Parametric and Dynamic Studies of an Iron-Based 25-kW_{th} Coal Direct Chemical
Looping Unit Using Sub-Bituminous Coal

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Abstract

The iron-based Coal-Direct Chemical Looping (CDCL) combustion process is an alternative to conventional oxy-combustion technologies where the oxygen used for fuel conversion in the CDCL process is provided by an iron-oxide based oxygen carrier, instead of an air separation unit. The iron oxide is reduced using coal in the reducer reactor, producing highly-pure CO₂ in the flue gas, and the reduced iron oxide is regenerated in a separate combustor reactor using air. The CDCL process at Ohio State has been developed and demonstrated in a 25 kW_{th} sub-pilot unit, and it is the first chemical looping demonstration unit with a circulating moving bed reactor for solid fuel conversion. To date, the CDCL sub-pilot unit at OSU has been operated for more than 680 hours, with a 200-hour continuous operation, providing important data on long term operability as well as parametric optimization. This paper discusses recent parametric operational experience with sub-bituminous coal as the fuel, where dynamic changes in variables were performed to observe the effects on the unit itself. Measurements included temperature, pressure, and gas concentrations from the reducer and combustor. Furthermore, effects of different variables, such as flue gas recycle ratios (enhancer gas flow rates), feed port injection, and temperature, were observed. Tests confirmed high coal conversions with high purity of CO₂ achieved in the flue gas. Overall, the moving bed design of the reducer results in nearly full coal conversion with a high purity of CO₂, eliminating the need for additional downstream fuel polishing and/or separation units. The combustor gas contained lean oxygen concentrations with minute amounts of carbonaceous gases detected, indicating proper regeneration of the oxygen carrier as well as good gas sealing between the reducer and combustor.

Key Words: chemical looping combustion; coal; CO₂ capture; energy; iron oxide; moving bed

1. Introduction

It is widely known that anthropogenic carbon dioxide in the atmosphere has been linked to global warming [1], and in recent years, it has been proposed that fossil-fuel power plants should capture the carbon produced and store it underground so that it is not added to the atmosphere to contribute to global warming. However, many present post-combustion capture technologies are capital intensive, have high energy penalties, and are difficult, if not infeasible, to retrofit to many present-day power plants. Chemical looping combustion is considered a promising technological alternative to direct fuel combustion because of its inherent ability to produce electricity from carbonaceous fuels without a significant carbon dioxide separation penalty[2–6].

In recent years, there has been an interest in solid fuel systems for chemical looping processes because of the ability to convert fuel directly without a need for external gasification or air separation[7–14]. As a result, The Ohio State University has developed an iron-based Coal Direct Chemical Looping (CDCL) process, shown in **Figure 1**. The iron-based CDCL process converts solid fuels into electricity with in-situ carbon capture by reducing and oxidizing iron oxide based oxygen carrier particles in separate reactors without using a traditional gasifier and an energy-intensive air separation unit. Like most chemical looping combustion processes, the system consists of a reducer reactor, which converts the fuel into carbon dioxide and reduces the oxygen carrier, and a combustor reactor, which reoxidizes the oxygen carrier with air. The reaction in the combustor is exothermic, and the energy from the combustor as well as the both flue gas streams is recovered for the steam cycle for electricity generation.

Many chemical looping processes use a fluidized bed for the reducer reactor. Two integrated, circulating fluidized bed units with a designed fuel capacity of 10 and 100 kW_{th} for

solid fuels have been designed and constructed at Chalmers University in Gothenburg, Sweden, with initial demonstrations performed on the 10 kW_{th} unit using fuels such as petroleum coke and a South African coal [15]. Oxygen carrier materials tested in the 10 kW_{th} unit include ilmenite, a manganese ore [16], ilmenite ore with lime, and manganese ore with lime mixtures [17]. Further work with the 100 kW_{th} unit includes tests with an ilmenite oxygen carrier and fuels such as Mexican petroleum coke and a Columbian bituminous coal [9,13,18–20]. The fate of pollutants such as sulfurous and nitrous species was also studied in the 100 kW unit at Chalmers University [21]. Hamburg University of Technology has developed and commissioned a 25 kW_{th} solid fuel CLC unit. To allow for a better fuel conversion, particularly for the volatiles, the fuel reactor was designed as a two-stage fluidized bed [12]. Tests include work with oxygen carriers such as Australian ilmenite and a synthesized CuO/Al₂O₃ oxygen-uncoupling material [12]. A 10 kW_{th} integrated chemical looping combustion unit was designed and constructed at Southeast University, China, for the purpose of converting biomass and coal using both iron oxide [22] and nickel oxide [23] as oxygen carriers. The fuel reactor consists of a spouted fluidized bed, which has the advantage of a longer solids residence time. As opposed to the 10 kW_{th} Chalmers University process, the solid fuel in the Southeast University reactor is conveyed into the bottom of the reducing reactor with carbon dioxide and steam instead of at the top. Southeast University has also studied using iron and calcium mixtures as an oxygen carrier for chemical looping in a fixed bed reactor [24]. A 1.5 kW_{th} chemical looping oxygen uncoupling (CLOU) demonstration reactor has been built and operated at the Instituto de Carboquímica in Zaragoza, Spain, with chemical looping oxygen uncoupling and ilmenite oxygen carriers [25], with further studies including work on the fate of sulfur with lignite coal using the 60% CuO and MgAl₂O₄ spinel oxygen carrier at temperatures around 930°C [26]. Although promising new

mixed-metal perovskite oxygen carriers have been mostly tested with gaseous fuels such as methane [27–30], perovskite oxygen carriers have also been tested with Mexican petroleum coke and Columbian coal in a batch fluidized bed [31]. It was found that gaseous sulfur species lowers the reactivity of the perovskite, most likely due to calcium sulfate formation [31].

The iron-based CDCL process developed at Ohio State uses a moving bed configuration, unlike any of the previously mentioned works. In the moving bed reducer, the oxygen carrier particles, solid fuels, and enhancing gas are introduced from the top, middle and bottom sections of the reducer, respectively. In order to effectively convert the solid fuels, the reducer is designed with two main stages [33,34]. In the top stage, the iron oxide based oxygen carrier converts the volatiles that are driven off the coal into carbon dioxide, while in the bottom stage, the iron oxide based oxygen carrier converts the devolatilized coal char. The moving bed reducer concept has also been proposed or used by National Taiwan University [35], as well as the Korean Institute of energy research [36]. The National Taiwan University of Science and Technology has tested polyurethane and polypropylene in an annular moving-bed type reactor with an alumina supported iron oxide oxygen carrier. It has been shown that chemical looping using a moving bed can be an effective method to treat solid plastic waste [32]. The countercurrent moving bed reducer configuration provides a number of advantages over a fluidized bed reducer. A moving bed reducer allows for better control of the fuel and oxygen carrier, unlike a bubbling fluidized bed which allows unconverted volatiles to bypass the bed. Because the oxygen carrier is not fluidized, the particle size can be an order of magnitude larger than the pulverized fuel, and this leads to more straightforward separation. By adjusting the gas velocity in the reducer, the flyash and attrited particle can be separated in-situ without needing a separate unit operation; the fines

exit through the reducer flue gas. Finally, a moving bed is compact compared to a fluidized bed, in that the vessel is smaller due to the dense nature of a moving packed bed.

The iron-based CDCL technology has been demonstrated at Ohio State in a 25 kW_{th} sub-pilot unit with high conversions of solid fuels such as sub-bituminous coal and waste products such as metallurgical coke fines with minimal carbon carryover [34]. Furthermore, the carbon dioxide purity in the flue gas is high with low values of carbon monoxide, methane, and hydrogen impurities [33]. As of this writing, over 680 hours of operation have been performed in this unit, with a successful 200 hour continuous campaign. Furthermore, extensive 2.5 kW_{th} laboratory bench unit studies have been performed that were used to verify the carbon char and volatile kinetics [37].

The main purpose of this work is to provide further insight into the effect of variables on the CDCL system with results from some of the testing provided after the 200 hour run from [33]. This paper presents steady state data on the overall performance of the system, including carbon dioxide purity and fuel conversion as a result of variables such as enhancing gas flow rate, coal injection location as well as coal flow rate. Insights into the comparison of variables and interpretations were performed based on both chemical concepts as well as hydrodynamics, as the system consists of heterogeneous reactions (iron oxide with fuel gas, in situ coal gasification, etc.) intertwined with hydrodynamics of solids of different sizes. Previous operations attempted to control the temperature of the reducer reactor as to make it isothermal; however, during commercial operation, the reducer reactor would have a decreasing temperature profile, as the solids would come in hot from the combustor and the temperature would decrease as the solids react with the coal volatiles and gasification products. Furthermore, since previous publications have mainly focused on steady state data, work has also been dedicated to studying transient data

from the system, particularly temperature profiles in the moving bed reducer section, and concentration of gases in the reducer, and later the combustor. The results of these analyses have helped to provide general insight into such items as the residence time of the iron oxide in different sections of the bed as well as temperature distribution.

2. Experimental Setup

The experimental system, shown in **Figure 2**, consists of a combustor, a reducer, a riser, a cyclone, a L-valve, two standpipes and other auxiliary devices. The total height of the system is 5 m. The details of the design of the 25-kW_{th} Coal Direct Chemical Looping subpilot unit, the velocities, and the hydrodynamic characteristics of the coal, ash, and oxygen carriers have been extensively described in previous publications [33,34].

For this work, several important modifications were made to the system. First, a second point for fuel injection was added to the lower section of the reducer in order to determine the effect of coal injection location on the system parameters. The coal injection port was placed 40 cm below the first coal injection location. For later trials, a second gas analyzer was used for measuring the gas concentration out of the combustor outlet while measuring the concentration out of the reducer gas outlet. Temperatures at four regions of the system were measured. The first region, containing thermocouple T₁, consists of the top of the reducer down to 116 cm from the top, and the thermocouple is 58 cm below the top. The second region is the middle of the reducer, containing thermocouple T₂, which is in the region where coal is injected, and the region ranges from 116 cm down to 260 cm, while the thermocouple is 200 cm below the reducer gas outlet. The third region containing T₃, is at the bottom of the reducer, measured from 260 cm below the top of the reducer and 300 cm below the top, which is at the entrance of the L-valve.

The thermocouple for the combustor, or T_4 , is 33 cm above the distributor plate in the combustor, which has a height of 60 cm.

The coal used in this experiment was a subbituminous, Powder River Basin coal from the Black Thunder mine of Wyoming, USA, whose ultimate and proximate analyses are shown in **Table 1**. The fuel was air dried overnight at 35°C and pulverized to 50% less than 200 mesh (74 micron) before injection into the unit. The carbon quantity on a mass basis with moisture was used to determine the carbon consumption during the runs. The molar flow rate of carbon at the reducer outlet was determined from knowledge of the nitrogen flow rate in as well as measuring the nitrogen concentration downstream. The coal feed was controlled with a volumetric screw feeder from Schenck Accurate, with the hopper walls of the coal feeder agitated for steady flow, and a stem-less screw was used to avoid coal aggregate formation and to maximize the coal flowability. The feed rate of coal was adjusted by varying the DC voltage to the screw feeder and a flow rate calibration curve was developed for use in operation. The flow rate and the corresponding voltage were checked after every trial in order to verify that the flow rate was as set.

Samples from the gas outlets of reducer and combustor were taken to quantify the performance of the integrated unit. Non-dispersive infrared analyzers, model ZRE Infrared Analyzer and Chemiluminescence Analyzer by California Analytical Instrument, were used for measuring the concentrations from the reducer and combustor. The infrared-based analyzers were used to measure CO_2 , CO , CH_4 , SO_2 ; a chemiluminescence-based analyzer was used for NO_x measurement, and O_2 was measured paramagnetically. The gas concentration data was continuously recorded at a rate of 1 sample per second. A diaphragm pump and needle valve were used to control the sample gas flow rate to the gas analyzer. A 2 μm sintered filter, chiller,

and desiccant bed were installed to condition the gas sample prior to measurements. For earlier runs shown in Table 2, only one analyzer bank was used, and the sample line was selected between the reducer and combustor using a manifold. Later runs, shown in Table 3, used two banks of analyzers that sampled continuously, one for the reducer and one for the combustor.

As there was significant heat loss at the lower fuel capacity systems, the system was encased in high-temperature ceramic heaters and insulation. Previously, the experiments performed in the system attempted to make the system isothermal, but for these experiments, the heaters were set to allow for a more natural profile for a moving bed system in commercial operation. For the system heating, the heaters were set to maximum power instead of having a set point temperature. This was performed in order to observe the temperature distribution in the system as a result of reactions and flow of oxygen carrier. The temperature distribution in the moving bed reducer side and on the fluidized bed combustor side were observed as a result of coal injection into the system for the various trials shown in **Table 2** and **Table 3**. Between each trial, the system was allowed to circulate without coal injection for 2 hours between coal injections to allow for regeneration of the particle and return to a steady state circulation. Furthermore, the solid level in the moving bed reducer was maintained at the same height for each trial.

3. Data Analysis

The concentrations and flow rates of gas species measured from the system outlets during operation were used for determining the performance of the CDCL system. For the overall results from **Table 2** and **Table 3**, the following equations were used. It should be noted that not all of the calculations apply to **Table 2** as not all of the gas analyzers were in use. For steady

state tests, the primary parameter that describes the performance of the reducer in the CDCL process is the once-through carbon conversion of the coal in the reducer $X_{C,R}$, defined as

$$X_{C,R} = \frac{F_{CO_2,R \text{ coal}}}{F_C} [1]$$

which is defined as the ratio of the flow rate of carbon dioxide from coal ($F_{CO_2,R \text{ coal}}$) emitted at the reducer outlet versus the flow rate of carbon from coal that is injected into the reducer (F_C). The carbon content was calculated based on the ultimate analysis, and the dry carbon content in the analysis was multiplied by one minus the moisture fraction of the material from the proximate analysis (**Table 1**). The carbon dioxide enhancing gas flow rate is removed from the CO_2 calculation so that only carbon from the coal is accounted for. This parameter describes how well the reducer can convert the coal into carbon dioxide and how well the reducer prevents carbon carryover into the combustor.

In order to determine the total flow rate of gases leaving the reducer, the total flow rate of nitrogen injected into the reducer was divided by the nitrogen volume fraction on a dry basis. The nitrogen volume fraction is estimated by subtracting all of the remainder species volume fractions ($x_{i,R}$) from one.

$$F_{total,R} = \frac{F_{N_2,R \text{ injected}}}{1 - (x_{CO_2,R} + x_{CH_4,R} + x_{CO,R} + x_{NO,R} + x_{SO_2,R} + x_{O_2,R})} [2]$$

Steam is not included as it is removed prior to the gas analyzers. The flow of nitrogen includes that calculated from the non-mechanical valve and from the coal injection carrier gas. The individual component flow rates are simply

$$F_{i,R} = F_{total,R} * x_{i,R} [3]$$

An important parameter of a chemical looping process is the carbon dioxide purity leaving the reducer. Overall, the carbon dioxide purity is reported on a nitrogen and moisture free basis because in a commercial plant, there would be little nitrogen being injected into the process and steam would be condensed before carbon capture and sequestration. Any carbon dioxide added from the enhancing gas is not included in the calculations because the enhancer can alter the outcome of the calculations. For instance, a large enhancing gas flow rate may make the stream more pure than it actually is. The concentrations in the transient analyses performed later in the paper are not shown on a nitrogen-free basis in order to more clearly observe system parameters. The carbon dioxide purity also measures how efficient the reducer is at converting coal volatiles and char gasification products into carbon dioxide. For carbon dioxide, the purity is calculated using the molar flow rate of each species in the reducer $F_{i,R}$ as follows:

$$CO_2 \text{ purity} = \frac{F_{CO_2,R \text{ coal}}}{F_{CO_2,R \text{ coal}} + F_{CH_4,R} + F_{CO,R} + F_{NO,R} + F_{SO_2,R} + F_{O_2,R}} [4]$$

The reducer carbon dioxide purity measures how much purification or further processing the carbon dioxide needs before carbon capture and sequestration; a high purity means a reduction in purification requirements for downstream CO₂ conditioning before sequestration.

The oxygen demand, adapted from Berguerand and Lyngfelt (2009), is also used to describe the performance of the reducer. The oxygen demand measures the additional oxygen needed to fully oxidize coal volatiles and coal gasification products leaving the reducer. It is possible to have a very low reducer coal conversion with a 0% oxygen demand. In this scenario, the reducer can oxidize any volatiles, but cannot keep the carbon in the reducer. The oxygen

demand measures the fraction of oxygen needed for complete conversion of the coal carbon leaving the reducer where

$$O_2 \text{ Demand} = \frac{\frac{1}{2}F_{CO,R} + 2F_{CH_4,R} + \frac{1}{2}F_{H_2,R}}{(F_{CO_2,R} \text{ coal} + F_{CH_4,R} + F_{CO,R})\phi} \quad [5]$$

and where

$$\phi = \frac{\%C + \frac{\%H_2}{2} - \%O_2}{\%C} \quad [6]$$

The theoretical best oxygen demand possible is 0%. The oxygen demand also measures how much oxygen polishing is needed on the reducer outlet stream. The way the oxygen demand is defined, sometimes the reducer coal carbon conversion is calculated as

$$X_{C,R \text{ } O_2 \text{ Demand}} = 1 - O_2 \text{ Demand} \quad [7]$$

However, when the oxygen demand is defined with the flow rates of carbon leaving the reducer, $X_{C,R \text{ } O_2 \text{ Demand}}$ is just a measure of the conversion of the measured gases at the reducer outlet and not how well the reducer can prevent carbon carryover. $X_{C,R \text{ } O_2 \text{ Demand}}$ does not incorporate the actual flow rate of coal injected into the reducer, just the flow rate of carbon leaving the reducer.

Additionally, the η_{CC} and η_{OO} , the carbon capture efficiency and the combustor oxidation efficiency, respectively, are calculations that can indicate how efficient the CDCL system is at capturing the coal carbon. The term η_{CC} is the ratio of carbon that leaves through the reducer to the carbon that the entire system emits. These calculations remove the effect of the enhancing gas flow rates to avoid any biases the enhancing gas might introduce. The calculation is as follows for η_{CC} :

$$\eta_{CC} = \frac{F_{C,R \text{ from coal}}}{F_{C,R \text{ from coal}} + F_{C,C}} \quad [8]$$

However, the η_{oo} is the ratio of oxygen used to oxidize the particles to the total amount of oxygen used in the combustor

$$\eta_{oo} = \frac{F_{O_2,C \text{ used}} - F_{CO_2,C}}{F_{O_2,C \text{ used}}} [9]$$

For both of these parameters, an efficiency of 100% is achieved if no carbon is carried over into the combustor.

The carbon carryover fraction to the reducer is an important factor for attempting to close the carbon balance in the system. Carbon carryover is the fraction of carbon from the coal that is carried over into the combustor and converted to carbon dioxide, and it is calculated by measuring the number of moles of carbon dioxide in the combustor gas outlet and comparing to the moles of carbon in the coal feed.

$$X_{C,C} = \frac{F_{CO_2,comb}}{F_{C,coal}} [10]$$

The flow rate of carbon dioxide is calculated from the fraction of carbon dioxide and nitrogen in the combustor gas outlet and calculated based on a nitrogen balance. The carbon carryover to the reducer can be added to the reducer carbon conversion to determine if the carbon balance is complete.

4. Experimental Results and Discussion

4.1 Overall Operational Parameters

During this experimental campaign, the system was operated for over 70 hours of continuous operation. The complete data table for this experiment is shown in **Table 2** and **Table 3**. As described previously, for Trials 1-3 the combustor was not continuously sampled because of the existence of only one bank of analyzers. Thus, those trials do not report any parameters

that use any of the combustor data. Ignoring all other factors such as carrier gas flow rate, enhancing gas flow rate, coal flow rate, etc., the coal carbon conversion in the reducer ranged from 84.8-99.9% with the thermal capacity ranging from 7.4-27.7 kW_{th}. Some of the trends can be described as follows.

The first four trials were performed with coal injection in the top location indicated in **Figure 2**. Comparing Trials 1 and 2, with the same flow rate of 3 L/min for the enhancing gas, the trial with a higher flow of coal had a slightly lower conversion. This could be a result of some of the coal char being entrained out the top with the ash before it is converted to CO₂, as the higher flow rate of coal produces a higher velocity in the reducer because of more volatile gases generated. This would decrease the residence time of the coal char. Another reason could be a small fraction flowing into the combustor with the reduced particles, unmeasured during these trials because of the single analyzer bank. Meanwhile, Trial 3 with a lower enhancing gas flow rate produced a carbon conversion that was higher than both Trial 1 and 2. While the enhancing gas flow was lower than the other two trials, the trial shows that the flow was still sufficient enough to sustain the gasification reactions of coal in the reducer. This can potentially allow for a lower flue gas recycle ratio in a commercial plant. A lower enhancing gas could increase the residence time of the coal char and allow it to further react. In terms of oxygen demand, the third trial had a slightly higher value than the other two, mostly on account of the higher methane and carbon monoxide concentrations. While Trial 2 had a higher concentration of methane and carbon monoxide than Trial 1, the oxygen demand was lower because there was more carbon dioxide produced, making the denominator larger in Eq. 5.

For later trials, the gas from the combustor was analyzed alongside the reducer. The coal injection for Trial 4 was in the top location, while the coal injection for Trial 5 was in the

bottom. Trial 4 produced most of the coal conversion in the reducer reactor, but a small percentage of carbon was converted in the combustor reactor. The same was seen for the bottom coal injection trials as well. While the reducer top injection carbon conversions were not as high for the bottom coal injection location most likely due to carbon carryover into the combustor, the carbon dioxide purities were improved, most likely as a result of the extended length for an increased gas residence time.

The location of the coal injection port, and hence the solid fuel residence time, on the reducer is an important factor that affects the coal carbon conversion and purity. Furthermore, it is possible that at the lower flow rates of coal, the gas velocity is such that it allows for sufficient residence time to convert all of the coal flowing upward. However, for the higher flow rates of coal, there is a greater amount of volatiles produced, which make the residence time lower for the unconverted coal char. There is some variability within the data that can be expected but the values in this experiment fall within acceptable ranges. Nevertheless, the CDCL system has shown to be very robust with respect to the coal injection location, coal flow rate, and carbon dioxide enhancing gas, as the oxygen demand for all six of the trials was less than 1.3% and carbon conversions were in the range of at least 90.2 %.

The results from the trials, given in **Tables 2** and **Table 3**, show that the purity of the carbon-dioxide flue gas from the reducer is high, with low concentrations of carbon monoxide and methane. Hydrogen is not included in the tables, as the hydrogen concentration measured with a gas chromatograph for all trials is less than 400 ppm. This validates one of the merits of the two-section counter-current moving bed reactor, i.e., the fuels can be fully converted. As at the gas outlet of the reactor, the gas contacts only with the fresh oxygen carrier particles, the

hydrogen concentration should be less than 13 ppm based on the thermodynamic equilibrium of hydrogen with fresh Fe_2O_3 at 1000 C.

Furthermore, the carbon carryover fraction to the combustor, defined by Eqn. 10 and obtained from Trial 4 and 5 is less than 5%, as shown in **Table 3**, and the carbon dioxide concentration is less than 0.4 vol%. Thus, it was determined that there was minimal carbon carryover and gas leakage from reducer to the combustor. The carbon carryover was controlled using knowledge of the hydrodynamics of the oxygen carrier and the unconverted fuel, where the enhancer gas helps to fluidize the unconverted char and prevent most of it from exiting through the L-valve. As the particle shrinks upon in-situ gasification, the particle becomes elutriated through the packed moving bed to exit out with the CO_2 flue gas. In comparison, fluidized bed reducer designs using iron oxide as the oxygen carrier have oxygen demands in the range of 10-20% [18] as opposed to less than 1.5% observed in this study for the countercurrent moving bed reducer design.

The general performance of the oxygen carrier, i.e., the attrition rate during the operation and the reactivity over multiple cycles, was also studied. The rate of attrition of the oxygen carrier and the required consumption rate are important parameters for the design and economics of a commercial unit. The lower the consumption rate, the lower the operating cost for a commercial unit. The rate of consumption of the oxygen carrier during the 70 hour run was 0.00426% inventory per cycle, based on a total cycle time of 20 minutes. The larger particle size and lower contact area between the particles in the moving bed allows for a reduced attrition rate as opposed to a fluidized bed reducer. Furthermore, a representative oxygen carrier sample was taken from the reducer inventory after the operation and was tested in a thermogravimetric analyzer for its ability to continue reduction/oxidation cycle under hydrogen/ air conditions.

During the 10 cycle tests of 30 minutes of reduction and oxidization at 900 °C, the sampled oxygen carrier particles reacted steadily and thus, the reacted oxygen carrier demonstrated its ability to retain reactivity.

4.2 System Profile of Trial 1

The temperature and concentration profiles of the sub-pilot unit provide approximate yet unique information about the system operation, such as hydrodynamics, cycle times, and reaction fronts. Thus, a good portion of this manuscript is devoted to the transient profiles. **Figure 3** shows the system temperature distribution for Trial 1, with the coal injection occurring at the left solid line. The moving bed reducer temperature profile shows that the top of the reducer before coal injection is around 1025°C, the middle of the reducer, where coal injection occurs, is around 980°C, and the bottom of the reducer is at 785°C, while the combustor is 900°C. Upon initiation of coal injection, the dynamics of the system were monitored to reveal important information about the moving bed circulation system.

For the temperature in the middle of the reducer, the temperature immediately decreases upon coal injection by 17°C (from 984°C to 967°C) and mainly stayed stationary during the entire injection time because of the high concentration of coal volatiles and gasification products in this region in addition to the injected coal carrier gas, which was room temperature. The temperature decreases slightly by 3°C as a result of a disturbance that is explained later. For the top of the reducer, the temperature instantaneously decreases because of endothermic generation of coal volatiles as well as gasification products passing through this region to the reducer gas outlet and reacting with the iron oxide. After 18 minutes, the temperature then increased because of the exothermic reactions in the combustor returning hot solids from the combustor. The temperature after this point in general then follows the trend of the combustor, however, the

overall temperature is higher in the top of the reducer (1025°C in the top of the reducer compared to 900-950 in the combustor) because the temperature measurement of the combustor is a mixture of cool, albeit slightly preheated 300°C, air and hot solids, while the reducer temperature measures mostly the temperature of the solids. The gas flowing at the top of the reducer is a lower flow rate and is hotter because it flows past the hot particle in the lower sections of the moving bed, and the temperature is also mitigated by the continued reaction of the coal volatiles and incomplete gasification products with the iron oxide. The solids from the middle section lose energy upon reaction with volatiles and gasified coal char. The region is cooler because of the endothermic reactions with the gasification of char with CO_2 to form CO and the corresponding reaction of CO, CH_4 , and H_2 with the iron oxide. It can be noted that the increase in temperature in the middle of the reducer follows the trend of the combustor; however, the temperature increase is not as great as in the combustor because of the endothermicity of the reducer reactions.

The temperature of the bottom of the reducer remains unchanged upon coal injection for around 9 minutes, which corresponds to the time for the reduced oxygen carrier to reach the thermocouple in the lower region. Once the cooled solids reach the thermocouple in the lower reducer region, the temperature drops by 8 degrees (from 782 to 774°C), and 19.5 minutes later, the solids increase in temperature as a result of the heated solids from the combustor coming in at the top of the reducer passing through. The time between when the temperature drops in the region to the time when the solids temperature increases is around 19.5 minutes, which is indicative of the cycle time of the system. Meanwhile, for the combustor, the temperature increases by 50 degrees after 11.5 minutes, but a slight increase in temperature is noted before the temperature excursion. The slight increase in temperature is a result of a small amount of

unconverted char carrying over to the combustor during this time, causing a small increase of temperature in the combustor. There is no decrease in temperature in the bottom of the reducer because the magnitude of the endothermic reverse Boudouard reaction in the reducer is much smaller than the exothermic coal combustion reaction in the combustor. Nevertheless, the temperature change is small. The combustor temperature delay for the excursion to occur is a result of the time it takes for reduced solids to come from the middle of the reducer, where coal injection occurs to initiate iron oxide reduction, to enter to the fluidized bed combustor through the L-valve.

A secondary observation shows temperature perturbations for the top, the middle, and the bottom of the reducer, and the combustor, on the graph. This perturbation is a result of an addition of a small amount of room-temperature makeup of the oxygen carrier solids (<1 kg) that was added to the top of the reducer through the cyclone. Each of these perturbations resulted in either an immediate dip in the combustor or a gradual temperature change, depending on the exact location of the thermocouple compared to the colder solid in the packed moving bed. More gradual changes were observed for point E for the middle temperature reducer which showed minimal change because of the high concentration of coal char and volatiles and their corresponding endothermic reactions with the iron oxide occurring in this area, and point F for the fluidized bed combustor, where the colder solids are well mixed. The time difference between D and E is 7.5 minutes, which corresponds to the residence time for the solids in the top of the moving bed region.

Using the same time scale as the temperature profile in **Figure 3**, a time profile of the reducer flue gas concentration of carbon dioxide, carbon monoxide, and methane upon coal injection is plotted in **Figure 4** for Trial 1. This figure plots the concentrations that include the

nitrogen from the aeration and coal injection gases, and carbon dioxide from the enhancing gas. Before coal injection, the main species in the reducer is carbon dioxide from the enhancer gas injection, which comes from an external gas cylinder. When the carrier gas for the coal is first turned on for the coal feeder, a small amount of residual coal from the injection lines enters the reactor, resulting in a small peak before the actual coal injection. When the precalibrated coal feeder is turned on, the concentration of all three species increases in the reducer. The concentration of carbon dioxide in the flue gas outlet fluctuates, but the concentration of unconverted carbon monoxide and methane is steady below 0.02% after the initial excursion period. The main source of methane in the flue gas is from the coal volatiles. The fluctuations in concentration are a result of slight variations in the flow rate of the coal feeding into the unit. It is noted that the time from coal injection to the peak of CO₂ is around 29 minutes, which mainly corresponds to the time for the coal char to fill the reducer and be gasified at a steady state. Initially, the carbon monoxide and methane are at a much higher concentration (>0.1 vol%) than at steady state, and the concentrations of CO and CH₄ begin to decrease after around 30 minutes; this is a result of the particle becoming activated after one oxidation and reduction cycle. Once the particle becomes reoxidized from the combustor, the particle is more readily able to oxidize the abundance of coal volatiles in the top of the moving bed reducer. Another factor is that as the temperature at the top of the reducer reactor increases (as shown in **Figure 3**), the volatile species are more easily converted to CO₂, and the concentration of methane as well as carbon monoxide decreases.

4.3 System Profile for Coal Flow Step Changes

For one set of trials, the coal flow rate was stepped up several times to study the system dynamics. **Figure 5** shows the temperature distribution in the moving bed as a function of time

for the coal feed step changes. Many of the same trends can be found from this graph as that for Trial 1. For this trial, since the initial flow rate of coal injection is higher, the difference between the initial and final temperatures is greater. The moving bed reducer temperature profile shows that the top of the reducer before coal injection is around 1075°C, the middle of the reducer, where coal injection occurs, is around 1030°C, and the bottom of the reducer is at 835°C, while the combustor is 920°C. Upon coal injection, the temperature in the middle of the reducer immediately decreases upon coal injection, to a much greater degree, from 1030°C to 986°C, and mainly stays stationary during the entire injection time similar to Trial 1 due to the high concentration of coal volatiles and gasification products in this region. The room temperature enhancing gases also help cool the middle of the reducer. Also similar to Trial 1, the temperature of the bottom of the reducer remained unchanged upon coal injection for around 5 minutes, and thereafter, the temperature more readily decreased than for Trial 1 to a minimum of 804°C. Then after 14 minutes, the bottom reducer temperature increases similar to Trial 1. The temperature at the top of the reducer decreases from 1075°C to 1035°C, and unlike the plot for Trial 1, the reducer top temperature does not increase as much, but an increase is noticeable (from 1033°C at the point of the third coal feed step change to 1057°C around 24 minutes later). For the combustor temperature, a small temperature increase was observed from 916 to 926°C over 13 minutes, but the temperature begins to rapidly increase after this point, increasing from 926 to 978°C around 25 minutes later. This is slightly different compared to Trial 1, where only a 2 degree increase occurred during this period, as the flow rate of coal and thus the extent of reduction during Trial 1 was lower.

The coal feed rate starts out at 35.8 g/min, and when the coal injection feed rate is bumped up to 62.5 and 67.4 g/min, the increase has limited effect on the temperature profile of

the system, but it has an effect on reducer CO_2 and CH_4 concentrations, causing them to increase slightly. A concentration profile over the same time period for trials with step change in the coal feeding rate is shown in **Figure 6**. Similar to Trial 1, it takes 23 minutes for the carbon dioxide profile to steady out, the steady point indicated by letter A in the diagram. After this point, similar to Trial 1, the methane and carbon monoxide concentrations decrease, as a result of the activation of the particle in the top moving bed section after one cycle of reduction and oxidation. Upon coal feed step changes, the carbon dioxide concentration increases and then slightly decreases as a result of the coal feed rate adjusted by the screw feeder controller, and then it steadies out. The first two step changes require around 5-6 minutes to steady out to the maximum CO_2 concentration, while the last step change requires 11 minutes. Meanwhile, the methane concentration increases slightly for each increment of coal feed rate change, peaking at 0.2 vol% for 62.5 g/min, but given sufficient time, the concentration decreases. The carbon monoxide concentration mainly stays the same through this time.

4.4 Comparison of Top versus Bottom Coal Injection

The concentration of the reducer and the combustor gases as a function of time for coal injection trials from the top port and the bottom port are shown in **Figure 7** and **Figure 8**, respectively. While the flow rates of coal for both trials are slightly different (approximately 30 g/min versus 40 g/min), a general trend can be observed from the two profiles. For coal injection from the top port, **Figure 7**, coal injection starts at the black vertical line. The oxygen concentration in the combustor decreases at around 18 minutes, which also coincides with a noticeable increase of the combustor carbon dioxide concentration above a baseline of 0.1%. The decrease in oxygen in the combustor also coincides with the carbon dioxide profile in the reducer steadying out. Similar to the other trials, the methane and carbon monoxide concentrations in the

reducer increase substantially, and then decrease, but the decrease is less sudden than the other trials. As in the other trials, methane is the more prominent component in the volatiles over carbon monoxide. For the bottom coal injection, **Figure 8**, the time for the oxygen concentration to decrease in the combustor is around 10 minutes instead of 18 minutes, as the distance from initial particle reduction at the injection point is closer to the combustor than is the top port. The carbon dioxide in the combustor is also slightly higher because some of the coal char is carried over into the combustor with the particle.

5. Conclusions

The operation of the coal direct chemical looping 25-kW_{th} sub-pilot designed and constructed at Ohio State has been successfully demonstrated for the conversion of sub-bituminous coal for 680 hours of smooth, continuous operation with voluntary shutdown. During this testing, the demonstration showed high conversion of solid fuels up to 27.2 kW_{th}, with high carbon dioxide purity, owing to the robust nature of the circulating moving bed system design as well as the oxygen carrier developed at OSU. The carbon dioxide purity during all testing during this run was up to 99.99%, and the single-pass carbon conversion was measured to be up to 99.9% in all of the trials. Measurements from the combustor reactor during fuel injection showed particle regeneration, and the measured consumption of oxygen from the combustor was helpful for verifying the solid fuel conversion in the reducer. For all of the trials, it was noted that the carbon monoxide and methane concentrations decreased dramatically after the particle completed one system residence time of around 20-25 minutes, and the values reached a low steady-state concentration. The oxygen demand was measured to be as low as 0.14%, which suggests that all of the coal volatiles and coal char gasification products were almost fully oxidized. Moreover, the carbon capture efficiency was as high as 94.9% in all the trials. All of

the trials produced a nearly pure stream of carbon dioxide that contained little unconverted carbon and few pollutants. The success of the sub-pilot unit can be attributed to the novel facets of its simple yet innovative design, allowing for a near-complete single-pass conversion of solid carbonaceous fuels to a sequestration-ready carbon dioxide product with a high amount of carbon capture, i.e. minimal carbon carryover into the combustor reactor. The advancement of this project from fundamental particle studies at fixed bed scale, proof-of-concept at the bench-scale, and demonstration at sub-pilot scale has allowed for the development of the technology to a greater level of readiness for potential commercialization.

Conflict of Interest Statement

The authors declare no competing financial interest.

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Figure 1. Diagram of the Ohio State Coal Direct Chemical Looping process.

Figure 2. Experimental setup for the 25 kWth Coal Direct Chemical Looping subpilot system. A – Reducer, B – Combustor, C – Riser, D – Cyclone.

Figure 3. Temperature profile from Trial 1 for both the reducer and the combustor.

Figure 4. Concentration profile of the reducer for Trial 1. The concentrations in these transient analyses are not shown on a nitrogen-free basis in order to more clearly observe the effects on the system.

Figure 5. System temperature profile for trials with coal step changes.

Figure 6. Reducer concentration profile for trials with coal flow step changes.

Figure 7. Concentration profile for top injection.

Figure 8. Concentration profile for bottom injection.

Table 1. Ultimate and Proximate Analysis of the Subbituminous Powder River Basin coal.

Component	Value	Units
Proximate Analysis		
Ash	7.91	wt %, db
Volatile Matter	41.29	wt %, db
Fixed Carbon	50.8	wt %, db
Moisture	13.505	wt %, ar
Ultimate Analysis		
Carbon	71.25	wt %, db
Hydrogen	4.54	wt %, db
Nitrogen	1.13	wt %, db
Sulfur	0.46	wt %, db
Oxygen (by difference)	14.68	wt %, db
Energy Content		
Higher Heating Value	28.543	MJ/kg, db
Higher Heating Value	30.994	MJ/kg, maf

Abbreviations: db – dry basis; ar – as received; maf – moisture and ash free.

Table 2. Experimental results of Trials 1 – 3.

Trial	1	2	3
Port	Top	Top	Top
Coal Flow (g/min)	20.6	67.4	18.1
Power (kW _{th})	8.5	27.7	7.4
CO ₂ (L _{std} /min)	3	3	1
Reducer Carbon Conversion (%)	99.4	98.1	99.9
Reducer CO ₂ Purity (%)	99.92	99.42	99.31
Concentration CO (%)	0.051	0.047	0.119
Concentration CH ₄ (%)	0.027	0.216	0.567
O ₂ Demand (%)	0.45	0.42	1.12

Table 3. Experimental results of Trials 4 – 5.

Trial	4	5
Port	Top	Bottom
Coal Flow (g/min)	29.2	43.5
Power (kW _{th})	12.0	17.9
CO ₂ (L _{std} /min)	3	5
Reducer Carbon Conversion	92.4	90.2
Reducer CO ₂ Purity (%)	99.418	99.88
Concentration CO (%)	0.153	0.020
Concentration CH ₄ (%)	0.391	0.065
Carbon Carryover Fraction (%)	4.7	3.8
Combustor CO ₂ concentration (%)	0.4	0.3
Combustor O ₂ concentration (%)	14.6	14.9
η_{cc}	93.8	94.9
O ₂ Demand	1.26	0.14
η_{oo}	94.2	96.4
η_{cc}/η_{oo}	99.5	98.5

List of Variables

η_{CC} = The total moles of carbon emitted from the CDCL reactor versus the number of moles of carbon emitted from the reducer

η_{OO} = The ratio of oxygen used to oxidize the OC in the combustor to the total amount of oxygen used in the combustor

ϕ = The number of moles of oxygen needed to combust one mole of coal

$CO_2 \text{ purity}$ = On a nitrogen and moisture free basis, the purity of carbon dioxide generated at the reducer outlet

F_C = The flow rate of carbon into the reducer from coal

$F_{C,C}$ = The flow rate of carbon at the combustor outlet

$F_{C,R \text{ from coal}}$ = The flow rate of carbon from coal at the reducer outlet

$F_{CO_2,C}$ = The flow rate of carbon dioxide at the combustor outlet

$F_{CO_2,R \text{ coal}}$ = The flow rate of carbon dioxide from coal at the reducer outlet

$F_{i,C}$ = The flow rate of gaseous species i at the combustor gas outlet

$F_{i,R}$ = The flow rate of gas species i at the reducer gas outlet

$F_{O_2,C \text{ used}}$ = The amount of oxygen consumed in the combustor

$F_{N_2,R \text{ injected}}$ = The flowrate of nitrogen injected into the reducer

$F_{total,R}$ = The total flow rate of gases at the reducer outlet

$O_2 \text{ Demand}$ = The amount of oxygen needed to combust any unburnt volatile species at the reducer outlet

$X_{C,C}$ = The fraction of coal carbon carried over to the combustor

$X_{C,R}$ = The coal carbon conversion based on the carbon dioxide generation at the reducer outlet

$X_{C,R \text{ } O_2 \text{ Demand}}$ = The coal carbon conversion in the reducer based on the oxygen demand

$x_{i,R}$ = The molar fraction of gas species i at the reducer outlet