VALIDATION, MODELING, AND SCALE-UP OF CHEMICAL LOOPING COMBUSTION WITH OXYGEN UNCOUPLING

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Executive Summary

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Chemical Looping Combustion (CLC) is a novel technology that selectively separates oxygen from air by utilizing reversible oxidation/reduction reactions of metals and metal oxides, resulting in a low energy penalty. This separation is commonly accomplished by utilizing a dual fluidized bed reactor that circulates metal-based "oxygen carrier" (OC) particles between an air reactor (AR) and fuel reactor (FR). In the AR, air oxidizes the active metal of the OC particles, which are then cycled to the FR. For a CLC system, a gaseous fuel directly reacts with the solid OC, reducing the metal oxide and producing H_2O and CO_2, which are easily separated by condensing the H_2O. If the fuel is a solid, it must first be gasified, either externally or within the system. The heat released from the system is the same as for conventional combustion processes. However, the CO_2 is inherently obtained in pure form and little or no energy is needed to separate it from the rest of flue gases.

Researchers at Chalmers University of Technology in Sweden recognized the limitations of using gasification for coal conversion in CLC systems. This led to focus on new oxygen carriers that spontaneously release O_2 when in a low oxygen partial pressure. Through thermodynamic analysis, three metal oxides were identified which have suitable oxygen partial pressures at fuel reaction temperatures: CuO/Cu_2O, Mn_2O_3/Mn_3O_4, and Co_3O_4/CoO. Of the proposed CLOU metal oxide systems, the copper oxides are most promising. Since oxygen is in the gaseous form, this allows the oxygen to react directly with the solid coal (char) in the same manner as in a conventional combustion system. Therefore, the carbon conversion takes place as a fast combustion reaction, not as a slower gasification process, and solid coal can be introduced directly into the fuel reactor, it is not necessary to gasify the coal.

Chemical looping combustion clearly has good potential for efficient, comparatively low-cost removal of CO_2 from coal-based energy production. The challenge is to reduce the risk

associated with a new technology by advancing the understanding of fundamental processes that occur within a CLC system, building pilot units of increasing size and developing computational models of reactors and processes that can be used for system evaluation and scale up.

The overall objective of this project was to advance the technology of chemical looping with oxygen uncoupling (CLOU) by investigating the hydrodynamics of the system and identify potential barriers to scale up. Key tasks were: hydrodynamic validation of Barracuda-VR® for CLOU systems in two different system configurations; perform Barracuda-VR® simulations with kinetics; and, complete initial process development and scaling.

Hydrodynamic validation of Barracuda-VR® occurred in two system configurations with two experimental systems: a cold flow unit and a 10 kWth hot unit. The cold-flow unit was designed as a dual circulating fluidized bed system, scaled from the 100 kW_{th} PDU. The bench-scale 10 kWth bench-scale unit was a dual bubbling bed. The CFD simulations were performed with Barracuda-VR® a product of CPFD LLC.

Barracuda-VR® has some limitations on the kinetic inputs. First, the rate equation has to follow a power law or Langmuir-Hinshelwood reaction mechanism. The coefficients, which cannot be multiplied, can be one of four methods: Arrhenius Chemical Rate; 4^{th} order polynomial; table-based coefficient with an independent variable of: fluid pressure, fluid temperature, fluid density, fluid volume fraction, particle temperature, particle volume fraction, particle mass per volume, particle area per volume, and particle diameter; or, catalyst deactivation.

Finally, an Aspen Plus process model for the CLOU process, as well as for conventional non-oxygen uncoupling CLC, was developed to evaluate material and energy balance scenarios.

The purpose of the process models was to investigate options to support the development of The University of Utah PDU.

Experimentally-measured and computationally-simulated oxygen carrier circulation rates for the dual CFB system found that the simulated global circulation rate was consistently higher than the experimental values. This result was due to the Wen-Yu drag model overestimating the drag force, resulting in an over prediction of particle carryover from the reactors. Future work will focus on implementing a drag model that better models the system. Choked flow occurred at a circulation rate of 22 kg/min and a volumetric flow rate above 180 m^3/min. The experiments showed a leveling off around the same flow rate, but at a circulation rate of 17 kg/min. From experiments and simulation, the stand of particles in the loopseal increased with increasing circulation rate (from 1 kg to upwards of 2.5 kg). This led to the conclusion that the smaller cross sectional area in the AR to FR loopseal design caused the choked flow; therefore, increasing the diameter of the loopseal would increase the circulation rate. The particle volume fraction for the AR ranged from 1% - 8% and the FR was 8% - 11% for the parameters explored. The results showed that the air reactor bed mass decreased with an increase in the fluidizing velocity, which, in turn, increased the fuel reactor bed mass. The increase in the bed mass for the fuel reactor did not equal the decrease in the air reactor's bed mass, indicating that the remaining particles were stored in the loopseal. The pressures between the two systems was balanced by the changes in the two bed masses. When the FR fluidizing velocity was increased, particle concentration increased in the top of the reactor. The increased bed particle concentration in the top of the reactor also resulted in a higher pressure at the outlet from the FR to the AR. Both reactors show that as the air reactor fluidizing velocity increased, the residence time decreased. The residence

times in the air reactor and fuel reactor ranged from 10 to 170 seconds and 50 to 150 seconds, respectively, over the range of gas flow rates examined.

For the dual bubbling bed system, the simulated global circulation rate did not agree with the experimental data. The simulated global circulation rate was relatively insensitive to air reactor flow rate while the experiments showed a strong dependency resulting in much higher observed circulation rates than predicted by simulation at the highest air flow rates. This inconsistency is likely due to the small reactor size and under predicting wall effects. Barracuda-VR® has been developed for larger-scale units where wall effects are less prevalent. For the dual bubbling bed system, the FTR for the AR was 0.9, indicating that the internal circulation rate was close to zero. The particle volume fraction for the AR ranged from 17% - 27% and the FR was approximately 41%. In addition, the air reactor bed mass was predicted to decrease with an increase in air reactor fluidizing velocity. The particles leaving the air reactor increased the loopseal particle mass. The predicted particle residence times varied from 150 to 300 seconds for the air reactor and from 100 to 200 seconds for the fuel reactor. As with the dual CFB, this system has a range of residence times and circulation rates.

Since the two systems were quite different in size, the results were normalized with respect to reactor diameter. The circulation rates for the dual circulating fluidized bed were an order of magnitude higher on the lower values and over four times the circulation rate of the dual bubbling bed. The dual BB system had enough time for both the reduction (FR) and oxidation (AR) of the oxygen carrier, between 35-60 s. On the other hand, the dual CFB reached the target residence times when volumetric flow rate was less than 25 $m^3/h/m^3_{reactor}$. At volumetric flow rates higher than this, the AR residence time dropped significantly while the FR residence time was close to the identified average residence time. The residence time range was slightly larger

for the AR dual CFB vs the dual BB – 160 to 150 seconds respectively, and both residence times were similar in the FR.

As compared to film mass transfer, metal oxides kinetic rates were slower; therefore, they are the rate controlling mechanism. For the combustion of char, gas diffusion was the rate controlling step. The results of the global reaction rate where comparable to those in the literature and experimental data.

The initial particle volume fraction, coal char fraction, particle radius, and CO_2 mole fraction were also calculated for the dual bubbling beds. Coal char carbon collected at the top of the fuel reactor and in the freeboard. Also, the small particle radius and high concentrations of CO_2, indicated that this was the combustion zone.

The carbon capture efficiency for the 10 kW case was 0.94. This is above the base US DOE target efficiency of 0.9, but there are incidences when the system runs below the 0.9 carbon capture efficiency. To improve the carbon capture efficiency one could install a carbon stripper between the FR outlet and the inlet to the AR or install a weir in the FR around the outlet that is open at the bottom. This would block the carryover of the char particles located on the top of the FR bed.

Process modeling was also performed to investigate the autothermal nature of the two systems. Autothermal implies that the fuel reactor does not need additional fuel to keep the reactor from going endothermic. For CLC, it was found that a temperature range of approximately 1040^{o}C to 1145^{o}C was acceptable where both reactors were exothermic. In this range of temperatures, the endothermic reaction of the oxygen carrier as well as the gasification of the coal can be overcome by the hot carrier solids. For CLOU, the range was found to be approximately 930^{o}C to 1035^{o}C. This temperature difference is nearly the same as CLC, but the

overall range is at lower temperatures. Operating the air reactor below 930ºC, places the fuel reactor slightly endothermic. Furthermore, increasing the copper content enabled a larger delta T for operation and increasing the fuel reactor temperature decreased the operation envelope for the autothermal and allothermal modes of operation.

Personal communications with industry has suggested that, for a variety of reasons, CLC technologies still need additional verification at larger scales for implementation. There are few pilot-scale facilities available and in particular, for CLOU, there are no large-scale production units for the oxygen carriers. Several industrial representatives have suggested that the next level of study should be 10 MWth. Other carbon capture technologies have been studied at this scale. Based on our work, there should be no limits with respect to increasing the size; it does appear as though a dual circulating fluidized bed system may be problematic in terms of the lower residence times in the air reactor. As oxygen carrier materials continue to be developed, care must be taken so that the residence times in the reactors are long enough for conversion at a reasonable level. If the conversion is too low, then more material will have to be circulated, increasing compression costs.

In conclusion, chemical looping combustion (CLC) is a promising technology for high carbon capture efficiency with lower impacts on cost of electricity as compared to other proposed CCS. The variant chemical looping with oxygen uncoupling (CLOU) is a well-suited technology for solid fuels processing.

Our results suggest that a large advantage of the CLOU system is the improved heat integration between the fuel reactor and air reactor. This improved heat integration is due to the fact that it is easier to maintain the fuel reactor at autothermal operation. In addition, we have examined the range for autothermal operation and found that increasing the copper content

increases the temperature range. In addition, decreasing the fuel reactor temperature also increased the range of autothermal operations.

Barracuda-VR® has successfully modeled, as validated with experimental data, the hydrodynamics of two different reactor configurations, dual CFB and BB. Future work should focus on better drag force models.

Kinetic expressions have to be altered to be included in the Barracuda-VR® framework. We have taken literature values and incorporated these into the simulation, yielding similar kinetics. Using these values we obtained concentration and temperature profiles for the dual BB, 10 kW unit. Very little carbon carried over and the system recovered over 90% carbon, making this a clear option for carbon capture.

As with all energy technologies involving CO_2 capture, chemical looping will make economic sense only if there is a cost associated with emitting CO_2. Recent actions as part of the President's Climate Action Plan, namely POWER+, which supports the continuation of carbon capture technologies, and the Clean Power Plan, which is set to reduce carbon emissions by 2030, suggest that economic incentives will be in place for technologies which potentially utilize coal, such as CLOU. However, coal will continue to be in competition with natural gas and renewables. The market for CLC technology is primarily utilities that seek solutions for low-carbon production of electrical power from affordable fuel such as Wyoming coal. The combination of Wyoming coal cost and quality, and chemical looping's minimal impact on cost of electricity should be attractive to utilities.

There has been an explosion of work on CLC over the last approximately 10 years. As previously discussed, personal communication with industry suggests that the next level of work needs to be done at the 10 MWth scale, still quite a jump from the largest existing scale which is

3 MW. In terms of oxygen carriers, there have been several studies conducted at the 1 MW scale; however, to date, CLOU has not reached this scale. As stated above, in many ways CLOU is potentially superior to traditional CLC, but the limitation will be on the carrier production, reliability, and stability.

The lower cost of CLOU versus other combustion carbon capture technologies will make it attractive. The challenge for chemical looping combustion, and the issue that may prevent its application or adoption, is that it is also the least proven of the technology alternatives. It is clear that larger-scale studies are still needed. As such, the University of Utah group has recently received a DOE grant to continue its work in this area, specifically at the PDU scale of approximately 100 kW. In addition, the group has also become a center of excellence for CPFD LLC and has a continued license for the Barracuda-VR® software. Finally, the project will also focus on the manufacturing of a CLOU oxygen carrier to use in the PDU, a key step in moving the technology forward for coal. In this way, we can investigate the role of coal ash and attrition for the oxygen carriers. This scale will serve as an important stepping stone toward the 10 MWth unit adoption which, as stated above, will be needed to build confidence in the technology for its adaptation.