State of Wyoming Clean Coal Technologies Research Program

Areas of Interest
D: Advanced cycle technologies
C: Post-combustion gas clean up technologies
F: Carbon capture and sequestration or use technologies

Novel Carbon Capture Technology Development for Power Generation Using Wyoming Coal

A Final Executive Report to the Legislature of the State of Wyoming
Clean Coal Technologies Research Program
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Wyoming is the largest producer of coal in the U.S. This coal accounts for nearly half of the U.S. power production. Thus, WY will be greatly affected by anticipated future carbon emissions legislation. Carbon capture and sequestration (CCS) will be critical to minimize the cost burden incurred on power generation facilities due to carbon emissions. Existing industry standard CO_2 separation technologies are too costly for large scale implementation. Hence, two novel technological pathways for energy efficient carbon capture were pursued.

The University of Kentucky, Center for Applied Energy Research (CAER) led investigations into the application of chemical looping combustion (CLC) technology to Wyoming coal. In the CLC process, an oxygen carrier (OC) transfers oxygen from air to the fuel in a reducing chamber for combustion. Since no N_2 is introduced for combustion, unlike conventional coal combustion technologies, nearly pure CO_2 is produced. Potential OCs, commercially available and developed at CAER, have been screened by TG for their reactivity towards a Wyoming coal char and the effects of Wyoming coal ash on OC reactivity were studied as well. The promised OC for large scale application has been tested in CAER's continuous bench scale FB fuel reactor using Wyoming coal char; the effect of the operational parameters was investigated and the optimal operating parameters are recommended

Los Alamos National Laboratory (LANL) led the development of novel ionic liquid (IL)-based materials for energy efficient CO_2 capture. ILs are promising materials for CO_2 capture due to their low regeneration energies, low volatilities, and high CO_2 selectivities and capacities. However, their industrial implementation as solvents for CO_2 capture is hampered by their high viscosities which lead to high pumping costs, slow sorption kinetics, and inefficient heat transfer. LANL synthesized and evaluated physically gelled ILs, polymerizable IL/IL composites, and polymer/IL composites as potential routes to advanced CO_2 capture materials. The effect of IL cation and anion functionality and polymer matrix chemistry were extensively explored and their impact on material properties and CO_2 separation performance assessed. Deployment platforms for the developed materials were identified. These carbon capture technology platforms include

solid sorbents, membrane contactors, and membranes. Potential commercial opportunities for each materials class are discussed and recommendations for further development made.

A brief synopsis of the development work conducted on the aforementioned two technological pathways is provided below.

Research Area 1: Investigation into the use of Wyoming Coal as the feed for Solid-Fueled Pressurized Chemical Looping Combustion Gasification (PCLCG)

Chemical looping combustion (CLC) is an emerging technology being investigated for future-generation to produce electricity from fossil fuel with in-situ CO_2 separation and without an external stand-alone air separation unit for oxygen production. Instead, CLC uses a solid oxygen carrier (OC), usually a metal oxide to transfer the oxygen from the air to the fuel. Air is not mixed with the fuel, and so the product CO_2 is not diluted with nitrogen in the flue gas. Nearly pure CO_2 is obtained in the exit gas stream from the reducer following condensation of H_2O. The produced CO_2 stream is ready for subsequent sequestration without costly purification. Much research has been done world-wide to develop a CLC process for the combustion of gaseous fuels. Only recently has there been interest in the application of CLC to solid fuels due to potential problems such as slow solid-solid reactions, possible effect of ash on OC reactivity, difficulties of the separation of OCs from ash for recycle, and the durability of the OC.

The ultimate goal for this project research area was to gather information that is critical to the development of an advanced, high-efficiency coal-fired power-generation technology that is capable of 90% capture of the carbon fed to the power plant with a low increase in the cost of energy. Since 2006, work at CAER has focused on the development of OCs for CLC application to solid fuels, the reactivity of solid-solid (OC-coal char) reactions, and identification of optimum CLC conditions such as OC to char ratios, temperature, particle size distribution, durability of the OC, effect of ash on reactivity, separation of the OC from ash and combustion efficiency.

Currently Wyoming coal is used to generate electricity in 38 states according to the Wyoming Mining Association representing 55% of the coal used in the US, and a feasibility study of the application of pressurized chemical looping combustion/gasification (PCLCG) to Wyoming coal would benefit its use under future carbon constraints.

Objectives of this project are (1) to obtain the performance of various OCs towards the gas fuel and the solid fuel (Wyoming coal char), and to identify the suitable OC for use with the Wyoming coal char; (2) to determine the effect of PRB coal fly ash on the performance of various OCs; (3) to find the water vapor effect on the OCs' performance; (4) to demonstrate the continuous run of the bench scale CLC setup, and investigate the effect of the operating parameters such as temperature, fluidizing gas composition, solid inventory, OC to char ratio and solid residence time on char conversion under continuous running.

Prior to the experiments, the possible reactions that took place in the project were identified, and the evaluation parameters were defined, which include the oxygen transfer capacity, average reaction rate, conversion of char, and the CO_2 selectivity.

Wyoming coal char and ash were prepared at the beginning of the project. In order to minimize the potential agglomeration of OC with coal particles at coal's initial combustion stage – devolatilization, the process CAER developed required a pyrolysis step of the coal prior to feeding to reducer. Two 55- gallon drums of the Wyoming PRB coal were acquired from a power plant in the State of Illinois. A bench pyrolyzer was setup for coal char preparation using a tube furnace connected with a three-stage cooling and gas cleaning system. The coal was treated at 550 °C with nitrogen purging for 5 hours to produce coal char. The char generated was then ground to a certain particle size. About 5 lbs. of PRB coal ash was collected from the same power plant. The particle size of the ash was in the range of 2-54 μm. Proximate and ultimate analyses of the PRB char were measured, and the ash was subjected to ash analysis.

Nickel, copper- and iron-based oxygen carriers were produced by freeze granulation from commercially available metal oxides and α-alumina powders. Typically, a slurry was prepared by ball milling a mixture of solids and additives (dispersant and binder) with deionized water. The well-mixed slurry (e.g. slip) was sprayed through a nozzle into liquid N_2 by pressurized air, resulting in a production of frozen spherical particles. The size of the spheres (OCs) was adjusted by air pressure, the liquid flow rate, and composition of the slip. Different ratios of metal oxide loadings to alumina were chosen as 100:0, 75:25, 50:50, and 25:75 of wt/wt %. Freeze granulation conditions, pump speed and air pressure, were optimized to maximize the particle yield in the desired size range. After freeze drying, the OC particles were heat treated in a high temperature oven at 1400°C for 6 hours to remove the organic additives and to improve the

crushing strength. The OC particles were subsequently sieved and those with size between 100-300 μm were selected as the oxygen carriers for tests and characterization. Characterization studies of the OCs included microscopic imaging, crushing strength, apparent density, surface properties, and phase identification by XRD.

The experiments were carried out in the TGA and in the bench scale reactor. The TGA was equipped with a water vapor furnace and coupled with MS. Gas flow rates and switching was controlled by a set of mass flow controllers operated by Lab View software on a dedicated computer. Times for oxidation/reduction and flows were programmed as needed and the entire operation could run continuously without intervention. The bench scale fluidized CLC fuel reactor includes a fluidized bed reactor (2 inches in inner diameter and heated by an electrical furnace), a volumetric solid feeding system for OC and coal char particles, a gas mix and delivery system comprised of a bank of MFCs, a steam generator, and gas sampling units (Rosemond X-stream infrared multi-channel gas analyzer) connected to a multichannel gas analyzer for CO, CO_2, CH_4 and O_2 detection.

The iron-, nickel-, and copper-based oxygen carriers were first screened in the TGA for 5 redox cycles using gaseous fuel in dry and wet conditions. The capacity and reaction rate were selected as criteria to evaluate the OCs. The results show that under dry conditions, CuO based OCs exhibited much higher oxygen carrying capacity than the other two types of metal oxides. Fe_2O_3 based OCs showed the smallest capacity. Capacities of NiO based OCs were higher than Fe_2O_3 OCs, and also presented a strong dependence on the metal loading. Water vapor played an important role in the solid-gas phase red-ox reactions. When 10% water vapor was added into the syngas, capacities of all the OCs decreased. Reduction of capacity was more severe for CuO and NiO based OCs; than for Fe_2O_3 OCs. Under wet conditions, CuO based OCs still possessed the highest oxygen carrying capacity among the three materials. NiO based OCs were the most vulnerable materials to water vapor, showing the highest reduction in capacity of over 95%, and performance which depended significantly on the metal loading. Compared to the other two metal oxides, the capacity of Fe_2O_3 based OCs exhibited much better resistance to water vapor degradation. The two samples with low Fe_2O_3 loadings presented almost no reduction in capacity under the wet conditions. The capacities of Fe_2O_3 based OCs in wet gases were at least 30% higher than that of NiO based OCs with the same amount of metal loading.

In terms of cycling reaction rate, in the dry gases, NiO based OCs showed the highest reaction rates among the three metal oxides. CuO based OCs had intermediate reactivity. Fe_2O_3 based OCs presented the slowest reaction rates with low metal oxide loadings. Although all the OCs exhibit slowed reaction rates compared to their dry gas performance, in the presence of water vapor, Fe_2O_3 based OCs outperformed the other two materials' moderate reaction rates.

In terms of cycling stability, Fe_2O_3 based OCs showed the best consistency among cycles for the three materials. CuO based OCs had the least stability, followed by the NiO based OCs. The samples with 100% CuO and NiO displayed severe deactivations in both dry and wet cycles. In this study, we found that for the freeze-granulated CuO and NiO based OCs, only those with high alumina support loadings could maintain stability/reactivity at 950 °C for at least 5 cycles without significant deterioration in performance.

The solid composition change of OC during reaction was identified by XRD analysis. For Ni and Cu OCs, the compounds of OCs from dry and wet gas reduction were not significantly different from each other. In the Fe OC, the iron oxide was reduced to FeO ($FeO.Al_2O_3$) owing to its good dispersion on the support, even in the wet gas reduction.

The water vapor (WV) effect on the surface area of OC samples with/without WV present during the reduction cycles was analyzed by conducting the surface measurement; specifically their BET surface area, pore volume and pore width. The results show that the reduced samples with and without WV present during the reduction had very similar specific surface area. For FG Fe_2O_3-50 samples, the wet reduced sample had a slightly larger surface area than the dry reduced sample. For the copper and nickel samples, the wet reduced samples showed a slightly lower specific surface area than that of the dry reduced samples, 10% for FG CuO-50 and 5% for FG NiO-50. Thus the percent differences in the specific surface areas were less than the degree of reactivity decrease caused by WV. Average pore diameter and pore volume measurements also showed close results, suggesting that the presence of WV did not alter the microstructure of the particles significantly.

In the solid-gas phase reactions, the presence of water vapor will drastically reduce the capacity and reaction rates of commonly used metal oxides, however, in the solid-solid reaction, considering the presence of water vapor can facilitate the in situ gasification which in turn will

accelerate the overall combustion rate. Therefore it will be ideal to use the metal oxide with moderate capacity and reactivity, but high resistance to water vapor as the active material in OCs. So, the Fe_2O_3-based OCs is selected for next step study - solid fuel combustion.

Solid fuel direct combustion using Wyoming coal char was another important task. It was also important to understand the water vapor effect on direct char combustions with various OCs. Comparative tests were performed by heating up mixtures of the char with various freeze-granulated OCs to 950 °C in Ar with or without water vapor. To avoid complexity, CO_2 was not present. In dry Ar, OCs were the only oxygen source for char combustion and in the wet gas test runs, water vapor was the only gasification agent. The baseline was measured which runs using pure Al_2O_3. Results showed that no significant weight change contribution was from the support material alone. The experimental on OCs with char suggest that WV facilitated the coal char combustion by *in situ* gasification perform well for solid fuel combustion. The synergistic effects of simultaneous gasification and carrier fuel reduction were obvious. However, they tend to require energy intensive processing to enhance their integrity and reactivity and are therefore expensive to produce. The application of CLC requires a large quantity of oxygen carrier inventory due to its slow reduction rate. Furthermore, the attrition loss of the OC during operation is inevitable, which necessitates the development of cost-effective OCs such as Ilmenite.

Ilmenite ore, supplied by QIT Iron and Titanium Corporation, Canada from the Lac Tio mine, was studied as a potential cost-effective OC. It is iron rich, which is suitable to be used as OC. Comparison study of reactivity and crushing strength between the natural OC and a synthetic OC was performed. The result showed that reactivity of the natural ilmenite OC is a little lower than the synthetic OC; however, the ilmenite exhibited a much higher crushing strength, and also has good chemical stability. The chemical stability was examined by conducting multi-redox cycles. The comparison of the reactivity and the phase change gave an indication of good or bad chemical stability. Overall, ilmenite proved to be a viable, cost effective OC candidate for large scale CLC application.

The PRB ash effect on the performance of OCs was studied by mixing ash with OC and char at varying ash concentrations. The ratio of char/OC was chosen to be above the stoichiometric ratio. The performance of the OC was determined by the amount of carbon converted from the char

based on carbon analysis from before and after the TG runs. All results were normalized to the base case of a char and OC only run without ash. Maximum rates of reduction of the OC were determined from the differential of the weight loss curves. The maximum and minimum levels of variation of the experimental results from the TG-MS testing procedures were determined previously from duplicate runs using the same materials and operating parameters. The result showed that the addition of PRB ash decreased carbon removal of the Fe_2O_3 based OC, but had positive effects on reduction rates at 25% and 50% ash concentrations. The PRB ash also had a small positive effect on the oxygen transfer capacity and average reaction rate of ilmenite. Overall, with the low ash concentration ($\leqslant$3%), which is a process relevant value; ash effect on ilmenite performance was negligible.

Prior to conducting the bench scale fluidized bed test, it was necessary to find the optimal operating parameters for the designed fluidizing bed reactor. A clear PVC reactor with the same dimensions as the bench scale fuel reactor was fabricated to study the phenomenon at incipient and bubbling fluidization. The hot and cold run of the stainless steel reactor were also conducted. By measuring the pressure drop, the minimum fluidization speed for both cold run and hot run bench scale tests were determined.

The bench scale CLC setup was also run for a continuous test using treated PRB coal char as fuel and Ilmenite as the oxygen carrier. During the experiment, the effect on char conversion and CO_2 selectivity of operating parameters such as bed temperature, fluidizing gas composition, solid inventory, OC to char ratio and solid residence time were investigated. A higher reaction temperature gave a higher conversion. However, the related higher CO level decreased the CO_2 selectivity. The addition of CO_2 and water vapor to the fluidizing gas was beneficial to the reaction rate. Water vapor was much better than CO_2 as char gasification agent and also gave the best CO_2 selectivity. Increasing the solid feed rate can produce a higher CO_2 concentration, but the conversion and reactivity do not always increase with feeding rate. OC inventory and OC to char ratio gave best conversion and CO_2 selectivity at certain values. Based on the results, the following optimized operating parameters are recommended: reaction temperature at $950^{\circ}C$, a gas composition of 25 vol. % water vapor balanced with CO_2, a 17.6 g/min solid feeding rate, 2L/min fluidizing gas flow rate, and an OC to char ratio of 100. Since higher temperature will increase the char conversion, a higher temperature of $1050\ ^{\circ}C$ could be used.

Research Area 2: Ionic Liquid-Based Materials for Carbon Capture from Existing Pulverized Coal Power Plants using Wyoming Coal

ILs are promising materials for CO_2 capture due to their low regeneration energies, low volatilities, and high CO_2 selectivities and capacities. However, their industrial implementation as solvents for CO_2 capture is hampered by their high viscosities which lead to high pumping costs, slow sorption kinetics, and inefficient heat transfer. The ultimate focus of this effort is to develop novel deployment platforms for ILs to address the challenges associated with their large scale industrial use. This work explored development of novel IL-based materials using design strategies employing IL gelation, polymerizable ILs, and IL impregnation into polymer matrices to achieve enhanced CO_2 separation performance. Specifically, physically gelled ILs, polymerizable IL/IL composites, and polymer/IL composites were synthesized and evaluated as potential routes to advanced CO_2 capture materials. The effects of IL cation and anion functionality and polymer matrix chemistry were extensively explored and their impact on the material properties and CO_2 separation performance assessed. The main outcomes of this work are summarized below.

Polymer/IL Composites: IL impregnation into polymer matrices was applied to successfully fabricate IL/polymer hybrid materials for CO_2 separation. Both polyethylene glycol (PEG) and polyvinylideneflouride (p(VDF-HFP)) based IL/polymer hybrid materials were synthesized. These polymer/IL hybrids showed promising high CO_2 affinity for potential deployment as sorbents and membranes for CO_2 capture from flue gas capture. IL/PEG sorbents were evaluated for CO_2 sorption near ambient temperature and realistic flue gas pressure conditions to understand the influences of IL cation and anion functionality and cation alkyl chain length on material performance. IL/PEG sorbents showed high affinity for CO_2 and improved sorption rates over the neat ILs. High CO_2 sorption capacity up to 1.5 mmol/g sorbent was measured for IL/polymer sorbent containing [emim][Ac], which is comparable to other high performing porous organic sorbents but significantly lower than that reported for high performing inorganic sorbents. The high sorption capacity of [emim][Ac]/PEG sorbent is attributed to the chemical reaction between CO_2 and acetate group leading to carboxylate formation. Interestingly, incorporation of electron withdrawing CF3 group on the acetate anion led to significant reduction in the CO_2 sorption capacity.

IL/p(VDF-HFP) materials were evaluated as thin films to understand the influence of IL impregnation on the gas transport properties. Both amorphous and semi-crystalline p(VDF-HFP) were used as polymer matrices. A 2 to 3 order of magnitude increase in CO_2 transport was observed following IL impregnation into each polymer matrix. A CO_2 permeability of 1000 barrer and CO_2/N_2 selectivity of 12 was obtained for [emim][Tf2N]/p(VDF-HFP) containing 60 % [emim][Tf2N] at 75 °C. During temperature cycling between 75 °C and near ambient temperatures, the amorphous polymer matrices showed dramatically improved IL retention capability as compared to the semi-crystalline polymer matrices comprising the same chemical compositions. Further development and deployment of these IL/polymer composites as membranes with thin selective layers (ca. 100 nm) would lead to unprecedented CO_2 permeances (10,000 GPU). Since CO_2 capture cost using membranes is significantly affected by the permeance (inverse relation), significant reductions in CO_2 capture cost are achievable with membranes having high CO_2 permeance. To fully realize the techno-economic benefits of the improved permeance, further improvement in CO_2/N_2 selectivity is required. While process schemes are accessible to utilize membranes with selectivities below 20, process designs combined with systems analysis efforts from non-profits, government, and industrial entities show efficiency and cost advantages if selectivities reach 20.

Gelled ILs: Gelled-IL materials were fabricated using physical gelation of ILs with a low molecular weight gelator. Extensive rheological characterization of the gelled-IL materials was conducted to understand and improve mechanical properties of the gelled-IL materials. The gelled-IL thermal history and fabrication protocols had profound impacts on gelled-IL mechanical properties. Gels prepared by mixing gelator and IL at temperatures above their gel point, typically 155 °C, followed by quenching in ice bath were found to have the highest moduli, followed by gels that had been rapidly quenched from 145 to 0 °C at -30 °C/min cooling rate in the rheometer. Gels prepared by slow cooling of a sol to 0 °C exhibited the lowest moduli, indicating that they are the weakest mechanically. Thus, rapid cooling appears to result in the formation of a stronger gel network with the low temperature and rate of the quench influences the extent of that enhancement. Increasing gelator concentration also led to improved gel strength and an increase in sol-gel transition temperature, an important factor for determining their utility in elevated temperature process environments. The sol-gel transition temperature identified for the gel containing 40 mg gelator is approximately 125°C, which is significantly

higher than that measured for gelled-IL with 15 mg/g gelator. Although the synthesized gelled-ILs had solid-like characteristics, the mechanical properties of the gelled-ILs were not sufficient to allow their deployment and use as solid sorbents or membranes utilizing any fabrication scheme. Further improvements in the gelled-IL mechanical properties are mandated to realize their potential as a medium for carbon capture.

Polymerizable IL/IL Composites: IL polymerization into solid particles was accomplished by incorporation of polymerizable functional groups including vinyls, methacrylates, acrylates, and epoxides into monomeric and oligomeric backbones incorporating IL moieties. Post-polymerization, these poly-IL materials were shown to have exceptional IL retention ability with free IL loadings up to 80%. As a result, these poly-IL/IL composites are attractive materials for CO_2 capture. Ultrasonic assisted atomization was used to synthesize poly-IL/IL particles. The influence of initiator type, concentration and reactive functional group were evaluated to obtain robust poly-IL particles. Although, the poly-IL materials fabricated showed solid-like characteristics and the ability to retain high fractions of free-IL, the long reaction times for the vinyl and methacrylate functionalized materials and short shelf-life of the highly reactive acrylates and epoxides rendered poly-IL sorbent fabrication using spray drying a significant challenge. Other techniques such emulsion polymerization should be explored to fabricate size controlled poly-IL particles while potentially mitigating the fabrication challenges encountered due to polymerization kinetic constraints.

Deployment platforms for the developed materials were identified. These carbon capture technology platforms include solid sorbents, membrane contactors, and membranes. Potential commercial opportunities for each materials class are discussed and recommendations for further development made.

The work conducted as part of this programmatic effort comprises the feasibility research required to progress the technology to the next stage of development and validation. As a result of the overarching conclusions and assessment of near term success potential of the technology/materials design approaches pursued as part of this project a single approach has been down-selected for continued development. Commercialization/Success potential was evaluated with input from potential end users of the technology both interested in deployment for their industrial CO_2/N_2 and CO_2/CH_4 separation needs. The selected materials design strategy

employs polymer/IL composites comprised of low crystallinity polymer matrices resulting in high IL loading potential, excellent IL retention under anticipated process conditions, high CO_2 affinity, and industrially attractive permselectivity. The near term path forward for continued progression of these materials as a separation media will be conducted as part of our continuing efforts with the cost share partners on this program. The materials will be deployed as membranes. It is our assessment that advancing these materials to the next stage of development and demonstration as high performing CO_2 capture membranes will involve the following critical tasking. •) Given the industrially attractive separation performance (permeability and selectivity) exhibited by these materials at ambient conditions, the next progression should involve translation of these materials into high permeance/ throughput membranes. This translation will comprise developing methods to fabricate ultra-thin selective layers of these materials on commercially attractive supports. •) Demonstration of the composite material and membrane performance over a broad range of industrially relevant operating conditions and environments to define optimum separation process parameters for use of this technology in Wyoming coal derived flue gas (temperature, trans-membrane pressure, impurity and water tolerance and performance influences). •) Continued materials optimization to further improve material selectivity at elevated process temperatures leading to improved process economics. Near-term efforts should be scoped to involve incorporation of hybrid additives targeting elevated selectivity.