ADVANCEMENT OF CHEMICAL LOOPING COMBUSTION WITH OXYGEN UNCOUPLING

A research program funded by the University of Wyoming School of Energy Resources

Executive Summary

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June 30, 2014

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Chemical looping combustion (CLC) is recognized as a promising technology for producing energy from fossil fuels, coal in particular, while isolating carbon dioxide (CO_2) as an almost pure gaseous stream suitable for compression and storage. The overall result is energy production from coal with little or no associated release of carbon dioxide. Economic evaluations have determined that chemical looping combustion can result in a lower cost of electricity than other combustion technologies with CO_2 capture, including oxy-fuel combustion, integrated gasification-combined cycle (IGCC), and CO_2 scrubbing of combustion flue gas with chilled ammonia or MEA. It is widely considered the most attractive technology under development for environmentally responsible energy production from coal.

Chemical looping combustion involves using a solid "oxygen carrier," typically a metal oxide, to separate and transfer oxygen contained in air to a vessel where it reacts (combusts) with a gaseous or solid fuel. Undesirable diluent species in air, such as nitrogen and argon, are not transferred by the oxygen carrier. In effect, a CLC system has a built-in air separation process that requires much less energy and complexity than cryogenic air separation units required for oxy-fuel combustion or gasification.

The chemical looping combustion process is configured with two reactors, an air reactor and a fuel reactor. Fuel is introduced into the fuel reactor where it reacts with the oxygen carrier (combusts) to form primarily CO_2 and H_2O. The reduced oxygen carrier then is transported to the air reactor where it is oxidized back to its original state by air. The oxygen carrier cycles, or "loops," between the two reactors, giving the process its name. Most configurations of chemical looping combustion systems, including the process being developed at the University of Utah, use fluidized bed reactors that allow easy transfer of granular oxygen carrier particles between reactors.

Chemical looping combustion is a relatively new technology and development has not yet progressed to the point where commercial systems are available. Most of the research being performed today is limited to lab-scale studies of process fundamentals, and most research focuses on processing of gaseous fuels.

Solid fuels such as coal are more challenging to process in a chemical looping system than e.g. natural gas, because reactions between gas and a solid oxygen carrier are much more efficient than reactions between two solids. Under most circumstances, in order for coal to be processed by chemical looping, it must be gasified to form a combustible gas, either in a separate gasifier that feeds into the chemical looping fuel reactor, or in-situ in the fuel reactor itself. A separate gasifier would require an

expensive air separation system to provide oxygen for gasification, and in-situ gasification with steam is slow and inefficient.

A relatively new concept to work around this challenge of processing solid fuels by CLC is a variant known as chemical looping with oxygen uncoupling, or CLOU. The CLOU process, which is the focus of the University of Utah's chemical looping research, involves using oxygen carriers that spontaneously liberate highly reactive gaseous oxygen (O_2) in the fuel reactor. In order to display this behavior, the equilibrium thermodynamic behavior of an oxygen carrier must be such that at combustion temperatures, the active metal will oxidize in gas environments with more than about 2-5% oxygen, such as that in the air reactor where incoming air contains about 21% oxygen. In environments with low oxygen concentrations, such as the fuel reactor where fuel will rapidly consume any available oxygen, thermodynamics will favor the reverse of the oxidation reaction, resulting in production of gaseous O_2. There are few oxygen carriers that exhibit this CLOU behavior. The most well-studied and understood is copper, cycling between cuprous (Cu_2O) and cupric (CuO) oxide ($2\ Cu_2O + O_2 \leftrightarrow 4\ CuO$). That has been the University of Utah's target oxygen carrier system, largely because of how well the copper carriers are understood. However, an industrial-scale chemical looping system will required several hundred tons of oxygen carrier material, so it must be affordable. Copper may be infeasible for large scale systems, but for the time being no less expensive CLOU carriers are available in the quantities needed for pilot-scale research.

The promise of the CLOU variant of chemical looping combustion as a comparatively simple and low-cost method to process fuels such as Wyoming PRB coal makes it an attractive alternative for carbon capture-ready energy production. Initial lab-scale studies on copper-based CLOU processing of solids fuels were very promising and showed rapid rates of conversion relative to conventional CLC processes. Subsequent studies by a variety of institutions focused on development of CLOU oxygen carrier materials, mostly copper-based, and several well-performing candidates resulted. However, no studies had gone beyond lab scale or focused on CLOU performance in a system with integrated fluidized beds.

The purpose of this project was to advance the understanding of CLOU-based conversion of Wyoming coal through a combination of lab-scale studies focusing on fundamental chemical processes, development of a pilot-scale system for large scale process studies of CLOU and computational simulations of a CLOU system. The project had four main technical tracks: (1) oxygen carrier design and performance, (2) evaluation of underlying chemistry in a CLOU system, (3) design and analysis of an integrated fluidized bed CLC system and (4) process modeling.

The key factor determining performance of chemical looping combustion is the oxygen carrier material. The oxygen carrier should have a high oxygen capacity, should be reactive during both oxidation and reduction, should be insensitive to impurities in the ash and gas such as chlorine and sulfur, should be able to maintain performance over several oxidation-reduction cycles, should be physically robust to withstand the turbulent fluidized bed environment, and should be low cost. Although several groups have developed copper-based oxygen carriers that perform well in lab-scale experiments, the carriers are generally highly engineered, expensive and not able to be economically produced in quantities needed for pilot-scale testing. The University of Utah therefore sought to develop relatively simple, low-cost copper-based oxygen carriers that could be used in its pilot-scale chemical looping system, with the understanding that the materials may not perform as well as the more complex materials developed by others.

Two comparatively low-cost oxygen carriers resulted. Both are prepared by impregnation of a support material with copper nitrate solution followed by calcining (heating) to high temperature to secure the copper within the substrate. It was determined that multiple addition/calcining cycles resulted in a more even distribution of copper, and a more reactive carrier material, than impregnating with all copper at once. Copper concentrations (as CuO) as high as 60 wt% could be achieved, although the carrier materials were observed to sinter in lab-scale fluidized bed tests at loadings of 50 wt% or higher. The two substrate materials were silicon carbide (SiC) and ilmenite. Silicon carbide is widely available in powder form for blasting/polishing applications, and is relatively inexpensive. Engineered silicon carbide catalyst supports are also available, and although the oxygen carriers resulting from these materials perform much better than those based on blasting grit, they are much more expensive. During calcining, SiC oxidizes to form SiO_2 (silica) and copper becomes intimately mixed with the substrate. The SiC-based carriers performed very well and showed little reduction in activity after multiple oxidation-reduction cycles. The other support material, ilmenite, is a relatively low-cost natural mineral common oxygen carrier for non-CLOU applications. The thought behind using ilmenite as a support was to take advantage of its availability and physical robustness. Ilmenite-based carriers were determined not to be as reactive as the SiC-based carriers, nor did they maintain reactivity over as many cycles. It was concluded that either of the carriers developed at the University of Utah would be able to be produced in quantities large enough for pilot testing, and could be produced at CuO loadings high enough to allow process studies under industrially-relevant CLOU conditions.

The second focus area was evaluation of underlying mechanisms responsible for oxidation and reduction of copper-based CLOU carriers. Scale-up of chemical looping combustion requires good understanding of these processes and associated rates as functions of the reactor environment (e.g. temperature, oxygen concentration, fuel concentration). Different copper-based carriers can display different performance due to differences in internal surface area, copper loading and uniformity of copper distribution. Several CLOU oxygen carriers from different sources were tested in a variety of lab-scale systems including thermogravimetric analyzers (TGAs) and batch fluidized beds to evaluate rates of oxidation and reduction both without and with addition of coal char. The carrier materials were also characterized through scanning electron microscopy, electron-dispersive x-ray analysis for determination of element distribution, BET porosimetry for measurement of internal surface area and crushing tests to determine physical robustness.

It had previously been observed that the rate of oxidation increases with temperature to roughly 850°C, after which it decreases. It was determined that this results from a decrease in oxidation driving force as the equilibrium partial pressure of oxygen increases with temperature. Through a series of experiments designed to keep the driving force constant at different temperatures, it was possible to determine the true activation energy of the chemical reaction of Cu_2O oxidation to CuO. Variation of oxidation rate with conversion of the carrier was evaluated for the range of carriers and was able to be modeled by taking into consideration physical developments in the oxygen carrier, in particular grain boundaries for the copper species. Universally-applicable rate expressions for oxidation of copper-based CLOU carriers were developed. At chemical looping combustion temperatures, oxidation of the CLOU carriers is rapid, particularly over the range of conversions targeted for the process. This helps keep the size of the air reactor reasonable and reduces the inventory of carrier material necessary.

Even more important than the rate of carrier oxidation is the rate of oxygen release, or "uncoupling" for the CLOU carriers. This was evaluated in a similar manner to oxidation, and was also found to be very sensitive to the amount of oxygen in the surrounding gas. The oxygen release rate increases strongly with temperature and is rapid under conditions representative of an industrial CLOU system. As with oxidation, it was discovered that carrier reduction (oxygen release) is affected by both the underlying chemistry and physical changes of the carrier material. A universally-applicable rate expression was developed which predicted rates of reduction for all tested carriers with reasonable accuracy over a range of temperatures, gas environments and ranges of carrier conversion. The models of oxygen carrier performance are valuable for modeling and scale-up of CLOU-based chemical looping systems.

The third technical track involved development of an integrated, semi-pilot scale chemical looping combustion process development unit constructed at the University of Utah's Industrial Combustion and Gasification Research Facility and targeted primarily for CLOU processing of Wyoming coal. This represented the largest activity in the program and was also the most challenging. Because chemical looping combustion has not developed to the point of commercialization, there were no operating systems to reference when designing the process development unit. It was necessary to determine an appropriate size for the system that would both replicate conditions in an industrial unit as closely as possible, yet be reasonably affordable and manageable. Based on process analysis, results from the laboratory experiments and experience with other combustion systems at the university facility, it was decided to design for a maximum of 250 kW thermal input (ca. 41 kg/hr, or 90 lb/hr PRB coal), but to target roughly 100 kW as standard operating conditions. For sizing the reactor, it was assumed that an oxygen carrier containing 25% CuO by weight would be used, and that it would be oxidized to an average 75% copper as CuO in the air reactor and be reduced to an average 30% CuO in the fuel reactor. For 100 kW feed of Wyoming Black Thunder PRB coal, that would require circulation of 2,330 kg/hr oxygen carrier. In order to achieve this circulation rate, it was determined that both reactors should be circulating fluidized bed (CFB) designs. CFB reactors are also the most suitable for scale-up to demonstration and commercial scale, since they primarily grow vertically, rather than horizontally like bubbling beds, at larger capacities. Each reactor was designed to be 0.25 m inner diameter and roughly 6 m tall, resulting in average oxygen carrier particle residence times of about 1.5 minutes. Cyclones on the outlets of the reactors separate oxygen carrier particles from the product gas. The separated oxygen carrier particles are returned to the system via loop seals. All output of the air reactor cyclone feeds into the fuel reactor, while the fuel reactor has an internal circulation loop and dedicated outlet near the bottom of the reactor to return solids to the air reactor.

Several other practical design issues needed to be resolved. The reactors could be constructed of metal and then externally heated, or refractory-lined and pre-heated before testing. Both solutions have their advantages, but it was ultimately decided to use refractory-lined reactors since they will be able to tolerate higher temperatures, will provide better thermal stability, and the engineers at the combustion facility are familiar with refractory-lined systems, which is how the other pilot systems are designed. It was also necessary to determine whether the fuel reactor would be fluidized with steam, carbon dioxide or a mixture of the two. Steam can be generated relatively easily, so it was decided to focus on steam fluidization but to make provisions for eventual recycle of CO_2-rich product gas from the fuel reactor. Separating coal ash from the oxygen carrier particles is important. Analysis of the expected cyclone performance indicated that much of the fine coal ash will pass through the cyclone with the gas, allowing natural separation of the two materials. Bag houses downstream of the reactors capture ash particles and any fine oxygen carrier particles resulting from attrition in the turbulent beds. A portion of the unconverted coal char will be carried over to the air reactor and burnt there, which will not allow capture of that CO_2. It was decided not to include a carbon trim cell at the outlet of the fuel reactor to help convert this carryover carbon since it was felt that proper design requires thorough analysis of fuel reactor performance. Provisions were made in the system layout to allow future installation of a carbon trim cell. System preheating will be achieved through a three stage approach involving electrical heating of fluidizing gas to heat the reactors to approximately 400°C followed by direct firing of natural gas into the fluidizing gases to heat the bed to roughly 650°C and finally direct injection of low flows of natural gas into the air reactor to achieve in-situ combustion to heat the system to the target operating temperature of roughly 950°C.

The chemical looping combustion process development unit was constructed at the University of Utah's Industrial Combustion and Gasification Research facility. The overall facility includes a basement level, main level and mezzanine and occupies approximately one-fourth of one of the facility buildings. The CLC PDU is tied in with the facility electrical system, distributed control system, closed cooling water circuit and flue gas handling system.

The fourth focus area was process modeling, which involved consideration not only of the chemical looping reactor but the overall plant. Analysis with the process models confirms that CLOU provides much more efficient conversion of coal, enabling much smaller reactor sizes, than conventional chemical looping combustion using e.g. ilmenite or an iron-based material as an oxygen carrier. Resulting capital and operating cost savings are diminished by the comparatively high cost of oxygen carrier material for CLOU processing. While an iron-based CLC system allows heat extraction from only the fuel reactor, in a copper-based CLOU system processing Wyoming coal, both the air and fuel reactors are overall exothermic, with most of the energy production associated with the air reactor. This may simplify process configuration and allow higher overall efficiencies.

Analysis of process scale-up to 1 MW, 10 MW and 100 MW indicates that non-CLOU systems become less attractive at larger scales due to the high costs associated with compressors required to fluidize the comparatively large beds. Practical considerations of operating such large non-CLOU systems are also a concern. The analysis did not consider costs associated with operation of carbon trim cells, which have the possibility to be very large for non-CLOU systems due to the very coal char conversion rates in the fuel reactor.

Much new and valuable information regarding performance and practical development of chemical looping with oxygen uncoupling resulted from this program. There is now good understanding of fundamental processes that take place in a copper-based CLOU system for processing coal. Models describing these fundamental processes, as well as models of the overall CLOU process, are available as tools for system design and scale-up. A robust process development unit design has been established and the PDU will continue to provide useful information on performance of chemical looping systems for processing Wyoming coal.