An investigation of steam production in chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU) for solid fuels

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Abstract

Chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU) are being actively explored as solid fuel combustion technologies that have the potential to facilitate CO₂ capture. While CLC and CLOU have similarities operationally, there are some key differences. In particular, the CLC process requires a coal gasification step where coal is first broken down into a syngas with the use of steam or CO₂. The resulting syngas is then oxidized with the metal oxide to release energy. In the CLOU process the metal oxide releases oxygen that combusts the solid fuel, resulting in a lower residence time, as the coal gasification reactions are avoided. The CLC and CLOU systems were modeled with ASPEN Plus at a 10 MW_{th} scale, and the process streams were analyzed by ASPEN Energy Analyzer to determine the amount of industrial process steam that could be generated from CLC or CLOU. Both the air and fuel reactor were analyzed as two circulating fluidized beds, with metal oxide circulating between the two reactors. The air reactor, where metal oxide is oxidized, was fluidized with air. The fuel reactor, where the metal oxide is reduced, was fluidized with steam for CLC and recirculated CO₂ for CLOU. It was identified that the CLOU process had the potential to produce more steam, approximately 7920 kg/hr, as compared to CLC (6910 kg/hr).

Keywords

Chemical-looping combustion (CLC), Chemical-looping with oxygen uncoupling (CLOU), Solid Fuel

1. Introduction

Recent interest in controlling CO₂ emissions has motivated research in carbon capture technologies for solid fuel combustion. Chemical-looping combustion (CLC) has emerged as a promising alternative technology for CO₂ capture. Research has been carried out in 0.3-140 kW_{th} pilot units (Lyngfelt, 2011) and 1-3 MW_{th} demonstration units are currently under construction (Lyngfelt, 2014). A typical CLC process consists of two interconnected fluidized beds which serve as a fuel and an air reactor. In the fuel reactor, the fuel is combusted with oxygen supplied by a circulating oxygen carrier, typically a metal oxide. The reduced oxygen carrier is then transported to the other reactor, the air reactor, where the reduced oxygen carrier is oxidized by air. The regenerated oxygen carrier is then carried back to the fuel reactor.

While chemical-looping combustion (CLC) and chemical-looping with oxygen uncoupling (CLOU) are very similar in configuration, they differ in the mechanism by which oxygen is accessed by the solid fuel (Mattisson, 2013). In the case of CLC the coal is gasified with steam, forming a syngas. The resulting syngas is then oxidized with the circulating oxygen carrier to form CO₂ and H₂O, accompanied with the release of energy. In the case of CLOU the oxygen carrier releases oxygen, which then combusts the coal. In CLOU the gasification step is avoided, resulting in a faster reaction time. A variety of materials have been explored for CLC processes and the CLOU process (Lyngfelt, 2011; Adanez et al., 2012; Mattisson, 2013; Imtiaz et al., 2013). In this particular study, the CLC process has been explored with an iron-based oxygen carrier Fe₂O₃ that releases oxygen by transitioning to Fe₃O₄. The CLOU process has been modeled using a copper-based oxygen carrier transitioning from CuO to Cu₂O (Sahir et al., 2014).

2. Overview of the CLC and CLOU process models

In this study, CLC and CLOU were modeled with ASPEN Plus to determine the material and energy balances (Sahir et al., 2014). The process stream data from those balances was then used in ASPEN Energy Analyzer to determine the steam production rate for each scenario. Wyoming Powder River Basin (PRB) coal was chosen as the feedstock basis, which is being utilized for a process development unit being built at the University of Utah (Lighty, 2012; Whitty, 2012). Specifications are given below and details can be found in Sahir et al. (2014).

2.1 CLC ASPEN Plus Process Model

The CLC ASPEN Plus model employed 60% Fe_2O_3 supported on Al_2O_3 oxygen carrier particles with a particle diameter of 150 μm . Within the CLC fuel reactor the following reactions take place:

In the air reactor the oxygen carrier is oxidized by the following reaction:

These aspects have been incorporated in the development of a process flow sheet shown in Figure 1 (Sahir et al., 2014), and whose model blocks are explained below:

Figure 1. ASPEN Plus flow sheet of CLC process model.

As mentioned in Sahir et al. (2014) the fuel reactor had three blocks (RGIBBS, RSTOIC, and RYIELD). While these are three separate blocks in the ASPEN Plus process model, in reality these reactions occur in a single fuel reactor representing a direct CLC process. The RYIELD block breaks the coal down into its constituent elements. The effluent stream from the RYIELD block is then fed into the RGIBBS reactor with the required steam, which generates the syngas. In the ASPEN process model the water consumption was based on an equal amount of carbon moles to water moles to affect the reaction $C_{(s)} + H_2O \rightarrow CO_{(g)} + H_{2(g)}$. The water requirements to produce steam for fluidizing the fuel reactor were 6.9 times larger than that required for the reaction. These were determined based on circulating fluidized bed calculations from Basu and Fraser (1991) and Lyngfelt et al. (2001). The reaction of the metal oxide particles with the syngas, represented by Reactions 1 and 2, was modeled in a RSTOIC block with 99.9% conversion of Fe_2O_3 to Fe_3O_4 . Due to the endothermic nature of gasification the air reactor was

operated at a higher temperature, 1050°C, so that the oxygen carrier could transfer energy for the fuel reactor operation, at 975°C, to maintain the gasification reaction in an autothermal operational mode. The residence time for the fuel reactor was 10 minutes, controlled by the char gasification.

The effluent gas/solid stream was then sent to a cyclone to separate out the solid particles from the gas. The gas was then cooled, and energy was recovered. Water was recycled to generate the steam for fluidization of the fuel reactor; a flash was used for this separation. The gas fed to the flash was cooled to 85°C in order to condense the water from the other gases.

The reduced oxygen carrier particles were then sent to the air reactor; Fe₃O₄ was oxidized (Reaction 3) with a stoichiometric conversion of 80%. Energy was recovered from the effluent gas of the air reactor. The regenerated oxygen carrier particles were separated with a cyclone and sent back to the fuel reactor. Air reactor residence time was 90 seconds.

2.2 CLOU ASPEN Plus Process Model

The oxygen carrier in the CLOU process model was 40% CuO on ZrO₂ with a size range of 125-180 µm. The kinetics of the copper-based oxygen carrier were based on previous experiments of Mattisson et al. (2009a, 2009b) and analyzed by Sahir et al. (2012). The CLOU process involves the release of oxygen by the decomposition of a metal oxide, as represented by Reaction 4. The oxygen consequently reacts with a carbonaceous feedstock, represented by carbon for a simplified representation in Reaction 5. The process flow sheet for the CLOU process is shown in Figure 2 (Sahir et al., 2014).

from the CLOU fuel reactor would be offset by more energy being needed to heat the recycle stream, resulting in no net benefit. The residence time of the fuel reactor was controlled by the reduction reaction resulting in a residence time of 35 seconds.

Conversion in the air reactor was 50% with a residence time of 42 seconds. The gas/solid mixture was separated with a cyclone. The gas stream was cooled for energy recovery and the solid oxygen carrier was sent back to the fuel reactor.

3. Methodology for analyzing energy streams

The resulting energy streams with their related temperatures, from the ASPEN Plus process models of CLC and CLOU, were utilized for determining the heating and cooling requirements using ASPEN Energy Analyzer. The material and energy balance information for CLC and CLOU, obtained from ASPEN Plus process models, is included in Tables 1 and 2 respectively. No heat loss was assumed so these numbers are the maximum amount of energy that can be recovered. These streams are then used in ASPEN Energy Analyzer to determine the amount of steam that can be generated. For generating the heat exchanger networks a minimum temperature difference of 10°C was chosen. This temperature difference was chosen based on an analysis of conceptual designs for chemical looping processes for hydrogen and power cogeneration for gasification processes (Cormos et al., 2013).

In this study, the effect of heat loss on circulating fluidized bed reactors was not included, as in addition to radiation and convection it is influenced by various other factors (reactor geometry, unburnt carbon, moisture content in fuel and air, enthalpy of steam, sensible heat in ash and slag and flue dust, energy content of flue dust and cooling water) (Ref. Website; Basu, (2006)). Since this was a comparative study instead of a detailed design there was no way of knowing these factors. In a 10 MWth CLC study by Marx et al. (2011) the heat loss has been

assumed to be of the order of 2%. If a loss of 2% is assumed for both units, and both units have a heat input of 10MW, then the 2% loss would be the same for both units. Since this was a comparative study instead of a detailed design, and due to the lack of experimental information, heat loss has not been included in this study.

Table 1. Summary of stream energies and temperatures for the CLC process for a 10MW_{th} scale.

	Stream Energy (kW _{th})	Initial Temperature (°C)	Final Temperature (°C)
Energy required to heat water to fuel reactor temperature, HEAT 4	-9,530	150	975
Air reactor	5,880	1050	1050
Energy associated with cooling air reactor exhaust, HEAT 2	2,055	1050	150
Energy required for heating air, HEAT 1	-2,795	25	1050
Energy associated with cooling flue gas from the fuel reactor, HEAT 3	10,190	975	90
TOTAL	5,800		

Table 2. Summary of stream energies and temperatures for the CLOU process for a 10MW_{th} scale.

	Stream Energy (kW _{th})	Initial Temperature (°C)	Final Temperature (°C)
Energy required to heat recycled gas, REC HEAT	-1,490	150	672
Energy associated with cooling air reactor exhaust, AIR COOL	2,545	935	150
Air reactor	5,515	935	935
Energy required for heating air, AIR HEAT	-3,455	25	935
Energy associated with cooling flue gas from the fuel reactor, GAS COOL	3,530	950	150
TOTAL	6,645		

4. Results and Discussion

The ASPEN Energy Analyzer uses pinch analysis to determine the amount of heating and cooling required. In this case, the cooling requirement represents the amount of steam that can be generated from the CLC and CLOU processes. This study assumed that water was entering at 600 psia and 15.6°C, and exited as steam at the same pressure and 307.8°C. The pressure and temperature chosen to simulate in this case are similar to those chosen by Marx et al. (2013) for their process integration study, and to those employed in an Industrial Carbon Management Initiative (ICMI) report for process design of a CLC system for natural gas (ICMI Report, 2012).

Figure 3 represents the heat exchanger network (HEN) diagram for the 10 MW_{th} CLC process unit, with details on the steam heat exchangers outlined in Table 3. Energy from the fuel reactor exhaust was used to generate steam for fluidizing the fuel reactor. Air for fluidization of the air reactor was preheated by the air reactor exhaust and a portion of the energy from the air reactor. High pressure steam was generated by the remaining heat from the fuel reactor exhaust and air reactor. Recovery of energy from the air reactor presents a significant source of heat for the generation of the steam. Also, the energy required to generate steam for the fluidization of the fuel reactor is a significant requirement. Optimization of the fuel reactor, namely, decreasing the residence time, would potentially help reduce this requirement and allow for additional high-pressure steam generation.

Figure 3. Heat Exchanger Network (HEN) Diagram for the CLC process – 10 MW_{th} case.

Table 3. ASPEN Energy Analyzer results for CLC.

Heat Exchanger Role	Heat Exchanger duty (kJ/h)	Heat Exchanger duty (kW _{th})
Generate HP Steam by supplying a portion of energy from the fuel reactor exhaust gas stream	2.37×10^6	660
Generate HP Steam by supplying a portion of energy from the energy extracted from air reactor	1.85×10^7	5130
Preheat air by recovering energy from air reactor exhaust	7.40×10^6	2055
Preheat air by recovering a portion of energy from air reactor	2.70×10^6	750
Heat steam for fluidization from fuel reactor exhaust	3.43×10^7	9530

Figure 4 represents the HEN diagram for the 10 MW_{th} CLOU process unit, with details on the heat exchangers outlined in Table 4. Fuel reactor flue gas is used to heat the CO₂ recycle stream. As with CLC, air for the air reactor is preheated with the air reactor exhaust and a portion of the air reactor. High pressure steam is generated by the remainder of the energy from the fuel

reactor exhaust gas and the air reactor. As with CLC, the majority of the high pressure steam is generated by recovery of heat within the air reactor.

Figure 4. Heat Exchanger Network (HEN) Diagram for the CLOU process – 10 MW_{th} case.

Table 4. ASPEN Energy Analyzer results for CLOU.

Heat Exchanger Role	Heat Exchanger duty (kJ/h)	Heat Exchanger duty (kW _{th})
Generate HP steam generation by supplying a portion of energy from the fuel reactor exhaust	7.34×10^6	2040
Generate HP Steam by supplying a portion of energy from the energy extracted from air reactor	1.66×10^7	4600
Preheat air by recovering a portion of energy from air reactor	3.28×10^6	910
Preheat air by recovering energy from air reactor exhaust	9.18×10^6	2550
Heat the recycle stream from fuel reactor exhaust	5.36×10^6	1490

Figure 5 represents a comparison of the heat exchanger duties for the CLC and CLOU processes. A comparison of both scenarios highlights the significant role of the fuel reactor exhaust stream. The energy required to generate steam for the CLC reactor is significantly higher than that needed to heat the recycled CO_2 . This is a result of three factors: the enthalpy of steam is larger than the enthalpy of CO_2 ; CLC reactor steam is heated to a higher temperature than the CO_2 of CLOU; and, the larger residence time of CLC means that more steam is needed to fluidize the bed.

Figure 5. Comparison between heat exchanger duties between CLC and CLOU processes.

While these heat exchanger networks may not be the most efficient in terms of exchanger duties, they were designed to be the most practical. A traditional pinch analysis, such as mentioned in Kemp (2007) yields a more efficient system, but often results in a stream being split up multiple times. This results in more exchangers and the likelihood that streams may not be close to each other in the plant. These networks were designed so that the effluent of each reactor would preheat its own feed, rather than possibly sending it to other areas of the process.

The network resulted in the CLC process generating approximately 6910 kg/hr of process steam, and the CLOU process generating 7925 kg/hr of process steam. The process steam had an outlet temperature of 307.9°C at 600 psia. In this comparison the CLOU case generated 14.7% more steam than CLC. This estimate is somewhat conservative as well since the fuel reactor exhaust was cooled to 150°C in CLOU, whereas in the CLC case it was 85°C. These temperatures resulted from the CLC system needing recycled water for steam fluidization, and in the CLOU system a portion of the flue gas was being purged at a higher temperature.

5. Conclusions

An energy integration analysis was performed by utilizing information from ASPEN Plus Simulations for CLC and CLOU for coal. It was identified that the CLOU process with a copper-based oxygen carrier has an advantage, in terms of process steam generation, as compared to the CLC process with an iron-based oxygen carrier transitioning from Fe_2O_3 to Fe_3O_4 . The studies have highlighted the requirement to analyze energy requirements in steam production and fluidization more closely. By fluidizing the CLC fuel reactor with steam there is a significant amount of energy dedicated to heating and cooling the fluidizing steam. The findings of this study reiterate the need for experimental studies to study operational considerations.

ACKNOWLEDGEMENTS

This material is based upon work supported by the Department of Energy under Award Number DE-NT0005015. The material is based upon work while Dr. Lighty served at the National Science Foundation. The views and opinions of authors expressed herein do not necessarily state or reflect those of the National Science Foundation, the United States Government or any agency thereof. The authors will like to acknowledge Dr. George Richards from NETL for insights on system analysis studies conducted at NETL.

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