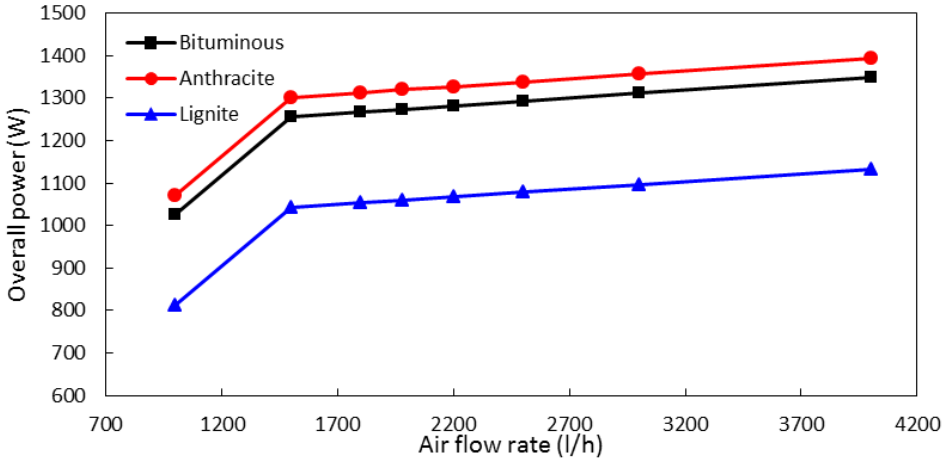

Figure 4. Overall energy output with increasing air flow rate using Co_3O_4 as OC for 256 g/h of coal feeding rate

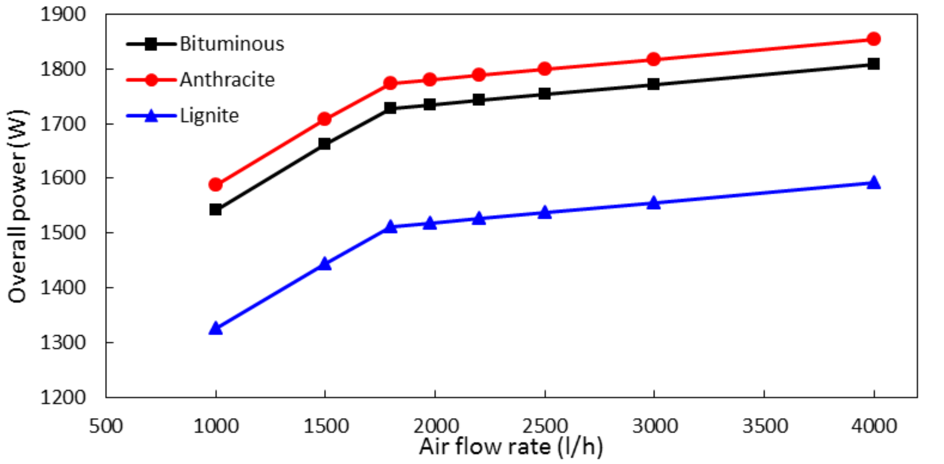

Figure 5. Overall energy output with increasing air flow rate using Mn_2O_3 as OC for 256 g/h of coal feeding rate

Table 5. Power output from three types of coal with increasing air flow rate using Co_3O_4 as OC with coal feeding rate of 256 g/h

Coal name	Air flow rate (l/h)							
	1000	1500	1800	1980	2200	2500	3000	4000
	Energy output (W)							
Bituminous	1025.4	1255.8	1266.8	1273.4	1281.5	1292.6	1311.0	1347.8
Anthracite	1071.1	1301.4	1312.4	1319.1	1327.2	1338.2	1356.6	1393.4
Lignite	811.3	1041.6	1052.6	1059.3	1067.4	1078.4	1096.8	1133.6

Table 6. Power output from three types of coal with increasing air flow rate using Mn_2O_3 as OC with coal feeding rate of 256 g/h

Coal name	Air flow rate (l/h)							
	1000	1500	1800	1980	2200	2500	3000	4000
	Energy output (W)							
Bituminous	1543.0	1661.5	1727.8	1734.4	1742.5	1753.5	1771.9	1808.8
Anthracite	1588.6	1707.1	1773.4	1780.0	1788.1	1799.2	1817.6	1854.4
Lignite	1326.1	1444.6	1510.9	1517.5	1525.6	1536.7	1555.1	1591.9

Next we consider the Case #5 – CLOU5 in Table 2. Keeping the amount of coal feeding rate to be the same at 256 g/h, we compare the maximum power output in Table 7 using the optimal air flow rate and three different OCs with varying amount for three different types of coal. It turns out that the amount of OC required for maximum power output is different depending upon its type. The amount of OC required varies as Mn_2O_3 > CuO > Co_3O_4 (the exact amounts are given in Table 7). This variation in the OC amount occurs due to the chemical reaction property of various OCs described below.
In the case of Copper and Manganese oxides, the overall reaction with carbon is exothermic in the fuel-reactor as shown in equations (5) and (6). On the other hand the reaction of the Cobalt oxide with carbon is an endothermic reaction as shown in equation (7) [9].

$$4CuO+C \rightarrow 2Cu_2O+CO_2 \quad \Delta H_r^{900°C}=-132.9 kJ/molO_2 \tag{5}$$

$$6Mn_2O_3+C \rightarrow 4Mn_3O_4+CO_2 \quad \Delta H_r^{900°C}=-201.9 kJ/molO_2 \tag{6}$$

$$2Co_3O_4+C \rightarrow 6CoO+CO_2 \quad \Delta H_r^{900°C}=11.7 kJ/molO_2 \tag{7}$$

Table 7. Comparison of maximum power output from three different types of coal using optimal air flow rate and optimal amounts of three different OCs

Coal type and amount	OC type	OC amount (kg/h)	Optimal air flow rate (l/h)	Maximum power output (W)
Bituminous - 256 g/h	CuO	9	1500	1573.71
	Co_3O_4	13.5	1500	1255.75
	Mn_2O_3	26	1800	1727.77
Anthracite - 256 g/h	CuO	9	1500	1619.39
	Co_3O_4	13.5	1500	1301.40
	Mn_2O_3	26	1800	1773.39
Lignite - 256 g/h	CuO	9	1500	1359.54
	Co_3O_4	13.5	1500	1041.59
	Mn_2O_3	26	1800	1510.89

5. Conclusions

In this paper, ASPEN Plus software is employed to model and study the CLOU process. The ASPEN Plus simulations are validated using information from a series of test cases conducted in a CLOU experiment [9]. Excellent agreement is obtained between the simulations and the experimental results for power output. It is demonstrated that the ASPEN Plus can provide a creditable process simulation platform for the study of CLOU process. More detailed validation results can be found in Zhou et al [8]. It is shown that the coal rank has significant impact on overall energy release; the Bituminous coal and Anthracitic coal show similar and better CLOU process performance compared to the Lignite coal. The similarity in the CLOU process performance of Bituminous coal and Anthracitic coal can be explained by the fact that both have similar carbon content. The results indicate that the char gasification is not a very significant factor in CLOU process performance since the presence of oxygen enables the solid-gas combustion to take place without gasification. More importantly, the effect of varying the air flow rate on overall energy output is investigated; there exists an optimal air flow rate to obtain the maximum power output for a given coal feeding rate and coal type. The effect of three different oxygen carriers on energy output is also investigated using the optimal air flow rate. Among the three oxygen carriers CuO, Mn_2O_3, and Co_3O_4, the best performance in terms of power output is achieved by Mn_2O_3. The results presented in this paper can be used to estimate the amount of various quantities such as the air flow rate and oxygen carrier (and its type) required to achieve near optimal energy output and CO_2 capture from a CLOU process based power plant.

References

[1] Leion H., Mattissson T., Lyngfelt A. The use of petroleum coke as fuel in chemical-looping combustion, Fuel 86, pp. 1947-1958, 2007.

[2] Adanez J., Abad A., Garcia-Labiano F., Gayan P., de Diego L.F. Progress in chemical-looping combustion and reforming technologies, Prog. Energy Combust. Sci. 38, pp. 215-282, 2013.
[3] Kvamsdal H. M., Jordal K., Bolland, O. A quantitative comparison of gas turbine cycles with CO_2 capture, Energy 32, pp. 10-24, 2007.
[4] Mattisson T., Lyngfelt A., Leion H. Chemical-looping with oxygen uncoupling for combustion of solid fuels, Int. J. Greenhouse Gas Control 3, pp. 11-19, 2009.
[5] Rydén M., Lyngfelt A., Leion H. Combined manganese/iron oxides as oxygen carrier for chemical looping combustion with oxygen uncoupling (CLOU) in a circulating fluidized bed reactor system, Energy Procedia 4, pp. 341-348, 2011.
[6] Leion H., Mattisson T., Lyngfelt A. Using chemical-looping with oxygen uncoupling (CLOU) for combustion of six different solid fuels, Energy Procedia 1, pp. 447-453, 2009.
[7] Shulman A., Cleverstam E., Mattisson T., Lyngfelt A. Manganese/iron, manganese/ nickel and manganese/silicon oxides used in chemical-looping with oxygen uncoupling (CLOU) for combustion of methane, Energy & Fuels 23, pp. 5269-5275, 2009.
[8] Zhou L., Zhang Z., Chivetta C., Agarwal R. Process simulation and validation of chemical-looping with oxygen uncoupling (CLOU) process using Cu-based oxygen carrier, Energy & Fuels 27, pp. 6906-6912, 2013.
[9] Abad A., Adanez-Rubio I., Gayan P., Garcia-Labiano F., de Diego L., Adanez J. Demonstration of chemical-looping with oxygen uncoupling (CLOU) process in a 1.5 kWth continuously operating unit using a Cu-based oxygen-carrier, Int. J. Greenhouse Gas Control 6, pp. 189-200, 2012.
[10] Mukherjee S., Kumar P., Hosseini A., Yang A., Fennell P. Comparative assessment of gasification based coal power plants with various CO_2 capture technologies producing electricity and hydrogen, Energy & Fuels 28, pp. 1028-1040, 2014.

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