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Looping Combustion of Solid Fuel---- Phase 1, 2004

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Project Summary

Chemical Looping Combustion is a novel combustion technology for the inherent separation of the greenhouse gas, CO₂. In 1983, Richter and Knoche¹⁵ proposed reversible combustion, which utilized both the oxidation and reduction of metal. Metal associated with its oxidized form as an oxygen carrier was circulated between two reactors – oxidizer and reducer. In the reducer, the solid oxygen carrier reacts with the fuel to produce CO₂, H₂O and elemental metal only. Pure CO₂ will be obtained in the exit gas stream from the reducer after H₂O is condensed. The pure CO₂ is ready for subsequent sequestration. In the oxidizer, the elemental metal reacts with air to form metal oxide and separate oxygen from nitrogen. Only nitrogen and some unused oxygen are emitted from the oxidizer. The advantage of CLC compared to normal combustion is that CO₂ is not diluted with nitrogen but obtained in a relatively pure form without any energy needed for separation. In addition to the energy-free purification of CO₂, the CLC process also provides two other benefits. First, NO_x formation can be largely eliminated. Secondly, the thermal efficiency of a CLC system is very high. Presently, the CLC process has only been used with natural gas.

An oxygen carrier based on an energy balance analysis and thermodynamics analysis was selected. Copper (Cu) seems to be the best choice for the CLC system for solid fuels. From this project, the mechanisms of CuO reduction by solid fuels may be as follows: a) If pyrolysis products of solid fuels are available, reduction of CuO could start at about 400°C or less. b) If pyrolysis products of solid fuels are unavailable and the reduction temperature is lower, reduction of CuO could occur at an onset temperature of about 500°C, char gasification reactivity in CO₂ was lower at lower temperatures. c) If pyrolysis products of solid fuels are unavailable and the reduction temperature is higher than 750°C, all reaction reactivities were improved, especially the CO₂ gasification reactivity of char. Thus, the reduction of CuO by the gasification product CO could proceed quickly.

Based on the results obtained, the following coal characteristics would be desirable for the Chemical Looping Combustion process: high volatile matter with a high reactivity of the char produced. PRB coal meets these criteria while being comparatively less expensive and also very abundant. The high moisture content present in PRB coal might also increase the reactivity for char gasification through the development of pore structure and specific surface area in the char during pyrolysis. Biomass materials are also suitable, considering the reaction mechanism of CLC system of solid fuels. The feasibility of the chemical looping combustion process of solid fuels was verified by focusing on PRB coal and biomass. Based on PRB coal as the preferred solid fuel in the development of the CLC system, the mass, energy and system in a dual reactor recirculation system has been determined.

In the Cu oxidation tests, it was confirmed that the heating rate is the most important effect on the Cu oxidation process. Lower heating rates and lower operational temperatures would result in incomplete conversion of Cu to CuO. Cu₂O may be the intermediate product. The operating temperature did not affect the reaction rate of the oxidation process. Under any operating conditions, the exothermic properties are clearly shown.

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2.1. Significance, Background Information, and Technical Approach

2.1.1. Identification and Significance of the Problem or Opportunity, and Technical Approach

2.1.1.1. Emission of Green House Gases (GHG) - Carbon Dioxide and Its Sequestration

Emission and Sequestration of CO₂. It has been known for more than 100 years that CO₂ is a greenhouse gas (GHG).¹ CO₂ is a heat opaque gas that traps and prevents heat from being transmitted through it when present in significant concentrations in the atmosphere. Atmospheric CO₂ concentration has grown dramatically, from about 280 ppmv (parts per million by volume) at the beginning of the industrial revolution (ca. 1850) to about 373 ppmv today,² an increase of 32%. Fossil fuel combustion is a major source of CO₂ emission. World-wide fossil fuel based power production contributes about one-third of the total CO₂ released annually.³ In the U.S., fossil fuels currently supply over 85% of the energy needs and their combustion is responsible for about 90% of the GHG emissions.⁴ During the 20th century, world-wide energy demand doubled approximately every 30 years and is expected to increase well into the 21st century. The Energy Information Administration in the U.S. Department of Energy (DOE) projects U.S. consumption of coal, oil and natural gas to increase by 40%, and carbon emissions to rise by 33% over the next 20 years.⁵ Compared to other fossil fuels, coal combustion suffers inherent CO₂ disadvantages because of its combustion characteristics and inefficient older combustion systems.

In recent years more concerns have arisen about controlling the emission of CO₂ due to its perceived acceleration of global warming. The intention of the Kyoto protocols (1997),⁶ was to provide binding limits on greenhouse gas emissions and begin the process of reducing the atmospheric concentrations of greenhouse gases. On February 14, 2002, President Bush announced the Global Climate Change Initiative (GCCCI) with the goal of significantly reducing U.S. greenhouse gas concentrations by 2012. The GCCCI calls for increased research and development investments to provide an improved basis for sound future decisions and for increased emphasis on carbon sequestration, since CO₂ is a major GHG. In 1997 DOE initialized a Carbon Sequestration Program to develop a portfolio of technologies that have a high potential for reducing GHG emissions. Two general approaches for CO₂ purification were listed as DOE potential developing projects, which includes pre-combustion de-carbonization and post-combustion capture.⁵ The program milestone is to demonstrate a series of systems that provide safe and cost effective GHG capture, storage and mitigation technologies at the commercial scale by 2012, followed by substantial market penetration beyond 2012.

There are three major measures to reduce CO₂ emissions in the fossil fuels combustion process. The first, and best method to reduce carbon dioxide is to use energy more efficiently or to use low-carbon intensity fuel such as natural gas to reduce the level of the carbon emission. The presently reported global average efficiency of coal-fired plants is around 31%. State-of-

the-art coal fired plants operating based on advanced technologies may increase its efficiency to around 47-50%. Power generation with natural gas combined cycle (NGCC) can reduce CO₂ emissions by increasing efficiency and use of a fuel with low-carbon intensity.⁷ However, the natural gas supply can not fully support the energy need of the country's electricity demand over a long term. Another way is to increase our energy supply from carbon-free energy (nuclear power and renewable sources such as solar energy, wind power, and biomass fuels). However, all these can not fill in the gap of energy supply which coal leaves. The third and the newest way is to separate, capture, and securely store carbon dioxide emitted from the global energy system (carbon sequestration). Capturing and storing carbon dioxide could slow down climate change and also allow fossil fuel to be a bridge to a clean hydrogen-based future. This method is the technical prolonging of the natural photosynthesis process which is slow in nature and presently could not be sustained at the high rates of industry CO₂ generation. It has been recently proposed that pure CO₂ sequestered from flue gas be stored in used oil and gas fields, in coal beds for oil or methane recovery,⁸ in aquifers,⁹ or in deep seas and sea bottoms.

However, in a conventional combustion system fuel and air are directly mixed and burned. This results in a low partial pressure of CO₂ in the presence of majority of nitrogen and other contaminants. This is the main limitation to controlling CO₂ emission and will create a significant energy penalty.¹⁰ The estimated cost of CO₂ disposal, ~\$4-8 US per ton of carbon,¹¹ is small compared to the costs for separation and purification of CO₂, which is typically in the range of \$100–200 US per ton of carbon.¹² This major loss in efficiency is a result of the energy needed for separation of CO₂ and for compressing it to a liquid form. For a coal-fired power plant, roughly one-fifth of the electricity produced will be lost to CO₂ separation and compression due to its low concentrations in flue gases.¹³ Faster CO₂ sequestration by chemical means at combustion sources with high CO₂ concentrations (i.e., stationary power plants) would be highly desirable.

Among available or proposed technologies^{14, 15} involving CO₂ purification, chemical looping combustion is the most promising technology to combine fuel combustion efficiently and pure CO₂ in-situ, thus easily followed by CO₂ sequestration. The process uses a solid oxygen carrier to transfer the oxygen from the air to fuel. The oxygen carrier is recycled as a fuel reactor (reducer), where it is reduced by the fuel, and as an air reactor (oxidizer), where it is oxidized by the air. Thus, air is never mixed with the fuel, and the CO₂ does not become diluted by the nitrogen of the flue gas. In this proposal, the technical development and pilot-scale demonstration of chemical looping combustion of solid fuels are focused on based on Phase I test results.

Chemical Looping Combustion (CLC) Process and Its Technical Challenges for Application to Solid Fuels. CLC is a novel combustion technology for the inherent separation of the greenhouse gas, CO₂. In 1983, Richter and Knoche¹⁵ proposed reversible combustion, which utilized both the oxidation and reduction of metal. Metal associated with its oxidized form as an oxygen carrier was circulated between two reactors – oxidizer and reducer. In the reducer, the solid oxygen carrier reacts with the fuel to produce CO₂, H₂O and elemental metal only, as

illustrated in Equation (1). Pure CO₂ will be obtained in the exit gas stream from the reducer after H₂O is condensed. The pure CO₂ is ready for subsequent sequestration. In the oxidizer, the elemental metal reacts with air to form metal oxide and separate oxygen from nitrogen, as illustrated in Equation (2). Only nitrogen and some unused oxygen are emitted from the oxidizer. The advantage of CLC compared to normal combustion is that CO₂ is not diluted with nitrogen but obtained in a relatively pure form without any energy needed for separation.

In addition to the energy-free purification of CO₂, the CLC process also provides two other benefits. First, NO_x formation can be largely eliminated. In a chemical-looping combustor, there is no fuel NO_x and prompt NO_x formation in the oxidation process of elemental metal since the combustion is fuel and flame free. Moreover, there is also no thermal NO_x formation due to the considerably lower oxidization temperature (around 900°C) as compared with conventional combustion.¹⁶⁻¹⁸ Secondly, the thermal efficiency of a CLC system is very high. Presently, the CLC process has only been used with natural gas. According to previous reports, the efficiency of the NGCC (natural gas combined cycle) system is higher than that of PF+FGD (pulverized coal furnace with flue gas desulfurization) system, IGCC (integrated gasification combined cycle) system and O₂/CO₂ recycle system on the basis of a 500 MWe power plant.¹⁹

The metal oxides used as solid oxygen carriers in the CLC must have sufficient rates of reduction and oxidation and enough strength to limit particle breakage and attrition. A number of metals have been discussed in the literature,²⁰⁻³¹ such as oxides of Fe, Ni, Co, Cu, Mn, and Cd, as well as metal blends. The investigation of the rates of oxidation and reduction of selected metal oxides were carried out in a TGA or lab-scale fixed bed using either H₂, CO or CH₄ as fuels.³² The rates of reactions vary widely depending upon the type of metal oxide, particle size (70 μm-2 mm), reduction gas (H₂, CO and CH₄) and temperature (600-1000°C). Generally, Ni and Co and their oxides showed higher oxidation and reduction rates than Fe and a greater durability after repeated oxidation and reduction cycles.³³ It was also found that an impregnated type of oxygen carrier could increase the reactivity and durability of the oxides, even with the particle size of oxygen carriers being as large as about 2 mm in diameter. Almost full conversion of reactants could be achieved in minutes for the impregnated type of oxygen carriers. The candidates for support materials could be Al₂O₃, yttria-stabilized zirconium (YSZ), TiO₂ and MgO. During the experiments a carbon deposit occurred while CH₄ was being used as the fuel gas. Carbon deposition on the solid metal causes the loss of solid activity, which will drop the rate of reaction significantly. In order to avoid carbon deposition, a high concentration of water vapor is added so that the ratio of H₂O/C is greater than 1.³¹

Starting from the introduction of CLC in 1983, the majority of studies have been with gaseous fuels such as methane and natural gas. Solid fuels such as coal and biomass have been ignored due to their technical problems. The adaptation of the CLC to the combustion of solid

fuels presents many challenges, however, this adaptation is very attractive because of rich coal deposits.

2.1.1.2. Technical Approach for CLC of Solid Fuels

Process Analysis and Technical Problems. There are two approaches to apply CLC to solid fuel combustion. The first approach is to gasify solid fuels in a separate gasifier with pure oxygen to produce a syngas of CH_4 , CO and H_2 without nitrogen. After cleanup, syngas is supplied for the CLC system to reduce metal oxides to metal, which is similar to the CLC using natural gas process. However, pure oxygen will be required to replace air (the cheapest oxidizing agent) for gasification to obtain a nitrogen free syngas. The fabrication of the separate gasifier and pure oxygen production system will increase the capital cost of the CLC system dramatically, which is not economical.

Approach 2, which is the proposed CLC process for solid fuels, is to directly supply solid fuel into the reduction reactor in the CLC system. It has advantages according to energy economics but has several technical problems. There are two reaction modes in this approach, including direct reduction of oxygen carrier by solid fuels, and gasification of solid fuels by CO_2 and H_2O , and then reduction of oxygen carrier by the gasification products. The actual reaction modes occurring in the chemical looping combustion of solid fuels is dependent on the properties of solid fuels and reduction mechanisms of oxygen carriers. If the first mode occurs in the reducer, the primary technical difficulties are that the reactivity between solid fuel and the oxygen carrier may be very slow because of low solid-solid contact efficiency. If the second mode occurs, the technical concern is that the solid fuel gasification speed is 100 times slower than its combustion at the same evaluated temperature, and thus a much longer residence time will be required to get the same carbon utilization. Therefore, reduction mechanisms of oxygen carrier by solid fuels and their kinetic properties occurring in the reducer of the chemical looping combustion process should be examined more closely. Other technical problems pertaining to the development of the chemical looping combustion of solid fuels include:

1. The separation of oxygen carrier particles from fuel and ash particles.
2. The prevention of the unburned carbon particles into the oxidizer, and also abatement and utilization of the unburned carbon produced.
3. The compatibility of two reaction processes for the oxygen carrier in two reactors.
4. Heat distribution between oxidization and reduction reactors in the presence of a gasification process.
5. Recycle of solid phase materials and system pressure balance, the prevention of gas leakage between reducer and oxidizer.

This proposed project is to be conducted in three phases. In Phase I, the major scientific and technical research should be focused on the reaction mechanisms of oxygen carrier and solid fuels in the reducer of the CLC system to provide necessary theoretical information and experimental results on the technical approaches and system configuration. In Phase II, a pilot

scale system of chemical looping combustion of solid fuels will be set up to investigate the system technical problems and demonstrate its technical feasibility. Consequently, if Phase II is successful, in Phase III external funding will be solicited to push the technical development of chemical looping combustion of solid fuels to a commercialization stage.

The Proposed Process. In order to overcome the technical difficulties mentioned above, it is proposed that a circulating fluidized bed (CFB) coupled with a combination of a moving bed and a bubbling fluidized bed (the reducer proposed in the Phase I proposal) or a combination of a bubbling fluidized bed and a turbulent fluidized bed (the reducer proposed based on Phase I tests) to be used for the chemical looping combustion of solid fuels, as briefly illustrated in Figure 1. In this approach, the facility will consist of three major components – a high-velocity riser acting as an oxidizer, a down-flow moving bed or a bubbling fluidized bed acting as a reducer where solid fuels are fed in after they are pyrolyzed (the process proposed in Phase I proposal for pre-handling of solid fuels) or pre-oxidized (the process proposed based on Phase I tests), and a low-velocity bubbling bed or a turbulent fluidized bed acting as a deep reduction reactor and separation device for the oxygen carrier from fuel ash as well as unburned carbon. The whole system uses three loop seals for oxygen carrier circulation. Among them, the reducer and separator are combined together to assemble a larger loop seal. The other two small loop seals will act as connectors of solid recycle between the oxidizer and the reducer with the separator.

In the riser, air is supplied as the fluidizing agent to oxidize elemental metal to its oxidized form. Oxygen is transferred from air to the oxygen carrier in this riser. The oxygen carrier is separated from the flue gas stream (consists of nitrogen and un-reacted oxygen only) by a cyclone attached to the riser. Pulverized coal is fed into the reducer after being pyrolyzed or pre-oxidized. The purpose of technical studies on pyrolysis or pre-oxidization of solid fuels is to economically improve their handling (to prevent caking occurred) in the reducer. Steam or recycling CO_2 is used as the aeration or transport media, or gasification agent in the reducer. Metal oxide is reduced to elemental metal in the reducer by direct or indirect reaction with solid fuels, which is dependent on the properties of solid fuel and oxygen carrier and their reaction mechanisms. In the bubbling bed or the turbulent fluidized bed, deep reduction of oxygen carrier, deep conversion of solid fuels and full separation of reduced oxygen carrier with fly ash will occur simultaneously. The reduced oxygen carrier will return to the riser (oxidizer) via another loop seal. The remaining unburned carbon is recycled to the fuel feeding port. Fresh oxygen carrier probably has to be added to maintain the reactivity of the oxygen carrier.

The volume of the gas flow in the oxidizer is much larger than that in a reducer because a large amount of nitrogen is carried in by the air. The oxidizing rate of the oxygen carrier is much faster than the rate of the reducing reaction. Thus, a high gas velocity has been chosen in the oxidizing reactor to keep a reasonable size reactor and to reduce the capital cost. In the reducer, relative long residence times, on the order of minutes, are needed for reduction of oxygen carrier directly by solid fuels or indirectly by syngas from gasification of solid fuels. Only a small amount of gas is needed for fossil fuel gasification, so a down-flow moving bed or a bubbling fluidized bed was selected. The ash produced is much lighter ($800\text{--}1200\text{ kg/m}^3$) compared to the

oxygen carrier (approximately 5000 kg/m^3). Thus, the oxygen carrier and fly ash are separated on the basis of different densities. By controlling the operating velocity, fly ash will be entrained out of a bubbling fluidized bed or a turbulent fluidized bed with “flue gas 2” and enter “cyclone 2” for cleanup. The flue gas exiting the bubbling bed will be nitrogen-free gases with CO_2 , H_2O , and possibly CO and H_2 .

Figure 1. The system configuration for the pilot scale chemical looping combustion process of solid fuels.

The gas velocity in the riser provides the driving force for the circulation of particles between the three components. The loop seals will allow solids flow from locations of lower static pressure to those of higher static pressure. Thus, the pressure balance and pressure profile along the solid routine will be one area needing a focused study. This will also result in the

selection of optimum reactor types for the reducer and separator. The temperature in the air reactor is somewhat higher because of the temperature fall in the fuel reactor in the presence of a gasification process. A heat exchanger can be installed in the air oxidizing riser to produce steam for power generation and the gasifying agent needed in the reducer and separator. Thus, the energy balance and its profile among the three components will be another area needing a focused study. All oxygen needed for the solid fuel combustion in the reducer is provided by the oxygen carrier. The necessary mass inventory of oxygen carrier and solid re-circulating ratio are determined by the oxidizing and reducing rates of the oxygen carrier, thermal input, attrition rate, and cyclone efficiency for the riser. Thus, the mass balance will be a third area needing a focused study.

The Proposed Oxygen Carriers and Analysis. An oxygen carrier based on an energy balance analysis and thermodynamics analysis was selected. Copper (Cu) seems to be the best choice for the CLC system for solid fuels.

A) Energy Balance Analysis.

The oxygen carrier reduction process in the CLC for solid fuel combustion is far more complicated compared to that of the CLC for gaseous fuels. The process is governed by the prevailing chemical thermodynamics and kinetics. There are two possible reaction paths for the reduction of oxygen carrier in the reducer, directly by solid fuels or indirectly by pyrolysis and gasification products of solid fuels. If the indirect path is dominant, the properties of pyrolysis and gasification of solid fuels should be considered. All reactions related to the pyrolysis and gasification of fossil fuel are endothermic, as illustrated by Equations (3), (4) and (5). During the endothermic reaction, heat input is needed to drive the reaction. In conventional gasification technologies, self-combustion of solid fuel particles is needed to provide the heat needed for the pyrolysis and gasification processes. This is called the auto-thermal process. In the proposed CLC system, the gasification process for solid fuel is combined with a reduction process for the oxygen carrier in the reducer where no oxygen exists. The only way to supply heat for the solid fuel gasification process is the reduction of oxygen carrier indirectly by the syngas produced and directly by solid fuels.

All enthalpy data are based on 1 atm and 25°C.³⁴ Until now, just a few metal oxides that have been examined as oxygen carriers for the CLC process show exothermic properties when reacted with carbon or syngas. The possible reactions related to oxygen carrier candidates and carbon in the reducer, are shown in Table 1. There are two steps (oxidizing and reducing) in the process of chemical looping for solid fuel combustion. Thus, the enthalpy of solid fuel combustion in the chemical looping process is equal to the sum of the enthalpies of the two steps. For the different oxygen carriers shown in Table 1, there is a different distribution of enthalpies for the two steps, and even the endothermic and exothermic reactions may be changed. For

copper oxides, its reducing reaction shows an exothermic reaction due to the smaller enthalpy of its oxidizing step than those of solid fuel direct combustion.

Table 1. Reaction Enthalpies at 1000°C and 1 atm (Calculations Based on Data from Reference ³⁴).

C + O₂ → CO₂, -392.75 KJ/mol	
<i>Endothermic</i>	<i>Exothermic</i>
2 NiO + C → 2 Ni + CO ₂ , 75.21 KJ/mol	
2 CoO + C → 2 Co + CO ₂ , 73.92 KJ/mol	2 CuO + C → 2 Cu + CO ₂ , -96.51 KJ/mol
1/2 Co ₃ O ₄ + C → 3/2 Co + CO ₂ , 53.9 KJ/mol	2 Cu ₂ O + C → 4 Cu + CO ₂ , -61.04
2 MnO + C → 2 Mn + CO ₂ , 378.98 KJ/mol,	2 Mn ₂ O ₃ + C → 4 MnO + CO ₂ , -33 KJ/mol
2 Mn ₃ O ₄ + C → 6 MnO + CO ₂ , 56.7 KJ/mol	
2/3 Fe ₂ O ₃ + C → 4/3 Fe + CO ₂ , 146.37 KJ/mol	
2 PbO + C → Pb + CO ₂ , 32.82 KJ/mol	

Based on the requirement listed in the DOE solicitation for development of an oxygen carrier in the CLC process,³⁵ the oxygen carrier should have the following properties: 1) high rates of reactivity for both the reduction and oxidation processes in a recycling base; 2) superior mechanical, thermal, and sintering properties; 3) low cost and 4) be environmentally sound. According to the DOE, lead is a hazardous element³⁶ and should not be used on a scale as large as a power generation process. Manganese oxides doped on alumina support could produce non-reactive compounds of spinel, MnAl₂O₄ and Mn₂AlO₄. That means that considerably less oxygen would be present for the reaction in the reducer.³⁷ Also, there is a thermodynamic limitation in the reduction reaction of manganese. When copper oxide was doped on substrate it was determined that most of its oxygen is active for reaction with methane, and the highest efficiency could be achieved with reduction rates up to 100%/min and oxidation rates up to 25%/min, although the formation of a melt phase was found on the surface of the particle during the reaction at higher temperatures over 950°C. Thus, copper oxides will be selected as the preliminary candidates for oxygen carriers for the proposed CLC application for solid fuel combustion.

B) Thermodynamics Analysis.

Chemical reaction thermodynamics are important for reaction control and reactor design. Fast reaction kinetics can always be obtained at high temperatures, with highly specific and pore-developed oxygen carriers. From the standard Gibbs free energy changes, the equilibrium constants can be calculated for the various reactions of metal oxide reduction and solid fuel gasification for a wide range of operating temperatures. The phase diagram for the reduction reactions using the reducing agents CO and H₂ produced from the solid fuel gasification process are shown in Figures 2 and 3, respectively.

Figure 2 shows the equilibrium gas ratio of P_{CO_2}/P_{CO} as a function of temperature for the reduction of various metal oxides. It shows that the ratio varies from approximately 10^5 for the reduction of Cu_2O to Cu , and Fe_2O_3 to Fe_3O_4 , to values on the order of 10^{-5} or less for the reduction of MnO and Cr_2O_3 to the elemental state of Mn and Cr . Information related to the Boudouard reaction, as illustrated in Equation (5), at atmospheric pressure is also presented in Figure 2. For the reduction of a metal oxide with CO in the absence of solid carbon, the oxides of copper, lead and nickel will be reduced to elemental form at gas ratios between 10^5 and 10^2 . Therefore, the completeness of the reaction could be achieved and a concentrated CO_2 stream will be obtained in the proposed CLC system. On the other hand, the reduction of manganese and chromium oxides requires a CO_2 -free environment, which is practically impossible for the CLC of solid fuel to achieve. Because carbon is also present in the reaction mixture in the proposed reducer, the reduction of metal oxide and carbon gasification to CO_2 occurs simultaneously. As shown in Figure 2, above the simultaneous equilibrium temperature where two curves for the reduction of metal oxides and the Boudouard reaction intersect, Fe_3O_4 will be converted to FeO above $650^\circ C$ and then to Fe above $700^\circ C$ under a low P_{CO_2}/P_{CO} ratio of ~ 10 . MnO needs to be above about $1600^\circ C$ at atmospheric pressure, which is impossible in the CLC since this temperature is above its melting point. In contrast, the curves for NiO , Cu_2O , PbO and Fe_2O_3 do not have intersection with the carbon curve even at low temperatures. The simultaneous reactions are not limited by thermodynamics, they are determined entirely by kinetics, which typically are fast in the CLC. In this case the gas constituents produced will have an intermediate impact on the value of the P_{CO_2}/P_{CO} ratio. Generally, the reduction reaction of metal oxide is faster than the solid fuel gasification in the CLC process. Thus, using NiO , Cu_2O , CuO and PbO as oxygen carriers could result in higher ratios of P_{CO_2}/P_{CO} .

H_2 is another product from the solid fuel gasification process using H_2O as the gasification agent. Figure 3 is the thermodynamics diagram for the P_{H_2O}/P_{H_2} equilibrium system, similar to the P_{CO_2}/P_{CO} system presented in Figure 2. The reduction of metal oxides with H_2 is less exothermic than its corresponding reaction with CO . Moreover, equilibrium of the water-gas reaction will occur and shift to the right at lower temperatures. This shows that H_2 at high temperature is a better reducing agent than CO for oxygen carriers. Solid fuel pyrolysis and gasification may produce some CH_4 in the reducing stream. Thermodynamics shows that CH_4 could be a better reducing agent than either CO or H_2 at high temperatures. However, CH_4 is unstable above $500^\circ C$ and decomposes into H_2 and C as soot. Any soot produced will be deposited on the metal oxides causing deactivation of the oxygen carrier.

The thermodynamic properties of the selected oxygen carrier ($Cu-CuO$) were set up in Phase I by the experimental tests.

Figure 2. Variation of the thermodynamic equilibrium factor for MeO-CO as a function of temperature (calculations are based on data from reference 31).

Figure 3. Variation of the thermodynamic equilibrium factor for MeO- H_2 as a function of temperature (calculations are based on data from reference 31).

2.1.2. Anticipated Public Benefits

The development of a chemical looping combustion process for solid fuels will produce several benefits.

- First, chemical looping will efficiently produce pure CO₂ in-situ which is ready for sequestration.
- Second, a major energy resource, coal, could be used for advanced combustion technologies, which will prolong its service time in efficiently and environmentally.
- Third, reduction of other pollutants emitted from coal combustion, such as sulfur and trace metals, can be controlled in an efficient way because of the very low volume of nitrogen-free flue gas that is generated in the reducer. NO_x formation can be almost eliminated.
- Fourth, the advanced CLC of solid fuels may provide a new choice for replacing the present available old PF system.

2.1.3. Degree to Which Phase I Has Demonstrated Technical Feasibility

2.1.3.1. Goal and Tasks of Project Phase I

In the proposed CFB chemical looping combustion process, research on the reducing reactor properties and solid material transfer is the major task. Understanding the mass balance, energy balance and pressure balance systems, as well as fluid dynamics is the key to the development of the concept. Due to the endothermic character of solid fuel gasification and reduction reactions for major oxygen carriers, a suitable oxygen carrier will be selected to achieve an exothermic reaction between syngas and the oxygen carrier. The oxygen carrier could be CuO-Cu impregnated onto a suitable support, which has properties of higher heat resistance, higher specific area, developed pore structure, and strong affinity for the impregnated reaction agent CuO-Cu. This will result in the adjustment of the distribution of heat release in the oxidation and reduction reactors which combined will equal the heat release from the combustion of solid fuel. The preliminary thermodynamic calculations show that using CuO-Cu as the oxygen carrier could control char deposition onto the oxygen carrier, which would result in an incomplete reduction of the oxygen carrier, followed by incomplete carbon combustion to release CO₂ in the oxidation reactor. Another benefit is that the ratio of P_{CO2}/P_{CO} could reach the 10⁵ level when CuO-Cu is used as the oxygen carrier. This means a very low concentration of CO will be generated at the exit of the reduction reactor. Based on reasonable assumptions, a theoretical basis of reaction enthalpy, chemical equilibrium and chemical reaction kinetics for three reaction units will be developed to understand the mechanisms for the chemical looping combustion of solid fuel and to develop the concept of the application of a circulating fluidized bed process to chemical looping combustion for solid fuels.

Three coal chars, prepared from sub-bituminous and bituminous coal samples with different volatile and sulfur contents, will be used in the gasification tests with CO₂ as gasifying agents in this phase. The evaluation of two CuO impregnated oxygen carriers under a simulated syngas atmosphere will be also conducted in this phase. The interaction between the oxygen carrier and ash will be studied. Three tasks were included in Phase I.

■ Task 1 - Theoretical frame analysis of reaction enthalpy, chemical equilibrium and chemical reaction kinetics for the chemical looping combustion of solid fuels. Researchers from the Paras Research Corporation and faculty and staff from the Combustion Laboratory at Western Kentucky University will carry out this task.

■ Task 2 - Studies of the basic data for coal char gasification with different particle diameters in a fixed bed reactor, the evaluation of two CuO impregnated oxygen carriers in a simulated syngas atmosphere and the interaction between the oxygen carrier and ash will be conducted in this phase. Researchers from the Combustion Laboratory will conduct this task.

■ Task 3 - Development of a system to monitor the mass, energy and pressure balances of the proposed CFB-CLC process. Researchers from the Paras Research Corporation and faculty and staff from the Combustion Laboratory at Western Kentucky University will conduct this task.

2.1.3.2. Test Results from Project Phase I

A series of experiments to support this application have been carried out in Phase I. The work done has been a thoughtful and programmed preparation for Phase II that gradually built up the mechanisms of CuO reduction by solid fuels and verified the feasibility of the whole process of CLC by solid fuels. In order to present results more logically, to give a clear picture of process feasibility and how to overcome technical problems, the data will be presented without maintaining the sequence of categories that were defined in the tasks in the Phase I proposal. The tasks have been completed as required in Phase I. Since the major technical bottleneck in developing the CLC of solid fuels is on the reduction mechanism of selected oxygen carriers by solid fuels, our primary results reflect our efforts in solving technical problems of the reduction process as outlined in the Phase I proposal. Also, the major technical issues about process integrity were also investigated by considering process pressure profiles and balance. Additional tests on the oxidization of oxygen carriers were also conducted concerning to keep the integrity of studies on the whole process.

2.1.3.2.1. Test Samples Preparation

A total of five solid fuels were studied in Phase I. Analytical data from the analysis of the solid fuels used are shown in Table 2. According to the test purpose, three categories have been set. In the first category, coal#1 and chemically pure CuO and their mixed samples were used to explore the possibility of direct reduction of oxygen carrier by solid fuel. In the second category, chars of Coal#1 and Coal #2, produced by a pyrolysis process and mixture of char with CuO were used to investigate the reduction mechanism of oxygen carrier by solid fuels. In the third category, a Powder River Basin (PRB) coal, a wood sample to simulate biomass, and a polymer to simulate MSW, and their mixtures with CuO were used to establish the process feasibility of the chemical looping combustion of solid fuels.

Table 2. Elemental Analysis Data (dry basis) for the Solid Fuels Used in the Study.

	Coal #1	Coal #2	PRB Coal	Wood	PE, Chemical
% Moisture	1.48	2.29	26.6	7.01	0.05
% Ash	15.34	12.28	5.18	0.29	0.02
% Vol Matter	16.5	31.4	32.0	76.1	99.8
Heating Value, BTU/lb	12,805	12,674	8,755	8,097	20,014
% Carbon	74.4	71.49	51.04	47.26	84.80
% Hydrogen	3.92	4.94	6.44	6.39	13.83
% Nitrogen	1.29	1.32	0.70	0.01	0.05
% Oxygen	3.09	12.28	36.35	46.00	1.21
% Sulfur	1.97	1.25	0.29	0.05	0.10
Chlorine, ppm	497	982	137	N/A	N/A
Mercury, ppm	0.18	0.10	0.07	0.0047	0.0015

2.1.3.2.2. Experiments and Instrumentation

Tests were conducted using SDT, or simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA), which simulates a micro-reactor. The following advanced characterization tools were used to study the products: FTIR and MS for gas phase characterization, XRD and SEM-EDX spectroscopy for solid characterization.

TGA-DTA (SDT). Approximately 10 mg of sample was placed in an alumina pan in an SDT (simultaneous TGA & DTA) 1960 V3.0F from TA Instruments and heated from ambient temperature at 10°C/min through 100°C/min to a range of 800°C through 1050°C. The experiments were carried out in ultra-high purity (UHP) CO₂ and UHP N₂ and also in air and oxygen. The actual test conditions are dependent on the test purpose. The following parameters were measured during testing: time (min), heating rate (°C/min), weight loss (%), weight loss rate (%/min), corrected heat flow of reaction (w/g), and corrected heat flow rate (w/g-min).

TGA-FTIR. Approximately 10 mg of sample was placed in a ceramic boat and heated from room temperature to 900°C at two heating rates (20°C/min and 50°C/min) in the TGA 951 under flowing (50 mL/min) UHP CO₂. The DuPont 951 TGA is interfaced to a Perkin Elmer 1650 series Fourier Transform Infrared Spectrometer (FTIR) with a permanent silicon transfer line (length one inch). The purge gas carries the evolved gas from the TGA through a 70 mL-sample cell with KBr crystal windows. For detection of the evolved gas, the cell is placed in the IR scanning path and is kept at 150°C by wrapped heating tape to prevent possible condensation. The IR detection range was from 450 cm⁻¹ to 4400 cm⁻¹. The 3D spectra and profiles of gaseous

species evolving from the TG system are recorded and analyzed using GRAMS/32 v4 software. CO₂ absorbs at 2356 and 3600-3700 cm⁻¹ and CO absorbs at 2178 cm⁻¹.

XRD. A THERMO ARL X'TRA X-ray diffractometer using CuK α radiation was used to analyze each of the samples. A tube voltage of 40 kV and a tube current of 20 mA were used for each sample. The samples were scanned every 0.04 degrees from 20 to 90 degrees. The XRD patterns are identified using a database of over 80,000 inorganic compounds.

SEM-EDX. The reaction residue samples were prepared by being doped onto carbon tape. The SEM analysis was performed using a JEOL LSM-5400 SEM. Attached to the SEM for energy-dispersive X-ray analysis (EDX) is a KEVEX Sigma 1 system with a Quantum detector for elemental analysis down to carbon in the periodical table. The instrument operating parameters were as follows: electron beam energy, 15 keV; working distance, 30 mm; sample tilt angle, 0°; In most cases, two elements, Cu and O, were selected to be analyzed at 2000X magnification.

TG-MS. A TA Instruments model 2950 TGA equipped with an evolved gas analysis (EGA) furnace was connected to a Pfeiffer ThermoStar mass spectrometer using a heated (200°C) capillary transfer line approximately 1.5 m long. Evolved species from the TGA were carried by the purge gas through the capillary for analysis by the MS. Two different purge gases were used for the TG-MS experiments — UHP CO₂ and UHP nitrogen. Samples were heated to 1000°C in flowing (100 mL/min) air or UHP N₂ at various heating rates around 30°C/min with some experiments having a 1 hr isothermal hold at the end of the heating segment to monitor continued mass loss/species evolution. The mass spectrometer (MS) was operated with scan ranges of 1-300 amu or 1-175 amu. The difference in scan range caused the total time for analysis to be cut by almost half — from over a minute to about 36 seconds. This allowed more data points to be taken during a given mass loss event. A calcium oxalate experiment was used to confirm correct operation of both the TGA and the MS prior to running the samples.

2.1.3.2.3. Test Sequences

Category 1: Three samples were used for the experiments. The first sample is referred to as chemically pure CuO to verify the thermodynamic properties of the selected oxygen carrier-Cu-CuO. The second sample, referred to as coal, consisted only of Coal #1. The third sample, referred to as the mixture sample to investigate the feasibility of CuO reduction by solid fuels, consisted of a 50% (by weight) CuO and 50% Coal #1.

Category 2: Two types of tests were conducted in this experiment. In the first type, char samples from two kinds of coal with different ranks (Coal#1 and Coal#2) were prepared in a nitrogen atmosphere using the ASTM standard procedure D5142 (LECO Instruments - TGA 601) for the determination and removal of volatile materials from the coal samples. These char samples were used to investigate their gasification reactivity in CO₂. In the second type of test, the evaluation of CuO reduction by coal char was conducted. The prepared char samples were

evenly mixed with chemically pure CuO at a ratio of 10:90 to investigate the reduction performance and mechanisms of CuO reduction in direct contact with coal char.

Category 3: In this test, PRB coal was selected as a model coal sample. Two fuels of opportunity, which are wood and PE were selected to simulate biomass and municipal waste. These samples were mixed with CuO at different ratios to investigate their reduction performance on CuO and to build up the technical feasibility of chemical looping combustion of solid fuels.

2.1.3.2.4. Category 1- Test Results and Discussion

Thermodynamic Tests of Chemically Pure CuO. For the chemically pure CuO sample, as the temperature increases, starting at ambient temperature in the SDT tests, the only peak for weight loss was found at about 893°C in N₂ and about 894°C in CO₂ atmospheres, respectively, as shown in Figure 4. The corresponding total weight losses in N₂ and CO₂ atmospheres, where no O₂ is involved, were about 11%. The heat flow of chemically pure CuO, which is shown in Figure 5 at the same conditions had apparent endothermic peaks at corresponding weight loss peaks. It appears that CuO decomposed to Cu₂O with the release of oxygen, as illustrated in Equation (6).

Chemical calculations indicate this reaction has endothermic properties and a corresponding weight loss of chemically pure CuO of 10%. If so, in air or oxygen atmospheres the decomposition of CuO should be shifted to higher temperatures as the partial pressure of O₂ increases due to its endothermic properties. As shown in Figure 4, the weight loss peak of chemically pure CuO was shifted to about 997°C in an air atmosphere and to about 1100°C in an O₂ atmosphere. In a test in a pure O₂ atmosphere, the decomposition process was accompanied by melting and vaporization due to the higher heating rate used in the SDT tests, thus the decomposition temperature and weight loss temperature of CuO could not be determined. A phase diagram with the corrected O₂ partial pressure and decomposition temperature are shown in Figure 6. This diagram shows the transformation of the CuO-Cu₂O system in inert and oxidizing atmospheres. In Figure 6, the equilibrium line divides the 2 D area into two zones, which correlates the temperature with the oxygen partial pressure. Above the equilibrium line the CuO could have a stable existence. Under this equilibrium line, Cu₂O could have a stable existence. All three phases of CuO, Cu₂O and O₂ are present simultaneously only at an equilibrium line correlating the system reaction temperature and oxygen partial pressure, P_{O2}. This reversible chemical reaction will go to completion if the system status is located in either of the zones. The temperature and oxygen partial pressure are the parameters that control the reaction direction and extent.

Figure 4. Weight loss history of chemically pure CuO sample in different atmospheres (N₂, CO₂, air, and O₂).

Figure 5. Corrected heat flow history of chemically pure CuO sample in different atmospheres (N₂, CO₂, air, and O₂).

Figure 6. The phase diagram for CuO and Cu₂O (P_{O₂} - T).

Mechanisms of Reduction of CuO by Coal (Coal #1) at Higher Temperature of 900°C. In this test, reaction paths, reactivity and reaction heat flows for the Coal#1 and mixture of Coal#1 with CuO at ratio of 50:50 were accurately evaluated using an SDT (DTA+TGA) to simulate a micro-reactor. Generally, the samples were heated at a heating rate of 10°C/min to 900°C in 2 different atmospheres (CO₂ and N₂), if not otherwise mentioned.

For the Coal #1 sample, as the temperature increases from ambient temperature in the SDT tests, the common peaks appear at a temperature of 50°C, which corresponds to the moisture loss in the coal sample, as shown in Figures 7 and 8. The small differences in peak heights and weight losses are attributed to the different moisture contents in the handling process. In a N₂ atmosphere, only one large peak appears at a peak temperature of about 505°C, with an onset at about 300°C and proceeds to 900°C. This weight loss is attributed to the release of pyrolysis products from coal. In a CO₂ atmosphere, similar to the peak temperature of about 505°C in the coal pyrolysis process, a weight loss peak at 520°C appears with a peak height of about half in comparison to the coal pyrolysis process. This phenomenon should be attributed to coal pyrolysis in a CO₂ atmosphere due to equilibrium abatement of release of pyrolysis products (the major product was CO₂, see FTIR spectrum) by CO₂. The apparent difference that occurred in the different atmospheres was at a higher temperature. In a CO₂ atmosphere, another large weight loss peak appears with an onset temperature of about 797°C and a peak temperature of 894°C. The likely reaction that occurs is CO₂ gasification of coal pyrolysis products and produced coal char. Thus, two decomposition stages of the coal sample occurred in a CO₂ atmosphere. The 1st stage was a pyrolysis process with an onset temperature of about 300°C and peak temperature of 520°C. The 2nd stage of the gasification process occurred at an onset

temperature of about 797°C and a peak temperature of 894°C. The corresponding weight losses were about 21% for the 1st stage and about 17% for the 2nd stage.

Figure 7. Weight loss history of the Coal #1 sample in a N₂ and a CO₂ atmosphere with a temperature ramp of 10 °C/min.

Figure 8. Corrected heat flow history of Coal #1 sample in a N₂ and a CO₂ atmosphere with a temperature ramp of 10°C/min.

The tests in a nitrogen atmosphere presented the simplest reaction mode for the reduction of the oxygen carrier by coal. Three different reactions could have occurred, (1) coal pyrolysis, which is endothermic, (2) reduction of CuO by coal pyrolysis products, which is an exothermic reaction, and (3) the decomposition of CuO to Cu₂O, followed by reduction of Cu₂O by coal pyrolysis products.

To explore the possible mechanism of CuO reduction during the coal pyrolysis process, comparisons of the weight loss history of a CuO sample in nitrogen, Coal#1 sample and the mixture sample of CuO and Coal #1 in a ratio of 1:1 are shown in Figure 9.

Figure 9. Weight loss history of CuO, Coal#1 and their mixture in N₂ and CO₂ atmospheres with a temperature ramp of 10°C/min.

As can be seen in the figure, as the temperature increases from atmospheric temperature, a peak appears at about 50°C for the mixed sample, which is attributed to moisture loss of coal in the mixed sample. Peak heights for the coal sample were a little higher than those of the mixed sample due to the fact that the mixed sample contained only half the coal of the Coal #1 sample. At about 300°C, the coal sample starts to partially release its pyrolysis products and loss rate reach its maximum value at about 505°C. The weight loss of the mixture sample starts a little later than the coal sample and reaches its maximum value at about 488°C, which is a little bit lower than that for the coal sample. The peak height of the mixed sample was even larger than that of the coal sample, but should be about half that of the coal sample. This indicates the CuO

is reduced by pyrolysis products of coal, and the reduction reaction has an onset at a lower temperature in the 300-400°C range. As the temperature approaches about 730°C, another weight loss peak of the mixed sample appears in comparison to a small peak in the coal sample thermal curve. The major weight loss in the coal sample at this temperature should result from the continuous reduction of the residual CuO by pyrolysis products of coal which is favored by kinetics at higher temperatures. As the temperature approaches 890°C, no apparent peaks are shown in the Figure 9 for both the coal and mixed samples, except for the large peak for the CuO decomposition process. This indicates that in a reducing atmosphere, CuO seemed to be directly reduced to Cu by coal pyrolysis, otherwise a major weight loss corresponding to Cu₂O reduction by coal pyrolysis products should appear. At the same operating conditions in a N₂ atmosphere, the total weight loss for coal was 23.1% and that of mixed sample was 23.5%. Thus, the calculated reduction efficiency of CuO was about 23.9% based on the mixture ratio of sample and weight loss of coal. The calculated value of 23.9% for CuO reduction was a little larger than its predicted theoretical value of 20% at complete reduction. Possibly, some materials in the mixed sample such as CuO and Cu had some effect on the improvement of the coal pyrolysis process.

In a CO₂ atmosphere, the reaction paths are more complicated. Two more reactions are added to the process compared with the results in the nitrogen atmosphere -- CO₂ gasification of coal pyrolysis products and coal char, the later has strong endothermic properties. Comparison of the weight loss history and the corrected heat flow history in CO₂ between chemically pure CuO sample, the Coal#1 sample and the mixture sample are shown in Figure 10.

Figure 10. Weight loss history of mixture sample in carbon dioxide with a temperature ramp of 10°C/min.

As the temperature increases from atmospheric temperature, a weight loss peak can be seen at about 50°C, which is attributed to the moisture loss from coal. The peak heights are different due to the difference in the amount of coal present, as explained above. At a temperature of about 515°C in the TG curves, a second peak appears in the TG curve from both samples, which can be attributed to the partial loss of coal pyrolysis products and/or the carbon dioxide gasification of coal pyrolysis products. If this is the only reaction that occurred, the peak heights of both samples should be the same. However, peaks with almost the same height appear, which indicates the reduction of CuO also occurred at this lower temperature. Before the temperature of 850°C was reached, the weight loss decreased smoothly for the coal sample, but another two peaks in the TG curve appeared at about 600°C and 825°C. These two weight loss peaks probably correspond to the process of reduction of CuO. Compared with the test results in an N₂ atmosphere, with the major CuO reduction peak at about 727°C, the weight loss peak was shifted to a lower temperature at about 600°C in the CO₂ atmosphere. This possibly indicates that the gasification of coal pyrolysis products could improve the reduction of CuO, due to the increase in the evolution of small molecular species, such as hydrogen, carbon monoxide and methane, which are more reactive toward CuO reduction compared with the large molecules present in the N₂ atmosphere.

Large peaks were observed for both chemically pure CuO and coal sample as the temperature approached about 894°C in the TG curve shown in Figure 10, which are attributed to CuO decomposition and coal char gasification, respectively. At the same temperature, a small peak appeared in the TG curve of the mixed sample. The calculation of CuO conversion can possibly explain what this peak corresponds to. Before reaching the temperature of 850°C in a CO₂ atmosphere, the total weight loss from coal was about 18% and that of mixed sample with a mixture ratio of 1:1 was 23%. Thus, the calculated reduction efficiency of CuO was about 28% based on mixed ratio of sample and weight loss of coal. The calculated value of 28% for CuO reduction was much larger than its predicted theoretical value of 20% for complete reduction. This may indicate that at least the complete conversion of CuO occurs before 850°C in the TG curve. Thus, the peak at a temperature of 894°C in the TG curve of the mixed sample should be attributed to coal char gasification in CO₂. The extra 8% weight loss can be attributed to the extra conversion of coal gasification in a CO₂ atmosphere. At this reaction stage where the temperature was above 850°C, the total weight loss of coal char was about 22.8% and that of mixture sample was 13.4%. The calculated gasification conversion efficiency of coal char in the mixed sample should be about 26.8% at 100% coal base in the mixed sample, compared to the result of 22.8%. It seems some materials in the mixed sample such as CuO and Cu had some effects on improvement of the coal pyrolysis process.

Characterization of Gaseous and Solid Products.

A) TGA-FTIR for the Evolved Gas Determination.

In TGA-FTIR experiments, evolved gases from TGA tests are sent through a heated transfer line to an FTIR cell for determination of gaseous components. It was determined that the main gas components from heating the mixture sample were CO₂ and H₂O, with some other species also present. Less CO was detected than CO₂. The TGA-FTIR spectra from the decomposition of the Coal #1 sample and mixture samples are shown in Figure 11 as 3D spectra of the total history and 2D spectra for the individual times. The vertical axis is marked in absorbance units, the horizontal axis is in wavenumbers (cm⁻¹), and perspective axis is in time.

Stretching modes that do not change the dipole moment of an absorbing molecule is an inactive mode in infrared spectroscopy. Homonuclear diatomic molecules do not have a permanent dipole moment. They do not absorb infrared radiation since stretching of the molecule produces no change in the dipole moment of the molecule. H₂, N₂, and O₂ are homonuclear diatomic molecules and can not be detected by infrared spectroscopy.

The Coal #1 sample produced only small peaks related to CO₂ and sulfur species below 670°C (Z = 766 s). This indicates low reactivity in a CO₂ atmosphere. At 860°C (Z = 1001 s), the Coal #1 sample produces large peaks at 3000 cm⁻¹ and 2359 cm⁻¹. The former is attributed to methane (CH₄) and the latter to CO₂. This indicates that the coal pyrolysis process still proceeds with the majority of the reductant in the form of CH₄. The peak at 674 cm⁻¹ may be attributed to 2 possible compounds, CO₂ or benzene. Due to the high temperature of evolution and the intense peaks found at a wavenumber of 2359 cm⁻¹, the peak at 674 cm⁻¹ can be attributed to CO₂, and not benzene. At 1374 cm⁻¹ there are peaks attributed to SO₂ and other sulfur species. At high temperature (900°C) and also long residence time (Z = 1355 s), all peaks which correspond to gas compositions approach the baseline in a high carrier gas stream. This indicates that all reactions are relatively complete. Peaks attributed to CO could be observed throughout the test.

The mixture sample exhibited small CO₂ peaks at 2359 cm⁻¹ and 674 cm⁻¹, some H₂O peaks at 3800-3900 cm⁻¹ and 1400-1500 cm⁻¹, and sulfur species at 1374 cm⁻¹ at a relatively low temperature range of 405°C (Z = 443 s). Some peaks attributed to CH₄ were also observed at this stage. This situation is consistent until all reactions in the system slow down, except the coal char gasification of CO₂. No CO peaks appeared at 2178 cm⁻¹ over the course of the experiment.

Figure 11. FTIR patterns for 100% Coal#1 and a mixture of Coal#1 with CuO at a ratio of 50:50 in a CO₂ atmosphere and heating rate of 50°C/min.

B) XRD for Solid Residues Characterization.

In order to conduct XRD experiments, a larger amount of sample was required. For the XRD tests, 100 mg samples were prepared by a DuPont 951 TGA system. The samples were heated from room temperature to 900°C, at a heating rate of 100°C/min and held for 1hr under a nitrogen or CO₂ atmosphere at a flow rate of 50 mL/min. Two samples were obtained -- mixture residue in N₂ and mixture residue in CO₂. A raw mixture sample was used for comparison purposes.

The 2θ angles listed in Table 3 were used to distinguish the CuO, Cu₂O and Cu in the samples. Figures 12-1, 12-2 and 12-3 show the XRD diffractograms of the samples. In Figure 12-1, the 2θ peaks with the highest relative intensities are at 35.5° and 38.7°, which correspond to CuO in the raw mixture sample. In Figure 12-2, the 2θ peaks with the highest relative intensities are at 43.3°, 30.5° and 50.4°. The 2θ peaks at 43.3° and 50.4° represent Cu in the residue of the raw mixture sample after CO₂ testing. The peak at 30.5° corresponds to sulfur species in the residue which may be a product of sulfur in coal. In Figure 12-3, the peaks with the highest relative intensities are at 43.2° and 50.3°, which show that Cu is in the residue. There is no obvious peak at 35.5° in either Figure 12-2 or 12-3 indicating most of the CuO was converted into Cu. In Figures 12-2 and 12-3, there are no apparent peaks at 36.4° and 42.3°, which indicated there is no Cu₂O in the samples. The relative intensity of the peak at 2θ = 50.4° in Figures 12-2 and 12-3 may indicate that the conversion rate of CuO to Cu in a CO₂ atmosphere is greater than that of the conversion rate in N₂, as shown in Table 4. However, this needs to be further verified.

Figure 12. XRD characterization of 3 mixture samples: 1) raw mixture sample, 2) reaction product of mixture sample in a CO₂ atmosphere, and 3) reaction product of mixture sample in a N₂ atmosphere.

12-2

12-3

Table 3. XRD Spectral Data from the XRD Library.

Item	2θ	Relative Intensity %
CuO	35.5	100
	38.7	96
Cu ₂ O	36.4	100
	42.3	37
Cu	43.3	100
	50.4	46

Table 4. XRD Spectral Data from Samples.

Item	2 θ	Relative Intensity %
CuO + Coal#1 (50%:50%)	35.5	100
	38.7	75.75
Residue of CuO + Coal#1 (50:50) exposed in N ₂	43.2	100
	30.48	9.71
	50.4	8.96
Residue of CuO + Coal#1 (50:50) exposed in CO ₂	43.2	100

C) SEM-EDX for Characterization of Solid Residues.

SEM images of chemically pure CuO at different magnifications are shown in Figure 13-1-1. The CuO sample was widely packed with dimensions from 1-3 μm . Pure CuO particles look like fish scales under smaller magnifications ranging from 500X to 2000X. As SEM magnification increases, the CuO looks more like a rod with a clear boundary. Two sites were selected to image with a magnification of 500X and are labeled 1 and 2. Atomic weight ratios of oxygen and copper of CuO are close to 40%:60% as determined by EDX analysis, as shown in Figure 13-2-1, which are different from calculated weight ratio of 20%:80%. The cause of this discrepancy needs to be further investigated by calibration of SEM-EDX. SEM images of a pure CuO sample change significantly after being treated at 900°C for 1hr in CO₂, as shown in Figure 13-1-2 at different magnifications. The pure CuO particles lose their original rod-like shape under treatment at high temperature. The CuO particles aggregated and developed into larger particles with dimensions of 5-10 μm . According to EDX analysis as shown in Figure 13-2-2, their atomic weight of oxygen decreased compared with EDX analysis of CuO. This may be formation of Cu₂O crystal.

The SEM images of the mixture sample at different magnifications, after being treated at 900°C in N₂ are shown in Figure 13-1-3. Due to the larger atomic weight of Cu, the images show Cu as being much brighter than the coal char. This is verified by EDX analysis of selected image sites in Figure 13-1-3 as shown in Figure 13-2-3. EDX analysis of the dark portion shows a very high carbon concentration of about 95%, and analysis of the brighter site gives a high Cu concentration of about 80% with the oxygen concentration below 10%. The original rod-like shape of the pure CuO particle is totally lost after treatment at high temperature in CO₂. The produced Cu particles melted, aggregated and developed into larger cauliflower-like aggregate materials with dimensions of 50 μm or more—in the size range of coal char. The observation of some small Cu balls served as a good proof that the Cu produced during the CuO reduction process is melted and splashed. Compared with Figure 13-1-3, which is an SEM image of the mixture sample after treatment in CO₂ at the same temperature, more splashed Cu particles were found in Figure 13-1-4. This is proof that the reduction of CuO is more intense. There is a clear boundary between the coal char and the Cu block. The smaller Cu balls were always associated with the coal char and doped onto coal char's surface. It could be logically inferred that CuO is reduced by the evolved gas from the coal pyrolysis process or CO₂ gasification of coal char, not

directly by contacting with the coal char. The CuO particles are reduced to Cu, which subsequently melts, aggregates and develops into a larger block. The outer surface of the produced Cu splashes at a higher temperature. As the splashed Cu particles come in contact with the relatively cool coal char surface, the smaller Cu particles cool down. Thus, the smaller Cu particles come from the larger Cu blocks and are not the reaction product of CuO in contact with the coal char. A faster reduction process of CuO occurring results in more melted Cu being produced. Thus, melting Cu will plug or even wrap the CuO core to prevent it from contacting reductant so that CuO reduction process stops. Now, we can answer the question raised in previous SDT tests that the later case dominates the process.

The melting and aggregation of Cu will result in several disadvantages. First, the melted Cu will wrap the CuO core preventing further reduction of the CuO, and thus loss of its oxygen producing capacity. Secondly, melting and aggregating of small particles of Cu will make it lose reactivity in the following oxidization stage. In order to prevent melting and to investigate the aggregation phenomena in the CuO-Cu system, lower temperatures were used in a CO₂ atmosphere to treat the mixture sample. A low coal to CuO ratio (1:10) was applied to the mixture sample which was closer to the stoichiometric ratio for the reaction of coal and CuO.

D) SEM-EDX for Characterization of Solid Residues Obtained at Lower Temperatures.

In this test, the reaction products of mixed sample with a ratio of 10% coal and 90% CuO were heated in a CO₂ atmosphere in an SDT furnace and the products evaluated and characterized using the SEM-EDX instrument. The melting phenomena of the previous tests were found to occur at a higher temperature. The end temperatures were set at 800°C and 850°C, respectively. The heating rate of the SDT furnace was maintained at 100°C/min.

The SEM images of the 10% mixture sample at different magnifications after being treated at 800°C in a CO₂ atmosphere are shown in Figure 13-2-5. The image of the reaction residue at lower magnification is very similar to that of the CuO sample which was treated in CO₂ atmosphere at 900°C. Some melted spots were observed in the images at higher magnification, but not severe. Several sites with different degrees of dark and bright were selected for EDX analysis, as shown in Figure 13-2-5. It was found that the majority of the sites selected were identified as Cu with an atomic concentration above 95%. It was not easy to find the coal char. The SEM images of the 10% mixture sample at different magnifications after being treated at 850°C in CO₂ are shown in Figure 13-1-6. The image of the reaction residue at 850°C at lower magnification is a little bit different from that at 800°C. Some cauliflower-like products are found like the ones at 900°C. However, no small ball-like materials were found in the higher magnification images. This may imply that melting is severe. Several sites with different degrees of dark and bright were selected for EDX analysis, as shown in Figure 13-2-3. It was found that the majority of the bright sites selected were identified as Cu with an atomic concentration above 95%. The dark spots were identified as un-reacted CuO and those in black as coal char, which were wrapped by a mixture of un-reacted CuO and produced Cu.

Figure 13-1-1. SEM images for sample of 100% chemically pure CuO at different magnifications

Figure 13-1-2. EDX analysis for sample of 100% chemically pure CuO at different magnifications

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	31.02	2.033	37.747	13.244	wt. %	
Cu	Ka	171.24	4.778	62.253	86.756	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	32.61	2.085	38.714	13.722	wt. %	
Cu	Ka	172.21	4.792	61.286	86.278	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Figure 13-2-1. SEM images for sample of CuO at 900 °C, CO₂ atmosphere and 100 °Cpm

Figure 13-2-2. EDX analysis for sample of CuO at 900 °C, CO₂ atmosphere and 100 °Cpm

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	9.40	1.119	28.071	8.947	wt. %	
Cu	Ka	83.02	3.326	71.929	91.053	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	8.52	1.066	26.621	8.370	wt. %	
Cu	Ka	81.28	3.291	73.379	91.630	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	13.63	1.348	37.197	12.977	wt. %	
Cu	Ka	77.19	3.208	62.803	87.023	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Figure 13-3-1. SEM images for mixture sample of 50% CuO+Coal at 900 °C, N₂ atmosphere and 10 °Cpm

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	0.21	0.119	21.852	6.577	wt. %	
Cu	La	20.63	1.173	78.148	93.423	wt. %	
				100.000	100.000		Total

kV 35.0
Takeoff Angle 25.0°
Elapsed Livetime 60.0

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
C	Ka	0.17	0.106	10.375	2.334	wt. %	
O	Ka	8.20	0.740	8.740	2.619	wt. %	
Al	Ka	4.50	0.548	0.926	0.468	wt. %	
Si	Ka	2.83	0.434	0.424	0.223	wt. %	
S	Ka	3.21	0.463	0.344	0.207	wt. %	
Ca	Ka	2.19	0.382	0.181	0.136	wt. %	
Cu	Ka	275.91	4.289	79.009	94.015	wt. %	
				100.000	100.000	wt. %	Total

Figure 13-4-1. SEM images for mixture sample of 50% CuO+Coal at 900 °C, CO₂ atmosphere and 10 °Cpm

Figure 13-5-1. SEM images for mixture sample of 90% CuO+Coal at 800 °C, CO₂ atmosphere and 100 °Cpm

Figure 13-5-2. EDX analysis for mixture sample of 90% CuO+Coal
at 800 °C, CO₂ atmosphere and 100 °Cpm

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	10.07	1.159	29.219	9.502	wt. %	
Al	Ka	0.41	0.233	0.242	0.133	wt. %	
Si	Ka	2.40	0.565	1.035	0.591	wt. %	
Cu	Ka	82.56	3.318	69.503	89.774	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	1.94	0.508	7.893	2.124	wt. %	
Al	Ka	0.25	0.182	0.207	0.094	wt. %	
Si	Ka	1.18	0.397	0.709	0.335	wt. %	
Cu	Ka	80.99	3.286	91.191	97.448	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	0.85	0.337	3.648	0.949	wt. %	
Al	Ka	0.74	0.314	0.644	0.282	wt. %	
Si	Ka	0.25	0.183	0.159	0.073	wt. %	
Cu	Ka	81.35	3.293	95.549	98.696	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	0.18	0.155	0.767	0.194	wt. %	
Al	Ka	0.03	0.064	0.027	0.011	wt. %	
Si	Ka	0.42	0.237	0.264	0.117	wt. %	
Cu	Ka	85.28	3.372	98.943	99.677	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
Al	Ka	0.49	0.254	0.552	0.236	wt. %	
Si	Ka	0.46	0.247	0.379	0.168	wt. %	
Cu	Ka	64.69	2.936	99.069	99.596	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Figure 13-6-1. SEM images for mixture sample of 90% CuO+Coal at 850 °C, CO₂ atmosphere and 100 °Cpm

Figure 13-6-2. EDX analysis for mixture sample of 90% CuO+Coal at 850 °C, CO₂ atmosphere and 100 °Cpm

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	0.44	0.243	2.808	0.726	wt. %	
Al	Ka	0.66	0.296	0.841	0.367	wt. %	
Si	Ka	0.17	0.149	0.155	0.070	wt. %	
Cu	Ka	55.50	2.720	96.196	98.836	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	0.46	0.247	3.290	0.858	wt. %	
Al	Ka	0.76	0.318	1.105	0.486	wt. %	
Si	Ka	0.71	0.308	0.753	0.345	wt. %	
Cu	Ka	48.09	2.532	94.853	98.310	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
Si	Ka	1.06	0.376	0.799	0.355	wt. %	
Ca	Ka	0.63	0.290	0.256	0.162	wt. %	
Cu	Ka	70.68	3.070	98.945	99.483	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Continued

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	0.66	0.298	3.562	0.924	wt. %	
Al	Ka	0.38	0.227	0.419	0.183	wt. %	
Ca	Ka	0.18	0.156	0.078	0.050	wt. %	
Cu	Ka	65.22	2.949	95.941	98.842	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0
Takeoff Angle 25.0°
Elapsed Livetime 30.0

Continued

El.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
O	Ka	44.62	2.439	69.712	51.044	wt. %	
Al	Ka	41.34	2.347	8.046	9.936	wt. %	
Si	Ka	86.16	3.389	14.729	18.931	wt. %	
K	Ka	9.52	1.126	1.279	2.288	wt. %	
Ca	Ka	1.08	0.379	0.151	0.277	wt. %	
Fe	Ka	1.96	0.511	0.479	1.225	wt. %	
Cu	Ka	11.22	1.223	5.604	16.298	wt. %	
				100.000	100.000	wt. %	Total

kV 15.0

Takeoff Angle 25.0°

Elapsed Livetime 30.0

2.1.3.2.5. Category 2 - Test Results and Discussion

Reduction of Oxygen Carrier (CuO) by Coal Char at 850°C. Two coal samples with volatile matter contents of approximately 15% (Coal #1) and 35% (Coal #2) were selected for this test. The coal samples were pyrolyzed to produce their char samples by a standard ASTM procedure for determining volatile matter values (ASTM D5142). The char samples were then ground to 100 μm and mixed thoroughly with CuO at a ratio of 1:9. The prepared mixtures were tested on an SDT instrument or TGA instrument in N_2 and CO_2 to investigate their reduction capability on CuO. The char samples were tested individually at the same heating rate and final temperature to explore the CO_2 gasification mechanism.

In order to obtain improved resolution and sensitivity, the samples were heated at a heating rate of $30^\circ\text{C}/\text{min}$ to 850°C , unless otherwise mentioned. A sample size of about 50 mg was used in all the tests. The test results are shown in Figure 14 for Coal char #1 and Figure 15 for coal char #2.

A) Reduction of CuO by Coal Char #1.

As the coal char #1 sample was heated from ambient temperature, peaks appeared at a temperature of about 50°C , which correspond to the moisture loss from the samples, as shown in Figure 14. The differences in peak heights and weight losses were attributed to the different moisture contents of the samples as a result of the handling process. In an N_2 atmosphere, two small peaks appeared at peak temperatures of about 450°C and 850°C . The weight loss of 3.34% corresponding to the first peak was attributed to the release of pyrolysis products from the coal char, which was not fully released during the ASTM procedure. In a CO_2 atmosphere, the pyrolysis peaks seemed to be abated due to the reaction of CO_2 with other pyrolysis products. The apparent difference that occurred in the CO_2 atmosphere was at a higher temperature with an onset of about 750°C and a peak at 850°C . The weight loss is definitely attributable to coal char gasification by CO_2 . In the given test conditions, the total weight loss was 14.8% and was due to the pyrolysis and gasification processes occurring in a CO_2 atmosphere.

For the mixed samples, the major peak appeared at a temperature of 848°C in an N_2 atmosphere and 836°C in a CO_2 atmosphere, with an onset temperature of about 620°C . These two peaks in both atmospheres can be attributed to pyrolysis, gasification and also CuO reduction. However, there was an apparent transition point observed in the weight loss rate curves at 750°C in both atmospheres. This implies the possibility of overlapping peaks between 600°C and 850°C . With regard to the peak heights of char samples in both atmospheres, the much larger peaks appearing in the mixed samples must correspond to CuO reduction by available reducing agents in both atmospheres. In an N_2 atmosphere, the reduction of CuO by pyrolysis products should be the major reaction occurring before the temperature of the transition point, and after that temperature, CuO should be reduced by char only since the test occurred in an inert atmosphere (N_2). However, in a CO_2 atmosphere, the situation is slightly more complicated. Before the transition point, the peak in the two atmospheres appears at nearly the same temperature. This implies that the reducing agents are char pyrolysis products in a CO_2 atmosphere. However, after the transition point, the peak height in a CO_2 atmosphere was higher

Figure 14. Weight loss history of coal char #1 sample and the mixed sample in nitrogen and carbon dioxide atmospheres with a temperature ramp of 30°C/min to 850°C.

than that in an N_2 atmosphere, which can be attributed to char gasification by CO_2 and then reduction of CuO by CO, even though the gasification reactivity was lower for coal char #1. It can reasonably be assumed that CuO reduction by char at a higher temperature and in a CO_2 atmosphere should include 3 main reactions: reduction of CuO by char directly, reduction of CuO by CO and also char gasification to produce CO, although it is not known exactly which of the first two reactions are the controlling reactions. The detailed mechanisms will be left for further study.

In a CO_2 atmosphere, the total weight loss from coal char #1 was about 14.8% and that of the mixed sample with a mixture ratio of 1:9 of char to CuO was 12.3%. Based on results in the previous report, it is reasonable to assume that no Cu_2O was produced in the final reaction product of the mixture sample -- Cu was the only reduction product. The calculated weight loss of CuO should be about 12.0% based on the mixture ratio of the sample and the weight loss of the char. However, 14.8% char conversion in the mixed sample can not supply enough reducing agent for CuO reduction based on the stoichiometric chemical calculations. This implies that the char gasification reactivity by CO_2 could be increased in the presence of Cu or CuO species, consequently, increasing its conversion rate to support reduction of more CuO. By the method of trial and error, the actual CuO reduction rate for coal char #1 was about 49.8%, and the char conversion was 33.6% after the one-hour isothermal stage in CO_2 .

B) Reduction of CuO by Coal Char #2.

For the coal char #2 sample, two runs of pyrolysis procedures were conducted (ASTM D5142 for volatile matter determination) in order to remove as much volatile material as possible from coal #2 sample. In the following CO₂ gasification process of coal char #2, there was no apparent peak found which corresponds to the release of volatile matter from the char sample. Reactivity of CO₂ gasification, which is represented by the DTG curve in Figure 15 for coal char #2, increased starting at 500°C, reached its maximum at 850°C, and then became almost flat.

For the mixed samples of coal char #2, two tests were conducted in N₂ and CO₂ atmospheres, respectively. Only one peak appeared at a temperature of 775°C in a N₂ atmosphere and 753°C in a CO₂ atmosphere. These were much lower than those found from the testing of coal char #1. Also, the onset temperature of about 500°C was much lower than that for coal char #1. Due to the release of reducing agents prior to testing, the peak seen can be attributed to CuO reduction by coal char alone without the influence of pyrolysis products. In the CO₂ atmosphere, CO₂ gasification could provide a reducing agent in the form of CO. The decrease of peak temperature might imply the higher reactivity of char #2 when compared to char #1 due to the higher specific surface area and pore structure of coal char #2, which was attributed to the higher volatile material content in coal #2.

Figure 15. Weight loss history of the coal char #2 sample and the mixed sample in nitrogen and carbon dioxide atmospheres with a temperature ramp of 30°C/min to 850°C.

In a CO₂ atmosphere, the total weight loss of coal char #2 was about 19.4% and that of the mixed sample with a mixture ratio of 1:9 char to CuO was 18.6%. Assuming that no Cu₂O

species were produced and Cu was the only reduction product, the calculated weight loss of CuO in the mixed sample was about 18.5% based on the mix ratio of the sample and the weight loss of the char. The calculated value of 18.5% for CuO reduction was very close to its predicted theoretical value of 20% for complete CuO reduction. However, 19.4% char conversion in the mixed sample similarly could not supply enough reduction agents for CuO reduction based on the stoichiometric chemical calculation. This implies that char gasification by CO₂ could increase in the presence of Cu species, so that its conversion rate should increase to support reduction of more CuO. Using a trial and error method, the CuO reduction rate by coal char #2 in CO₂ atmosphere was about 75.3%, and the corresponding char conversion was 50.8%. Compared with the case of char #1 with a CuO reduction efficiency of 49.8%, higher CuO reduction was found for char #2, possibly due to the higher reactivity of char #2.

TG-MS Characterization – Mechanisms of CuO Reduction Reaction by Char. In the TGA-MS experiments, evolved gases from the TGA tests were sent through a heated transfer line to a mass spectrometer for determination of evolved gaseous components. The main gaseous components present in the evolved gas of the mixture sample should be H₂O, CO₂ and CO, with some other pollutant species. For CO₂, the mass-to-charge (m/z) values monitored were 44, 28, 16, 12 and 45, and for CO, they were 28, 16, 12 and 29. The general carrier gas of N₂ has 3 m/z's -- 28, 14 and 29. It should be noted that some interesting gaseous species have the same mass numbers. The TGA-MS results from the decomposition of coal char #2 and the mixture samples in N₂ and CO₂ atmospheres are shown in Figures 16 through 18 as 2D spectra of intensity with respect to time. Figure 19 gives the test results for calcium oxalate, which was always used as the standard material to verify TGA-MS performance. Three mass spectra peaks appear in the TGA decomposition test of the calcium oxalate sample, which represent the loss of water, carbon monoxide and carbon dioxide. The second peak was hard to explain for a sample heated in the absence of oxygen (when UHP N₂ and argon gas were used as the carrier gas in the TGA-MS tests). However, this behavior can be explained based on further reaction of some of the CO initially formed. Specifically, the CO can decompose to produce carbon and CO₂. The presence of the secondary reaction was verified by the color of reaction product and also some related tests.

Only one MS peak was found for the mixed sample in an N₂ atmosphere, which corresponded to the major peak from the DTG test, and was a CO₂ peak with a mass number of 44. This peak did not return to its baseline as the temperature increased. Other peaks were found at m/z's of 16 and 12, which correspond to the peak for CO with the same m/z. Normally, m/z = 28 would be used to monitor CO evolution, but since the carrier gas of N₂ produces a huge m/z = 28 peak, no intensity change could be detected as a result of CO. Similarly, no distinct peaks were found for CO₂ for the reaction in a CO₂ atmosphere due to the strong background and corresponding ion current (A) from the carrier gas -- CO₂.

The TG-MS testing in N₂ strongly supports the occurrence of the direct reduction of CuO by coal char with onset temperatures as low as 500°C. The following equation represents the proposed reaction:

Combined with the TGA tests in a CO₂ atmosphere for individual coal char samples, which showed that coal char gasification had an onset at low temperatures (about 500°C), the following reaction mechanisms for CuO and char in CO₂ can be proposed. This reaction will proceed at a high temperature due to the continuous evolution of CO₂ at higher temperatures, such as 850°C, in a N₂ atmosphere.

1. At the lower temperature range starting around 500°C:

2. At higher temperature range above 750°C, the reactivity of all reactions was improved, especially gasification reactivity:

Figure 16. Total ion current versus the time (minutes) for the mass-to-charge values of 16, 28 and 44 resulting from the reaction of the mixed sample of coal char #2 and CuO to determine weight loss by TG and evolved gases by mass spectra in a CO₂ atmosphere.

Figure 17. Total ion current versus the time (minutes) for the mass-to-charge values of 16, 28 and 44 resulting from the reaction of the mixed sample of coal char #2 to determine weight loss by TG and evolved gases by mass spectra in a CO₂ atmosphere..

Figure 18. Test results for the coal char #2 sample to determine weight loss by TG and evolved gases by mass spectra in a CO₂ atmosphere.

Figure 19. Test results for calcium oxalate sample in the determination of weight loss by TG and evolved gases by mass spectra in an N₂ atmosphere.

Gasification Reactivity of Coal Char with CO₂ The previous results identified the possible reduction reaction of CuO by coal char with reaction onset temperatures of about 500°C. As the temperature increases, char gasification by CO₂ starts. The gasification product, CO, may further reduce CuO. Thus, at higher temperatures, the reaction of char gasification by CO₂, which produces CO, should become more important due to the increased reactivity of the reaction between CO and CuO since gases react more readily with solids than solids with solids. The overall reaction rate should be controlled by char gasification in a CO₂ atmosphere. In this regard, a test matrix was developed to evaluate reaction kinetics of char gasification by CO₂. The test results of coal char gasification reactivity by CO₂ are shown in Figure 20 for coal char #1 and Figure 21 for coal char #2. Coal char #1 came from coal #1 which has a lower volatile matter content (about 15% by weight) while coal char #2 came from coal #2 which has a higher volatile matter content (about 35% by weight). Four final temperatures were selected to evaluate gasification reactivity, 900°C, 950°C, 1000°C and 1050°C. The heating rate of the SDT instrument was set at 100°C/min. The residence time of char at the final SDT temperature was in the range of 60 minutes.

In all the curves in Figures 20 and 21, showing the weight loss rate of coal char samples, the first peak can be attributed to moisture loss from the coal char sample and the second peak attributed to the loss of volatile material, which was not fully removed during the pyrolysis procedures. Except for the experiment with a final temperature of 900°C, the char gasification reactivity initially increased and then decreased gradually as the reaction proceeded. A reactivity peak was found in all DTG curves in the range of 950°C through 1050°C. The decrease of the gasification reactivity was mainly due to the onset of coal char carbonization in CO₂. This has been attributed to the change of the coal char crystal structure and subsequent loss of active surface area of coal char. The loss of gasification reactivity even occurred at 1050°C with an onset conversion rate of about 80%. This means that the major portion of coal char was difficult to be gasified. Correspondingly, the reduction of CuO was difficult due to low and inefficient contact of un-reacted coal char with the outside ash layer and to CuO encased in an outer layer of reduced Cu in the fixed bed contact mode such as that which occurred in the SDT instrument. The effect of the outer ash layer on un-reacted coal char could be minimized to some extent by introducing this reduction reaction in a moving bed or a fluidized bed mode. An alternative reaction mode could have been the reduction of CuO by gaseous CO, which can proceed with relative ease. CO will be provided by the gasification of coal char in a CO₂ atmosphere. Thus, the improvement of the gasification reactivity was the main technical issue in the present studies.

Several measures could help to improve the gasification reactivity. As shown in Figures 20 and 21, a higher operating temperature would make sense. For the comparison of gasification performance of the two coal chars, which were shown in Figures 20 and 21, the final conversion and maximum reaction rates under the same test conditions showed an apparent difference. For coal char #1, the final conversions in a CO₂ atmosphere were 11.4%, 23.5%, 33.3% and 42.48% at the four temperature levels from 900°C through 1050°C, respectively. Correspondingly, the maximum gasification rates by CO₂ were 0.81%/min, 0.63%/min, 0.39%/min and 0.18%/min, at the four temperatures, respectively. For coal char #2 under similar test conditions, the final conversions in a CO₂ atmosphere were 13.4%, 29.9%, 52.6% and 59.5%, respectively.

Correspondingly, the maximum gasification rates by CO₂ were 1.57%/min, 0.99%/min, 0.49%/min and 0.21%/min, respectively. The improvement of gasification reactivity should be attributed to developed pore structure and specific surface area in coal char #2 due to its higher volatile content. However, improvement in gasification reactivity was not significant with volatile contents ranging from about 15% to 35%. Further work should extend the test coal types to low rank coals with higher moisture and volatile contents. The idea behind this is to increase the gasification reactivity by increasing the pore volume and specific surface area as large amounts of moisture and volatile content in low rank coals are released. The biomass and solid waste were selected in these tests based on their much higher volatile contents, which could be regarded as an extreme case of solid fuels in view of gasification reactivity.

Figure 20. Weight loss history for gasification of coal char #1 in CO₂ at a temperature ramp of 100°C/min to four final temperature levels from 900°C through 1050°C.

Figure 21. Weight loss history of the gasification of coal char #2 in CO₂ at a temperature ramp of 100°C/min to four final temperature levels from 900°C through 1050°C.

2.1.3.2.5. Category 3 - Test Results and Discussion

CuO Reduction by Biomass and Solid Waste. Several combustible resources have been listed as so-called opportunity fuels, which will soon emerge and be developed as popular commercial energy sources when the industry learns how to handle them. In view of the volatile content and corresponding gasification reactivity, biomass and municipal solid wastes are more attractive for utilization in the developing chemical looping combustion process.

Crops, such as switchgrass, have been grown for energy purposes at Ottumwa Generating Station in Chillicothe, IA, and at Plant Gadsden in Gadsden, AL. Miscanthus, a fast-growing grass product, is being grown for Dynergy Company for energy purposes. Willow and hybrid poplar are also being grown experimentally as energy sources. Willow is being grown and used in the United Kingdom experimentally as well; the UK has an extensive program to use biomass fuels. Post-customer materials provide another category of opportunity fuels. Representative post-customer materials include waste oil and refined oil, paper-derived fuel (PFD), plastics-derived fuel, refused-derived fuel (RDF) and sewage sludge. In this test, two types of these opportunity fuels, wood and polyethylene (PE), were selected as models to evaluate their utilization potential in the developing Chemical Looping Combustion process.

A) CuO Reduction by Solid Waste - PE.

The volatile material content in the PE sample (chemically pure) was 99.8%. Correspondingly, the total weight loss was 99.7% in N_2 , which was very close to its proximate analysis, as shown in Figure 22. The peak and its onset of weight loss rate were approximately 470°C and 370°C, respectively. The maximum rate of weight loss was 24.6%/min. Due to the release of CO_2 in the PE pyrolysis process, the onset of weight loss in CO_2 was slightly delayed when compared to the weight loss in N_2 . However, the weight loss in CO_2 reached its peak faster (459°C) than that in N_2 due to the possible gasification of pyrolysis products of PE or PE itself occurring in a CO_2 atmosphere. In CO_2 , the peak rate of weight loss reached as high as 26.9%/min at a temperature of 459°C, while it was less than 0.26%/min for coal char #2.

Figure 22. Weight loss history of the PE sample and the mixed sample in a nitrogen and carbon dioxide atmosphere with a temperature ramp of 10°C/min to 850°C.

For the mixed samples of PE with CuO, two tests were conducted in N_2 and CO_2 atmospheres. There were two peaks at temperatures of 388°C and 448°C in a N_2 atmosphere. Similarly, there were also two peaks in a CO_2 atmosphere. However, weight losses were delayed due to the reasons mentioned previously. Between these two peaks, there was an apparent transition point. This implies that two different processes occurred in the mixed samples in both N_2 and CO_2 atmospheres. The first peak in the DTG curve should be attributed to the pyrolysis of PE and the 2nd peak should be attributed to the pyrolysis of PE with the simultaneous reduction of CuO in the mixed sample. That the mixed sample proceeded a little faster in CO_2 might be explained by the fact that smaller reduction molecules have more reduction capability.

Both peaks for the mixed samples in different atmospheres came out a little earlier than those of pure PE samples due to the reversible nature of the CuO reduction reaction.

In both atmospheres, the total weight loss from the mixed sample of PE was 72-73%, which was close to 100% of the theoretical conversion efficiency of CuO reduction. Apparently, in this case, there was still no Cu₂O species to be found in the reaction products -- Cu was the only reduction product. Higher reduction conversion efficiency of CuO resulted from the higher reactivity of pyrolysis and gasification of PE and also higher gas-solid contact between gaseous reducing agent and CuO.

CuO Reduction by Biomass – Wood. The volatile material content of the wood was 76.1%. However, the total weight loss was 100% in CO₂. There was no apparent boundary between the pyrolysis of volatile material and the gasification of the fixed carbon in the wood sample, as shown in Figure 23. This was due to the larger temperature ramp (100°C/min) used for wood sample testing. Generally, a higher heating rate occurs in industrial-scale facilities, which are always in the range of 500-1000°C/min. Thus, wood test results with a heating rate of 100°C/min should be closer to the actual performance of CuO reduction by wood in a future chemical looping facility. Also, the total residence time for full conversion of CuO was just 5 min. The peak temperature of CuO reduction by wood occurred as low as 375°C. The peak rate of weight loss reached as high as about 110%/min. All these results show very attractive and promising opportunities for the utilization of opportunity fuels in the chemical looping combustion process. In both atmospheres, the total weight loss from the mixed sample of PE was 60%, which was very close to 100% of theoretical conversion efficiency of CuO reduction. Apparently, in this case, there was still no Cu₂O species found in the reaction products; Cu was the only reduction product.

SEM images of the reaction product from a mixture of wood and CuO at different magnifications are shown in Figure 24. The product sample looked like thick leaves with holes inside at a small magnification and a solid block at larger magnification. Compared with the original CuO sample, it was found that the Cu product kept the shape and structure of its raw material – CuO. There were no apparent melting phenomena to be found. The reason for the lack of melting was the lower temperature at which this experiment was run allowing the CuO a temperature cushion before the melting point of Cu — this allowed hotspots to form, but they were still below the melting point.

Figure 23. Weight loss history of the wood sample and the mixed sample in a nitrogen and carbon dioxide atmosphere with a temperature ramp of 100°C/min to 900°C.

Figure 24. SEM images for the mixed sample of wood and CuO (25%:75%).

CuO Reduction by PRB Coal.

A) Reduction Performance of PRB Coal.

Coal #1 and Coal #2 are bituminous coals, while the PRB coal used in this study is a subbituminous coal with higher moisture and volatile content as shown in Table 2. The TGA weight loss curve for this coal is shown in Figure 25. Typically, there are 3 peaks shown in the curve as the temperature rises to 800°C in a CO₂ atmosphere. The first large peak representing a weight loss comes at a temperature of 138°C, which is attributed to a moisture loss of 19%. The second peak comes at 459°C, which is attributed to the partial pyrolysis process of some volatile materials and this weight loss is approximately 30%. The last peak appears at 830°C, corresponding to the combined pyrolysis and CO₂ gasification of the fixed carbon of the PRB coal with a weight loss in this stage of about 50%. At the end of the gasification reaction in a CO₂ atmosphere, at a temperature of 850°C, only ash with a weight content of 6% is left. These tests indicate that the PRB coal has higher gasification reactivity than the other coals tested.

Figure 25. Weight loss curves for PRB coal and mixture samples in carbon dioxide and nitrogen atmospheres with a temperature ramp of 30°C/min to 850°C.

For the mixture samples of PRB coal with CuO (ratio: 25%:75%) in N₂ and CO₂ atmospheres, the two weight loss curves show trends similar to the PRB coal alone with 3 weight loss peaks. Due to the mixture ratio of PRB coal and CuO, the mixture sample shows a small peak at the moisture loss stage. However, starting at the partial pyrolysis process (second peak), the weight loss peaks in the mixture samples are larger. The second peak sizes from the mixture samples approach the size of the peaks of the coal by itself, and the sizes of the third peaks are larger than that of the coal sample. This indicates that CuO reduction occurs at a lower temperature, even though its reactivity is limited at the lower temperature. At higher

temperatures, the weight loss peaks appear earlier and are also stronger than that of the PRB coal. The reduction of CuO appears to occur quickly and thoroughly. The tests also indicate the improvement of char gasification reactivity by coupling with the CuO reduction, due to the fact that its products are consequently and continuously used for the reduction of CuO.

At the end of reduction reaction of the mixed samples, about 69% and 64% of solid residues are left in N₂ and CO₂ atmospheres, respectively. Stoichiometric calculations show that more than 90% of the CuO has been reduced in the CO₂ atmosphere. A smaller reduction conversion of CuO is found in a N₂ atmosphere, probably due to some fixed carbon not being gasified in a N₂ atmosphere to continue supporting the CuO reduction reaction. It is apparent that the CuO reduction reaction occurs with higher reactivity by using PRB coal.

B) Heat Flow Analysis of the Reduction Process.

Corresponding to three thermal decomposition peaks in the TGA curves, 3 heat flow curves (DSC curves) are shown in Figure 26 for the individual samples. For the PRB coal, the first peak is attributed to the endothermic moisture loss and the second and the third peaks are attributed to the endothermic partial pyrolysis process and combined pyrolysis and gasification process in the CO₂ atmosphere. Similarly, the mixture samples heated in N₂ and CO₂ atmospheres also show the endothermic moisture loss stages. However, in the partial pyrolysis and combined gasification processes, the mixture samples show an exothermic behavior. This indicates the reduction of CuO occurs due to its exothermic property and the heat released by CuO reduction reaction is greater than the heat needed to support the endothermic reactions of pyrolysis and gasification processes for the PRB coal. This supports the choice for oxygen carrier selected in the Phase I project, since CuO can be used as the oxygen carrier to compensate for the heat needed for the endothermic coal gasification reaction.

Figure 26. Heat flow curves for the PRB coal and mixture samples in carbon dioxide and nitrogen with a temperature ramp of 30°C/min to 850°C.

C) CO₂ Gasification Performance of PRB Coal

Figure 27 shows the weight loss curves for the PRB coal sample in a CO₂ atmosphere at different ending temperatures. At different final temperatures, the major differences in peak height are shown at the stage of the combined pyrolysis and gasification process. The difference in peak heights at the moisture loss stage is just the difference of handling the initial samples due to different moisture contents in test samples. There are no large differences in peak heights of weight loss at the partial pyrolysis process (second peaks). However, the char gasification quickly proceeds, which shows sharper peaks as the final temperatures increases. Compared with the previous two coal char samples, the effect of coal char structure and subsequent loss of active surface area of coal char does not happen in the gasification process of the PRB coal. This results from the high reactivity of the PRB coal and its lower fixed carbon content. Thus, the reduction of CuO proceeds easily with the PRB coal.

The final temperatures do change the reactivity of the CO₂ gasification of PRB coal, although it is not much of a change. When the final temperatures varied from 850°C through 1050°C, the CO₂ gasification reactivity changes from 6.47%/min, through 13.3%/min and 17.6%/min to 19.7%/min. The PRB coal's reactivity is much higher than that of chars obtained from Coal #1 and Coal #2. The improvement of gasification reactivity can be attributed to the more developed pore structure and specific surface area caused by moisture loss and pyrolysis processes, and also the reactivity of PRB coal itself. PRB coal, together with biomass, seems to be the solid fuel types for developing the CLC system for solid fuels. This indicates the gaseous products of the pyrolysis and gasification process should be the major reducing agents for reduction of CuO in the CLC process and the dominant reduction reaction path should be gas solid reaction between gaseous reducing agents and CuO. The CuO can be reduced by solid char, as shown in the previous tests with chars from Coal #1 and Coal #2, but its reduction reactivity is largely limited due to inefficient contact between the reactants.

Figure 27. Weight loss curves for the gasification of coal #3 -- PRB coal -- in CO₂ at a temperature ramp of 30°C/min to four final temperatures from 850°C through 1050°C.

C) XRD Characterization of Solid Residues

The XRD characterization of the solid residues from a 15 minute reaction of the mixed sample in a CO_2 atmosphere at 800°C is shown in Figure 28. The Cu peak was identified and there is no CuO or Cu_2O found in solid residue. This implies that all CuO is reduced by the PRB coal in a CO_2 atmosphere even in the shorter reaction time at the lower temperature of 800°C . This reduction time scale is suitable for the application of a bubbling fluidized bed as a reducer. The reduction reactivity of CuO can be improved by a faster heating rate, which is always at a level of several hundred Fahrenheit degrees per second (in the fluidized bed system). The actual reduction reactivity of CuO by a PRB coal should be much faster than the reaction in the TGA test (slow heating rate). The reactivity and conversion rate of CuO reduction by a PRB coal and biomass would be very practical in the CLC process for solid fuels. PRB coal is inexpensive, readily available, and has lower sulfur and chlorine contents. Thus, the use of PRB coal and biomass (to be demonstrated later in the proposal) shows promise in the development of the chemical looping combustion of solid fuels. Tests results based on solid (TGA, DSC, SEM, and XRD) and gaseous state (evolved gas analysis using FTIR and MS) information obtained in Phase I demonstrated the proposed reaction mechanism and strongly supports the feasibility of the chemical looping combustion process for selected solid fuels.

Figure 28. XRD characterization of three solid residue samples: 1) chemically pure CuO sample, 2) reaction product of chemically pure CuO at 800°C in a CO_2 atmosphere, and 3) reaction product of mixture sample (25%PRB:75% CuO) at 800°C in a CO_2 atmosphere.

2.1.3.2.7. Other Tests

Oxidization of Oxygen carrier-Cu. Figure 29 shows the weight gain and heat flow curve for the oxidation of chemically pure Cu during a temperature increase from room temperature to 800°C at the heating rate of 10°C/min. No weight change for the Cu sample is found until the temperature reaches 233°C. There are three thermal decomposition stages in Figure 29. The first stage appears at a temperature of 322°C, the second stage at a temperature of 567°C, and the third stage at temperature of 661°C. However, the three peaks overlap some so that it is not easy to distinguish the exact boundaries of the stage changes, even under high-resolution mode testing conditions. The total weight gain is 24.5% under experimental conditions, which is very close to the theoretical weight gain of complete oxidation of Cu with product of CuO. Three exothermic peaks in the heat flow curves correspond to three weight change peaks. The oxidation of Cu is an exothermic reaction, thus heat exchanger tubes can be installed inside the oxidizer to maintain the reaction temperature and also produce steam for electricity generation. It is apparent the total reaction should occur according to the following equation:

However, the actual reaction path is not as simple as shown in equation (7) based on the results of the oxidation process for Cu. The staged oxidation process is clearly shown in Figure 30-1 and 30-2. It seems that Cu₂O may be the intermediate product at a lower temperature under the slow oxidation process. At the high temperature stage, whether it is Cu or Cu₂O, it should be completely oxidized to CuO, which is based on theoretical calculations. With fast heating rates of 50°C/min and 100°C/min, only one strong peak could be found and was shifted to a higher temperature with an increased heating rate. The final peaks appear at 640°C, 662°C, 725°C, and 783°C, respectively, as the heating rate is increased from 5°C/min to 100°C/min. This implies that the minimum temperature for the completion of Cu oxidation increases as the heating rate increases. Due to the test limitation of the heating rate (100°C/min) using the available TGA instrument, the optimum reaction temperature to complete the oxidation of Cu could not be determined. However, the results indicate that higher operating temperatures in the range of 900

to 1000°C should be selected in the design of the oxidizer, considering that heating rates of several hundred Fahrenheit degrees per minute exist in the riser of the CFB.

The oxidation rate was increased from 0.5%/min to 8.5%/min when the heating rate was changed from 5°C/min to 100°C/min under our experimental conditions. Thus, the oxidation reactivity of Cu increases with an increase in the heating rate. Thus, it can be predicted that the oxidation of Cu should be completed within a few seconds in the riser area. The heating rate is the controlling factor in the oxidation reactivity of Cu and not the reaction temperature as illustrated in Figure 31.

Figure 29. Weight gain and heat flow history of chemically pure Cu in an air atmosphere at 800°C.

Figure 30-1. The effect of heating rate on CuO oxidation (X scale = time).

Figure 30-2. The effect of heating rate on CuO oxidation (X-scale = temperature)

Figure 31. The effect of final temperature on CuO oxidation.

Oxygen Carrier preparation. The conventional impregnated oxygen carrier has disadvantages of lower load capacity of the active component. Thus, the circulation rate of oxygen carrier in a CLC system will be largely increased. This will increase the reactor scale and power supply, and consequently, increases the capital cost. In Phase I, an effort was made to resolve this problem by mechanical mixing of Cu or CuO with a substrate of TiO_2 . The mixing ratio was kept at 50:50. The test purpose was focused on the oxidation and reduction performances of the mixture and variation of its mechanical strength.

Figures 32 and 33 show the oxidation performance of a mixture of Cu with TiO_2 . The oxidation performance of a mixture of Cu and TiO_2 is exactly the same as that of Cu alone which was based on the maximum oxidation temperature, the rate of reaction, and the final product. TiO_2 does not take part in the chemical reaction with either O_2 or Cu. The heating rate is still the important factor in the oxidation process of the mixture sample, with regard to the reaction rate and final product. Figure 34 shows the reduction of the CuO mixture with TiO_2 by PRB coal. The CuO- TiO_2 mixture is from the oxidation of the Cu- TiO_2 mixture. It seems that the mixture of CuO- TiO_2 can also be easily reduced by PRB coal. However, the mechanical strength is much better in the case of mixture sample, which shows higher mechanical strength. It can endure compression pressure as high as 14,000 PSI, which is suitable for use in the recycle system of the CLC process. The Cu sample broke under 1,500 PSI.

Figure 32. Oxidation performance of the mixture of Cu and TiO₂ at 800°C.

Figure 33. Comparison of the oxidation processes of Cu and its mixture with TiO₂.

Figure 34. Reduction of a mixture of CuO with TiO₂ by PRB coal (CuO mixture from Cu mixture with TiO₂ after exposed to an air atmosphere).

2.1.3.2.8. System Analysis for the CLC of Solid Fuels Based on a Mass-Energy-Pressure Balance-Design Consideration

In the chemical looping combustion process of solid fuels, the technical issues to be solved are mainly included in the reducer section, in which the reduction of the oxygen carrier may occur by solid fuels directly or by gasification products of solid fuels indirectly. Based on studies of mechanisms of CuO reduction by several kinds of solid fuels in Phase I, we found the reactivity of solid fuels plays the key role. The solid fuels with higher char reactivity, which is dependent on the physical and chemical properties of solid fuels, can be easily incorporated into the chemical looping combustion process. Tests results showed PRB coal, which is inexpensive and abundant, and some biomass or polymer-based waste solid fuels could be the best choices for further development of a chemical looping combustion system for solid fuels. These selected solid fuels have similar properties, such as higher moisture and volatile matter contents and lower ash contents. As is generally known, pyrolysis is more easily conducted with higher reactivity fuels. The increase in pore structure and surface area of solid fuels during pyrolysis will result in the increase of the gasification reactivity of char produced and also the reactivity of the char for reduction of the oxygen carrier. Thus, in Phase II, we will first focus on solid fuels such as PRB coal and biomass in our pilot-scale demonstration of the chemical looping combustion of solid fuels. Results collected in Phase II will continue to provide essential results for basic system design, improvement of reactor type, and system development for the chemical

looping combustion process of solid fuels for an industry scale demonstration. A second area of interest for Phase II will be on system compatibility for higher rank coals (bituminous coals) with relative lower reactivity.

Based on properties of the solid fuels selected and mechanism studies of the reduction of oxygen carrier directly by solid fuels, we are proposing the first major change in the handling process of solid fuels. In the Phase I proposal, it was proposed that the solid fuels would be first pyrolyzed to form char and then the char would be directly fed into the reducer. In this Phase II proposal, we are excluding the pyrolyzer, and propose the direct feeding of solid fuels into the reducer. It is apparent that excluding the pyrolyzer also simplifies the whole system and reduces its cost. Second, solid fuels, with higher moisture and volatile matter contents which show higher “sticky” trends, will be fed into the reducer after a special treatment. The special handling of solid fuels will include a pre-oxidation fuel feeder to treat the solid fuels which may become sticky in the following reducer. Generally, the pre-oxidation feeder is operated at a lower temperature, which is about 200°C. The only change of solid fuel properties in the pre-oxidation process is adsorption of oxygen and increase in oxygen functional groups, which will be beneficial for the reduction of the oxygen carrier. The third modification is the enlargement of the operating range of the reducer, which is designed to be in a large loop seal. In the originally proposed configuration, the reducer was to be operated as a moving bed in one component of the loop seal and the other side as a bubbling fluidized bed. Due to the fact the reactivity of oxygen carrier with solid fuels is higher than that predicted in the Phase I stage, and also the bubbling fluidized bed may be not the optimum device for the separation of oxygen carrier and fly ash, we propose to modify the reducer configuration as a bubbling fluidized bed in one side and a turbulent fluidized bed in the other side. The bubbling fluidized bed will be connected with the downcomer via a small loop seal, and the turbulent fluidized bed will be connected with the riser via another small loop seal. Thus, the final configuration of the proposed chemical looping combustion of solid fuels is shown in Figure 1. Two small loop seals are important for solid recycle and gas leakage prevention between the oxidizer and reducer. It will be discussed in the following chapter on system pressure balance.

System pressure balance is essential to the buildup of solid recycle and also the adjustability of the recycle rate. The function of the loop seal could assist the flow of solids from a location with lower static pressure to a location with higher static pressure inside the cycle system. The actual pressure profiles for several operating conditions are shown in Figure 35. In this figure, points 4 through 8 represent the upper loop seal, points 8 through point 12 represent the middle loop seal (reducer and separator), and points 12 through point 16 represent the down loop seal. The pressure difference is distributed in these loop seals to fulfill the task of transporting recycled solids from a lower pressure at point 4 to a higher pressure at point 17.

Generally speaking, the higher recycle rate of solids needs a higher pressure difference in the CLC system. In the original design, as shown in the Phase I proposal (indicated by red and green lines), the middle loop seal is made up of a moving bed on one side, which acts as the

reducer, and combined with a bubbling fluidized bed, which acts as a separator for ash and oxygen carrier. The pressure difference in the moving bed is always smaller, as shown in point 8' and point 9' (red for the high mass flow rate and green for the low mass flow rate operating conditions). If solids flow is intended to be operated at the higher mass flow rate condition, the upper and the down loop seals must work at the larger pressure difference. However, these two loop seals are both small and can not create the large pressure difference to support the higher mass flow in the whole system. This means the pressure profiles with the red marks are impossible. The static pressure at the point 5' location will move to the point 5'' location in the dashed line, which may be actually lower than that at the point 8' location. The normal pressure profiles in the upper loop seal may collapse. In this case, the solids flow may back-flow in the upper loop seals. The cycle system of the CLC will not be sustained. If recycled solid is operated at a lower mass flow rate condition, as shown in the pressure profile marked with green, it is very difficult to control and adjust the system under such narrow pressure differences between loop seals.

In this proposal, we will modify the operating conditions of the larger loop seal (black line) which acts as a reducer and separator, respectively. The reducer works under fluidized bed conditions and the separator works under turbulent conditions. In this new configuration, the larger loop seal works at larger pressure differences (point 8 through point 9 in black), and small loop seals (upper and down) work at a smaller pressure differences. Also these two loop seals have similar pressure differences. This modified system also will provide the flexibility of mass flow rate control (higher or lower). Thus, it is suitable for system setup, startup, stabilization and condition testing at the pilot scale stage. The investigation of solids flow and recycle will be conducted at a cold-model facility with the height of the riser (oxidizer) to be 3 m and a reducer to be 0.5 m. The operating gas velocity of the riser in the fast fluidization state is 5 times the terminal velocity of selected oxygen carrier. The operating gas velocity of the reducer in the bubbling fluidization state is 5 times the minimum fluidization velocity of the selected oxygen carrier, and the operating gas velocity of the separator in the turbulent fluidization state is the terminal velocity of the fly ash.

The mass balance of the hot model test facility is shown in Table 5. Based on calculations of the designed facility's thermal capacity of 5 KWt, 0.89 Kg/hr PRB coal will be fed into the reducer. The recycle oxygen carrier can be 6.7 Kg/hr for CuO in the reducer and 5.35 Kg/hr for Cu in the oxidizer. The air needed in the oxidizer is 4.90 NM³/hr. The purified CO₂ stream is only 0.84 NM³/hr. The load of separation of ash from oxygen carrier is 0.05 Kg/NM₃. These parameters will be used to build the hot model of the CLC process for solid fuels.

Figure 35. The pressure profiles of the proposed system of chemical looping combustion of solid fuels.

Table 5. Mass Balance Calculations for the Chemical Looping Combustion of Solid Fuels.

1. The proximate and elemental analysis of PRB coal (wt)					
C, wt	H, wt	O, wt	Moisture, wt	Ash, wt	LHV, BTU/lb
51.04%	6.44%	36.35%	26.60%	5.18%	8755
2. Actual contents of free hydrogen and oxygen					
H in Moisture	O in Moisture	Free H	Free O		
2.96%	23.64%	3.48%	12.71%		
3. Assuming partial free H oxidized by free O in coal through					
$2H + O \rightarrow H_2O$					
Thus, remaining hydrogen and carbon for reduction of CuO is					
H =		1.90%			
C =		51.04%			
Molar C and H in 1 Kg PRB coal as reducing agents of CuO					
C as reducing agent		H as reducing agent			
42.5		19.0			
4. Actual reactions with Cu-CuO occur as follows:					
In Reducer					
$C_{42.5}H_{19} + (2 \times 42.5 + 19/2)CuO \rightarrow (2 \times 42.5 + 19/2) Cu + 42.4CO_2 + (19/2) H_2O$					
In Oxidizer					
$(2 \times 42.5 + 19/2) Cu + [(2 \times 42.5 + 19/2)/2]O_2 + [3.75 \times (2 \times 42.5 + 19/2)/2]N_2 \rightarrow (2 \times 42.5 + 19/2)CuO + [3.75(2 \times 42.5 + 19/2)/2]N_2$					
Assuming extra air is 1.1 for oxidization reaction of Cu					
In Oxidizer					
$(2 \times 42.5 + 19/2) Cu + 1.1 \{ [(2 \times 42.5 + 19/2)/2]O_2 + [3.75 \times (2 \times 42.5 + 19/2)/2]N_2 \} \rightarrow (2 \times 42.5 + 19/2)CuO + 1.1 \{ 3.75 \times [(2 \times 42.5 + 19/2)/2]N_2 \} + 0.1 \times [(2 \times 42.5 + 19/2)/2]O_2$					

Continued

5. Thus, mass flow streams in oxidizer and reducer listed as follows:

<u>PRB Coal</u>		1.00	Kg
<u>CuO</u>		7.56	Kg
<u>Cu</u>		6.05	Kg
<u>Air</u>		5.53	NM ³
<u>Stream 1</u>	N ₂	4.37	NM ³
at oxidizer outlet	O ₂	0.11	NM ³
<u>Stream 2</u>	CO ₂	0.95	NM ³
at reducer outlet	H ₂ O	0.21	NM ³
<u>Ash discharge</u>		0.05	Kg

6. If design scale of facility is 5 KWt

<u>PRB Coal</u>		0.89	Kg/h
<u>CuO</u>		6.70	Kg/h
<u>Cu</u>		5.36	Kg/h
<u>Air</u>		4.90	NM ³ /h
<u>Stream 1</u>	N ₂	3.87	NM ³ /h
at oxidizer outlet	O ₂	0.09	NM ³ /h
<u>Stream 2</u>	CO ₂	0.84	NM ³ /h
at reducer outlet	H ₂ O	0.19	NM ³ /h
<u>Ash discharge</u>		0.05	Kg/h

2.1.3.2.9. Conclusions for Phase I

CuO can be decomposed into Cu₂O at higher temperatures in inert or oxidizing atmospheres. However, there is no evidence to show Cu₂O exists in reducing atmospheres. CuO can be converted into Cu in a reduction process, either in a direct path by coal or in an indirect path by pyrolysis and gasification products of coal. Evidence showing direct reduction of CuO by coal has been verified by tests to remove interferences from the coal pyrolysis process. CuO reduction by gaseous reducing agents can start at lower temperatures, approximately 400°C, and reduction by coal char can start at 500°C. However, its reduction reactivity at lower temperatures is not acceptable. CuO is not suitable for temperatures higher than 900°C since it appears to melt and aggregate which would result in a loss of its reactivity and also inhibit separation from fly ash. Keeping the temperature between 800°C and 850°C could control the extent of melting. For the case of CuO powder used in the reaction system, no carbon deposit was found on the surface of the reduced Cu, which was characterized SEM-EDX analysis. The existence of CuO or Cu could improve the gasification reactivity of coal char by CO₂. The major gaseous product was CO₂ in reduction tests of CuO by coal char, which was identified by monitoring the evolved gas using a mass spectrometer. CO could not be clearly identified due to its trace amount and also possible interference from the carrier gases of CO₂ and N₂ used for testing. In the case of CuO reduction by coal, the majority of the gases produced were found to be CO₂ and H₂O, which are the desired products.

Mechanisms of CuO reduction by solid fuels may be as follows:

a) If pyrolysis products of solid fuels are available, reduction of CuO could start at about 400°C or less:

b) If pyrolysis products of solid fuels are unavailable and the reduction temperature is lower, reduction of CuO could occur at an onset temperature of about 500°C, char gasification reactivity in CO₂ was lower at lower temperatures.

c) If pyrolysis products of solid fuels are unavailable and the reduction temperature is higher than 750°C, all reaction reactivities were improved, especially the CO₂ gasification reactivity of char. Thus, the reduction of CuO by the gasification product CO could proceed quickly.

Based on the results obtained so far, the following coal characteristics would be desirable for the Chemical Looping Combustion process: high volatile matter with a high reactivity of the char produced. PRB coal meets these criteria while being comparatively less expensive and also very abundant. The high moisture content present in PRB coal might also increase the reactivity for char gasification through the development of pore structure and specific surface area in the char during pyrolysis. Biomass materials are also suitable, considering the reaction mechanism of CLC system of solid fuels. The feasibility of the chemical looping combustion process of solid fuels was verified by focusing on PRB coal and biomass.

Based on PRB coal as the preferred solid fuel in the development of the CLC system, the mass, energy and system in a dual reactor recirculation system has been determined. The system configuration has been set up with the technical approach to be used in Phase II.

In the Cu oxidation tests, it was confirmed that the heating rate is the most important effect on the Cu oxidation process. Lower heating rates and lower operational temperatures would result in incomplete conversion of Cu to CuO. Cu₂O may be the intermediate product. The operating temperature did not affect the reaction rate of the oxidation process. Under any operating conditions, the exothermic properties are clearly shown.

References:

1. Arrhenius, S. "On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground," *The London, Edinburgh and Dublin Philosophical Magazine and Journal of Science* [Fifth Series], **1896**, *41*, 237–277.
2. Hermansen, S. "Impacts of Global Warming and Environment Design for Mitigation," 2004, <http://www.tuins.ac.jp/jm/library/kiyou/2004chiiki-PDF/Ando.pdf>
3. Herzog, H.; Drake, E.; Adams, E. "CO₂ Capture, Reuse, and Storage Technologies for Mitigating Global Climate Change," *A White Paper*, Jan, 1997, U.S.DOE/DE-AF22-96PC01257, Washington, DC.
4. U.S.DOE and U.S. "Environmental Protection Agency. Carbon Dioxide Emissions from the Generation of Electric Power in the United States," Washington, DC, Oct 15, 1999, available at <http://www.epa.gov>.
5. Klara, S.M.; Srivastava, R.D. "U.S. DOE Integrated Collaborative Technology Development Program for CO₂ Sequestration and Capture," *Environmental Progress*, **2002**, *21*(4), 247-253.
6. United Nations: 1997, Report of the Conference of the Parties on its third session held at Kyoto, Dec.1-11, 1997, Kyoto Protocol, FCCC/CP/1997/ 7/Add.1, United Nations, New York, NY.
7. Norman J. Rosenberg and Roberto C. I. "Storing Carbon in Agricultural Soils: a Multi-purpose Environmental Strategy," Kluwer Academic Publishers, 2001.
8. White, C.M.; Strazisar, B. R.; Evan J.J.G.; James S.H.; Henry, W.P, 2003, "Separation and Capture of CO₂ from Large Stationary Sources and Sequestration in Geological Formations – Coalbeds and Deep Saline Coalbed Aquifers," *J. Air & Waste Manage. Assoc.*, **2003**, *53*, 645-715.

9. Anon, L. "Testing CO₂ — Enhanced Methane Recovery," *Greenhouse Issues*, 1999, 9(45), 1–3.
10. Herzog, H.; Eliasson, B.; Kaarstad, O. "Capturing Greenhouse Gases," *Scientific American*, **2000**, 282(2), 72–79.
11. Yu, J.; Corripio, A.B.; Harrison, D.P.; Copeland, R.J. "Analysis of the Sorbent Energy Transfer (SETS) for Power Generation and CO₂ Capture," *Advances in Environmental Research*, **2002**.
12. Riemer, P. "Greenhouse Gas Mitigation Technologies. An Overview of the CO₂ Capture, Storage and Future Activities of the IEA Greenhouse Gas R& D Programme," The IEA Greenhouse Gas R&D Programme, 1998. <http://www.ieagreen.org.uk/paper2.htm>.
13. Freund, P. "Abatement and Mitigation of Carbon Dioxide Emissions from Power Generation," Powergen 98 Conference, Milan, June, 1998. <http://www.ieagreen.org.uk/pge98.htm>.
14. Lyngfelt, A.; Leckner, B. "Technologies for CO₂ Separation." In: Lyngfelt, A.; Azar, C., eds, *Minisymposium on CO₂ Capture and Storage*, pp. 25–35. Chalmers University of Technology and University of Gothenburg, Goteborg, October 22, 1999, available on <http://www.entek.chalmers.se/~anly/symp/sympco2.html>.
15. Croiset, E.; Thambimuthu, K. "Coal Combustion with Flue Gas Recirculation for CO₂ Recovery," In: Riemer, P.; Eliasson, B.; Wokauun, A. eds, *Greenhouse Gas Control Technologies*, Elsevier, New York: 1999, pp 581–586.
15. Marion, J.; Naskala, Y.N.; Griffin, T. "Controlling Power Plant CO₂ Emissions: a Long Range Approach," *Proceedings of the First National Conference on Carbon Sequestration*, 2001, Washington, DC, DOE/NETL-2001/1114. (on CD-ROM).
16. Richter, H.; Knoche, K. "Reversibility of Combustion Processes." *ACS Symposium Series*, **1983**, 235, 71–86.
17. Podolski, W. F.; Swift, W.M.; Miller, S. A. *Air Emissions from Pressurized Fluidized Bed Combustor, Pressurized Fluidized Bed Combustion*, Cuenca, M. A. and Anthony, E. J., eds., Chapman & Hall, London: 1995.
18. Jin, H.; Okamoto, T.; Ishida, M. "Development of a Novel Chemical-Looping Combustion: Synthesis of a Looping Material with a Double Metal Oxide of CoO-NiO," *Energy & Fuels*, **1998**, 12(6), 1272.
19. Ryu, H. J.; Bae, D. H.; Han, K.H.; Lee, S.Y.; Jin, G. T. "Reactivity Study on Ni-based Oxygen Carrier Particle in a Fixed Bed Reactor for Chemical-Looping Combustor," *Theories and Applications of Chem. Eng., KICChE*, **2002**, 8, 1329.
20. IEA Greenhouse Gas R&D Programme Report, "Carbon Dioxide Capture from the Power Stations," available on <http://www.ieagreen.org.uk/sr2p.htm>.
21. Hatanaka, T.; Matsuda, S.; Hatano, H. "A New-concept Gas–Solid Combustion System 'MERIT' for High Combustion Efficiency and Low Emissions," *Proceedings of Intersociety Energy Conversion Engineering Conference*, 1997, Vol. 30, pp 944–948.
22. Herzog, H.; Eliasson, B.; Kaarstad, O. "Capturing Greenhouse Gases," *Scientific American*, **2000**, 282(2), 72–79.
23. Ishida, M.; Jin, H. "A Novel Combustor Based on Chemical-looping Reactions and its Reaction Kinetics," *Journal of Chemical Engineering of Japan*, **1994**, 27, 296–30.

24. Ishida, M.; Jin, H. "Novel Chemical-looping Combustor without NO_x Formation," *Industrial and Engineering Chemistry Research*, **1996**, *35*, 2469–2472.
25. Ishida, M.; Jin, H.; Okamoto, T. "A Fundamental Study of a New Kind of Medium Material for Chemical-looping Combustion," *Energy & Fuels*, **1996**, *10*, 958–963.
26. Ishida, M.; Jin, H.; Okamoto, T. "Kinetic Behaviour of Solid Particle in Chemical-looping Combustion: Suppressing Carbon Deposition in Reduction," *Energy & Fuels*, **1998**, *12*, 223–229.
27. Ishida, M.; Yamamoto, M.; Saito, Y. "Experimental Works on Innovative Chemical-looping Combustor," ECOS'99, *Proceedings*, International Conference on Efficiency, Costs, Optimization, Simulation and Environmental Aspects of Energy Systems, Tokyo, June 8–10, 1999, 306–310.
28. Ishida, M.; Yamamoto, M.; Ohba, T. "Experimental Results of Chemical-looping Combustion with NiO/NiAl₂O₄ Particle Circulation at 1200C," *Energy Conversion and Management*, **2002**, *43*, 1469.
29. Jin, H.; Ishida, M. "Reactivity Study on Natural-gas-fueled Chemical-looping Combustion by a Fixed Bed," *Ind. Eng. Chem. Res.*, **2002**, *41*, 4004–4007.
30. Jin, H.; Okamoto, T.; Ishida, M. "Development of a Novel Chemical-looping Combustion: Synthesis of a Looping Material with a Double Metal Oxide of CoO–NiO," *Energy & Fuels*, **1998**, *12*, 272–277.
31. Jin, H.; Okamoto, T.; Ishida, M. "Development of a Novel Chemical-looping Combustion: Synthesis of a Solid Looping Material of NiO–NiAl₂O₄," *Industrial and Engineering Chemistry Research*, **1999**, *38*, 126–132.
32. Wolf, J.; Anheden, M.; Yan, J. "Performance Analysis of Combined Cycles with Chemical Looping Combustion for CO₂ Capture," *Proceedings*, 18th Pittsburgh Coal Conference, 2001, CD-Rom, Session 23.
33. Mattisson, T.; Jaders, A.; Lyngfelt, A. "Reactivity of some Metal Oxide Support on Alumina with Alternating Methane and Oxygen-application for Chemical-looping Combustion," *Energy & Fuels*, **2003**, *17*, 643–651.
34. P.W. Atkins. *Physical Chemistry*, fifth edition, W.H. Freeman and Company, New York.
35. Department of Energy Solicitations for the Small Business Innovation Research and Small Business Technology Transfer Programs – Program Area Overview, 2003, (Subject 43. *Combustion Technologies and Water Resources*), <http://www.ofes.science.doe.gov>.
36. <http://www.epa.gov>
37. Mattisson, T.; Jarnas, A.; Lyngfelt, A. "Reactivity of some Metal Oxides Support on Alumina with Alternating Methane and Oxygen – Application for Chemical-looping Combustion," *Energy & Fuel*, **2003**, *17*, 643–651.