

Investigation of Chemical Looping Combustion by Solid Fuels. 2. Redox Reaction Kinetics and Product Characterization with Coal, Biomass, and Solid Waste as Solid Fuels and CuO as an Oxygen Carrier

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This paper is the second in a series of two on the investigation of the chemical looping combustion (CLC) of solid fuels. The first paper put forward the concept of the CLC of solid fuels using a circulating fluidized bed as a reactor and Cu–CuO as the oxygen carrier, which was based on an analysis of oxygen transfer capability, reaction enthalpy, and chemical equilibrium. In this second paper, we report the results of the evaluation of the reduction of CuO reduced by solid fuels such as coal and some other “opportunity” solid fuels. Tests on the reduction of CuO by the selected solid fuels were conducted using simultaneous differential scanning calorimetry and thermogravimetric analysis, which simulates a microreactor. An attached mass spectrometer (MS) was used for the characterization of evolved gaseous products. The X-ray diffractometer (XRD) and scanning electron microscope (SEM) were used for the characterization of the solid residues. Results strongly supported the feasibility of CuO reduction by selected solid fuels. CuO can be fully converted into Cu in a reduction process, either in a direct path by solid fuels, which was verified by MS analysis under a N₂ atmosphere, or in an indirect path by pyrolysis and gasification products of solid fuels in the reducer. No Cu₂O exists in reducing atmospheres, which was characterized by an XRD analysis and mass balance calculations. No carbon deposit was found on the surface of the reduced Cu, which was characterized by SEM analysis. CuO reduction by solid fuels can start at temperatures as low as approximately 500 °C. Tests indicated that the solid fuels with higher reactivity (higher volatile matter) would be desirable for the development of the chemical looping combustion process of solid fuels, such as sub-bituminous Powder River Basin coal and solid waste and biomass.

1. Introduction

In the first paper of this two-part series, the theoretical framework of the chemical looping combustion process (CLC) of solid fuels was established on the basis of an analysis of the process, as well as the oxygen transfer capability, reaction enthalpy, and chemical equilibrium of oxygen carriers. Results indicated that Cu-based, Ni-based, and Co-based oxygen carriers should be the optimum oxygen carriers for the development of the CLC of solid fuels. However, Cu-based oxygen carriers are the only ones that may make the reducer self-sustaining on heat, or autothermal, with characterization of the exothermic enthalpy in its reduction process. This will be beneficial to simplify the reducer operation. The tendency toward the agglomeration of Cu-based oxygen carriers can be eliminated by decreasing the operating temperature because of their high reactivity at the interested temperature range in the reducer (600–900 °C) in the previous studies.^{1–4}

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(1) Ishida, M.; Yamamoto, M.; Saito, Y. Experimental Works on Innovative Chemical-looping Combustor. *ECOS'99, Proceedings of the International Conference on Efficiency, Costs, Optimization, Simulation and Environmental Aspects of Energy Systems*, Tokyo, Japan, June 8–10, 1999; pp 306–310.

(2) Mattisson, T.; Janders, 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.

Thus, in the second part of this series, we focus on reduction kinetics and the mechanism and morphology of reaction products of the selected Cu-based oxygen carrier. Coal and some “opportunity solid fuels” such as solid waste and biomass were evaluated for their reduction capability on Cu-based oxygen carriers. Tests were conducted by using a simultaneous differential scanning calorimetry and thermogravimetric analysis (DSC–TGA or SDT) as a simulating microreactor. An attached mass spectrometer (MS) was used for the characterization of gaseous products. The morphology and chemical properties of the reduced product were characterized using an X-ray diffractometer (XRD) and a scanning electron microscope (SEM).

2. Experimental Section

2.1. Preparation of Test Samples. In this study, sub-bituminous Powder River Basin (PRB) coal was selected as a model coal sample. Wood and low-density polyethylene (PE) were selected to simulate two fuels of opportunity, biomass and municipal waste, respectively. The proximate and elemental analyses of tested solid fuels are shown in Table 1. All solid fuel samples were ground

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Table 1. Approximate and Elemental Analysis of the Solid Fuels Used in the Study

	PRB coal	wood	PE
moisture (as received basis), %	26.6	7.01	0.05
ash (as received basis), %	5.18	0.29	0.02
volatile matter (as received basis), %	32.0	76.1	99.8
heating value (as received basis), kJ/kg	20 364	18 834	46 553
carbon (dry basis), %	51.04	47.26	84.80
hydrogen (dry basis), %	6.44	6.39	13.83
nitrogen (dry basis), %	0.70	0.01	0.05
oxygen (dry basis), %	36.35	46.00	1.21
sulfur (dry basis), %	0.29	0.05	0.10
chlorine, ppm	137	N/A	N/A

under atmospheric conditions, sieved into particles with a size fraction of 50–150 μm , and stored in a sealing bottle. The CuO sample was directly from the manufacturer—Fisher Scientific—with a purity of 99.9%. Its size fraction was also in the range of 50–150 μm . For handling the mixture of solid fuels and CuO, a mixture of 10–50 mg was prepared before each test began according to the desired ratio.

The mixed ratios were dependent on the mass balance of solid fuels and the selected oxygen carrier, as shown in Table 2 for the CLC system with PRB coal as solid fuels. Mass balance calculations indicated that, if 1 kg/h of PRB coal is fed into the reducer with the designed facility's thermal capacity of 5.6 kW, the recycling of CuO can be 5.56 kg/h in the reducer and 4.44 kg/h for Cu in the oxidizer. Other operating parameters included the air feeding rate in the oxidizer at 4.06 N m³/h, the purified CO₂ streamflow rate at 0.70 N m³/h, and the ash separated from the oxygen carrier at 0.05 kg/N m³. The chemical stoichiometric ratio (by weight) of PRB coal to the total mixture (PRB coal + CuO) should be about 15.5:84.5%. Considering the gas–solid contact mode in the SDT, the mixture ratios of CuO with PRB coal were determined to be 75:25%. Similarly, the mixture ratios of CuO with wood and PE were determined to be 75:25% and 90:10%, respectively. These samples were thoroughly mixed with CuO to investigate their reduction performance to build up the technical feasibility of the chemical looping combustion of solid fuels.

2.2. Experiments and Instrumentation. Tests were conducted using SDT, which simulates a microreactor. An attached MS was used for the characterization of gaseous products. XRD and SEM spectroscopy were used for solid characterization. The samples of solid residues, which were subjected to the XRD analysis, came from tests in a fixed bed setup to obtain samples with the amount required by the XRD instrument.

2.2.1. SDT. Samples of approximately 10–50 mg were placed in a ceramic pan in an SDT 1960 V3.0F instrument from TA Instruments and heated from ambient temperature at 10–100 °C/min to a range of 800–900 °C. The experiments were carried out in ultrahigh purity (UHP) CO₂ or UHP N₂. 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), and the corrected heat flow of the reaction (w/g).

2.2.2. TGA–MS. A TA Instruments model 2950 TGA equipped with an evolved gas analysis 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. UHP nitrogen was used as the purge gas for the TGA–MS experiments. Samples were heated to 1000 °C at 100 mL/min at various heating rates around 30 °C/min with some experiments having a 1 h isothermal hold at the end of the heating segment to monitor continued mass loss and species evolution. The MS was operated with scan ranges of 1–300 amu or 1–175 amu. The difference in the scan range caused the total time for the analysis to be cut by almost half—from over 1 min to about 36 s. This allowed more data points to be taken during a given mass-loss event. A calcium oxalate experiment was used to confirm the correct operation of both the TGA and the MS prior to running the samples.

Table 2. Mass Balance Calculation for the Chemical Looping Combustion of PRB Coal

1. The Proximate and Elemental Analysis of PRB Coal (wt)					
carbon, wt	hydrogen, wt	oxygen, 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 (wt)					
hydrogen in moisture		oxygen in moisture		free hydrogen	free oxygen
2.96%		23.64%		3.48%	12.71%
3. Assuming Partial Free H Oxidized by Free O in Coal Through					
2H + O → H ₂ O;					
Thus, Remaining Hydrogen and Carbon on Dry Basis for Reduction of CuO Are as Follows:					
H = 1.90%					
C = 51.04%					
Moles of Carbon and Hydrogen in 1 kg of PRB Coal as Reducing Agents of CuO					
C as reducing agent, kmol			H as reducing agent, kmol		
31.2			13.9		
4. Actual Reactions with Cu–Cu0 Occur as Follows:					
in reducer					
C _{31.2} H _{13.9} + (2·31.2 + 13.9/2)CuO → (2·31.2 + 13.9/2)Cu + 31.2CO ₂ + (13.9/2)H ₂ O					
in oxidizer					
(2·31.2 + 13.9/2)Cu + [(2·31.2 + 13.9/2)/2]O ₂ + [3.75(2·31.2 + 13.9/2)/2]N ₂ → (2·31.2 + 13.9/2)CuO + [3.75(2·31.2 + 13.9/2)/2]N ₂					
Assuming Extra Air Ratio is 1.1 for Oxidization Reaction of Cu					
in oxidizer					
(2·31.2 + 13.9/2)Cu + 1.1[(2·31.2 + 13.9/2)/2]O ₂ + [3.75(2·31.2 + 13.9/2)/2]N ₂ → (2·31.2 + 13.9/2)CuO + 1.1[3.75(2·31.2 + 13.9/2)/2]N ₂ + 0.1[(2·31.2 + 13.9/2)/2]O ₂					
5. Thus, Mass Flow Streams in Oxidizer and Reducer Are Listed as Follows:					
PRB coal			1.00	kg	
CuO			5.55	kg	
Cu			4.44	kg	
air			4.06	N m ³	
stream 1		N ₂	3.20	N m ³	
at oxidizer outlet		O ₂	0.08	N m ³	
stream 2		CO ₂	0.70	N m ³	
at reducer outlet		H ₂ O	0.16	N m ³	
ash discharge			0.05	kg	

2.2.3. XRD. A THERMO ARL X'TRA X-ray diffractometer using Cu K 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° from 20 to 90°. The XRD patterns are identified using a database of over 80 000 inorganic compounds. Because the amounts of solid residue samples were required by gram level, a small fixed bed facility was applied to produce solid residue samples, which were subjected to the XRD analysis.

2.2.4. SEM. The reaction residue samples were prepared by being doped onto carbon tape. The SEM analysis was performed using a JEOL LSM-5400 SEM. The instrument operating parameters were as follows: electron beam energy, 15 keV; working distance, 30 mm; and sample tilt angle, 0°. In most cases, two magnifications at 200 \times , 500 \times , 2000 \times , and 10 000 \times were selected to be analyzed.

3. Test Results and Discussion

3.1 Thermodynamics of Chemically Pure CuO. **3.1.1. Tests by SDT at Different Atmospheres and Determination of the Phase Diagram.** For the chemically pure CuO sample, as the

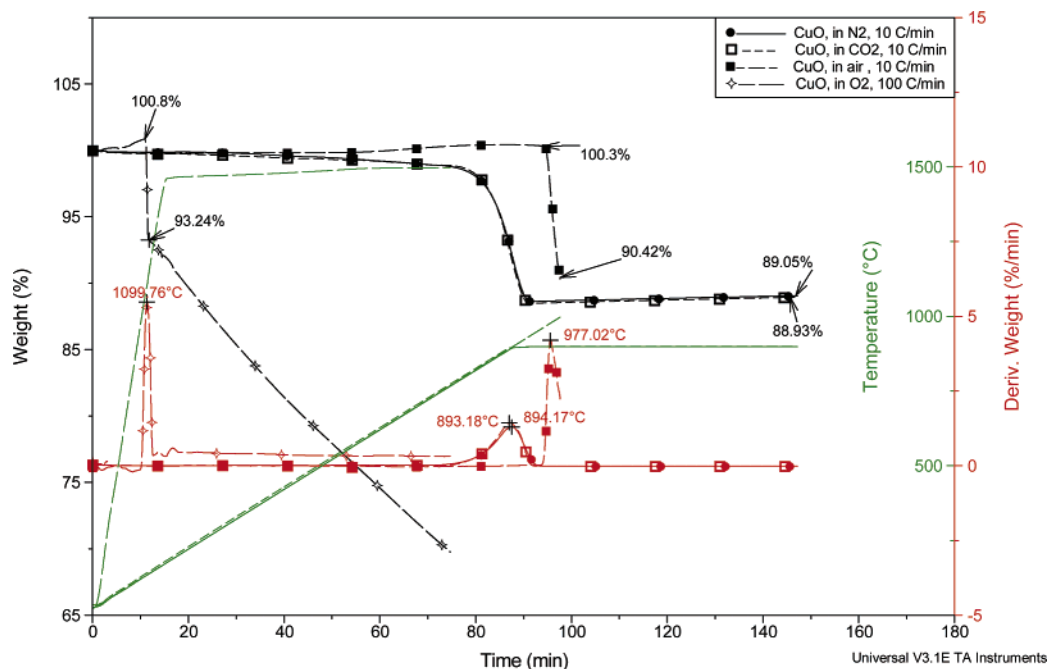


Figure 1. Weight loss history of a chemically pure CuO sample in different atmospheres (N₂, CO₂, air, and O₂).

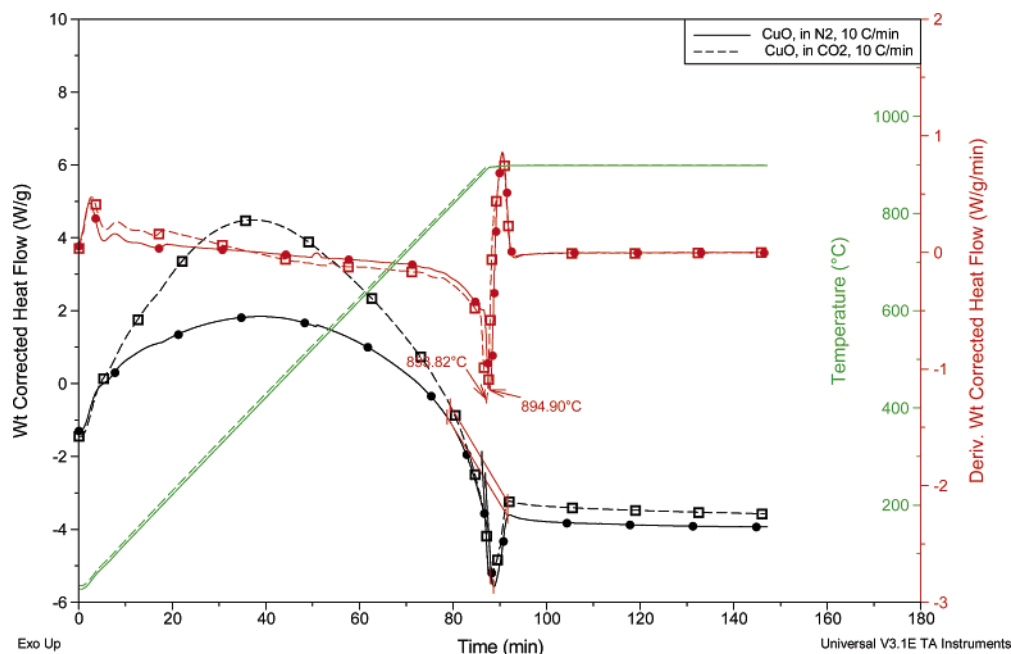


Figure 2. Corrected heat flow history of a chemically pure CuO sample in different atmospheres (N₂, CO₂, air, and O₂).

temperature increases, starting at ambient temperature in the SDT tests, the only peak for weight loss was found at about 893 °C in a N₂ atmosphere and about 894 °C in a CO₂ atmosphere, as shown in Figure 1. 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 2 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 eq 1 at 900 °C.



Chemical calculations indicate that 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 because of its endothermic properties. As shown in Figure 1, the weight loss peak of chemically pure CuO was shifted to about 997 °C in an ambient 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 because of the higher heating rate used in the SDT tests; thus, the decomposition temperature and weight loss temperature of CuO could not be accurately determined in this study. A phase diagram with the corrected O₂ partial pressure and decomposition temperature is shown in Figure 3. This diagram shows the transformation of the CuO–Cu₂O system in inert and oxidizing atmospheres. In Figure 3, the equilibrium line divides the 2D area into two zones and correlates the temperature with the oxygen partial pressure.

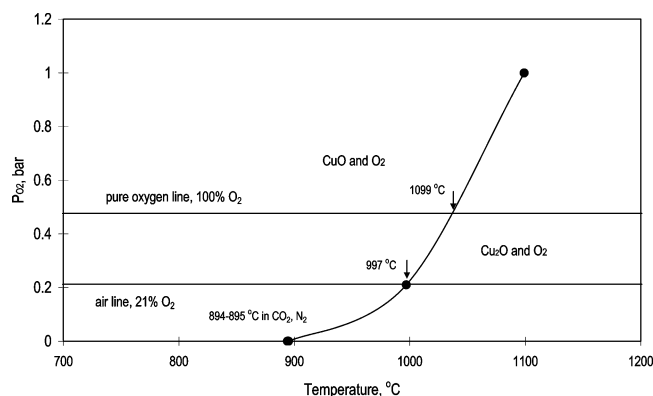


Figure 3. Phase diagram for CuO, Cu₂O, and O₂ (P_{O_2} – temperature).

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_{O_2} . 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. This phase diagram showed, at least in theoretical thermodynamic calculations, the possibility of eq 1 occurring with the production of Cu₂O in the reducer and CuO as the only oxidation product, both under ambient pressure and at the temperature range of interest of 800–900 °C.

3.1.2. Characterization of SEM–Energy Dispersive X-ray (EDX) and XRD. SEM images of chemically pure CuO at different temperatures are shown in Figure 4a and b. At the ambient temperature, as shown in Figure 4a (a-1 and a-2), the

CuO sample was widely packed with dimensions from 1 to 3 μm . Pure CuO particles look like fish scales under smaller magnifications ranging from 500 \times to 2000 \times . As SEM magnification increases, the CuO looks more like a rod with a clear boundary. SEM images of chemically pure CuO samples change morphology after being treated at 900 °C for 1 h in CO₂, as shown in Figure 4b (b-1 and b-2) at different magnifications. The pure CuO particles lose their original rodlike shape at high temperatures, being replaced by a solid block with holes inside. However, they almost keep their original size under treatment. The XRD test gave clear evidence that there were Cu₂O particles existing in the solid residue samples as chemically pure CuO was subjected to higher temperatures, as shown in Figure 5-2.

3.2. CuO Reduction by Coal (PRB Coal). The PRB coal used in this study is a sub-bituminous coal with higher moisture and volatile contents, as shown in Table 1. The TG weight loss curve for this coal is shown in Figure 6. Typically, there are three peaks shown in the curve as the temperature rises to 800 °C in a CO₂ atmosphere. The first large peak represents a moisture loss of 19% at a temperature of 138 °C. The second peak comes at 459 °C with a weight loss of approximately 25%, which is attributed to the partial pyrolysis process of some volatile materials. The last peak appears at 830 °C with a weight loss of about 50%, corresponding to the combined pyrolysis and CO₂ gasification of the fixed carbon of the PRB coal. At the end of the gasification reaction in a CO₂ atmosphere, at a temperature of 850 °C, only ash with a weight content of about 5.8% is left. Tests indicate that the PRB coal has higher gasification reactivity.

For the mixture samples of PRB coal with CuO (ratio 75: 25%) in N₂ and CO₂ atmospheres, the first two weight loss curves show trends similar to those of the PRB coal alone with three weight loss peaks. Because of the mixture ratio of PRB

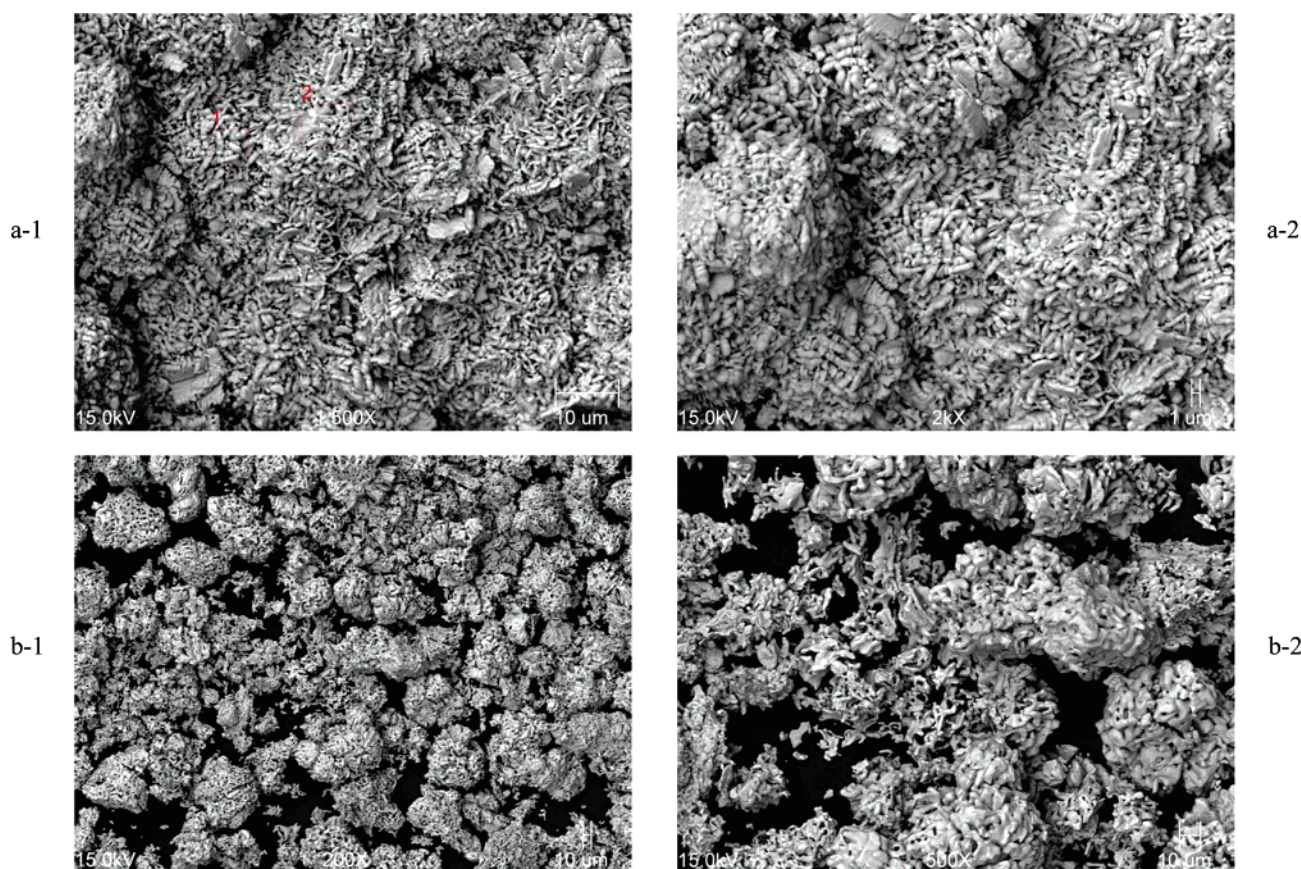


Figure 4. SEM images for example of 100% chemically pure CuO at different temperatures: (a) at atmospheric temperature and (b) at 900 °C.

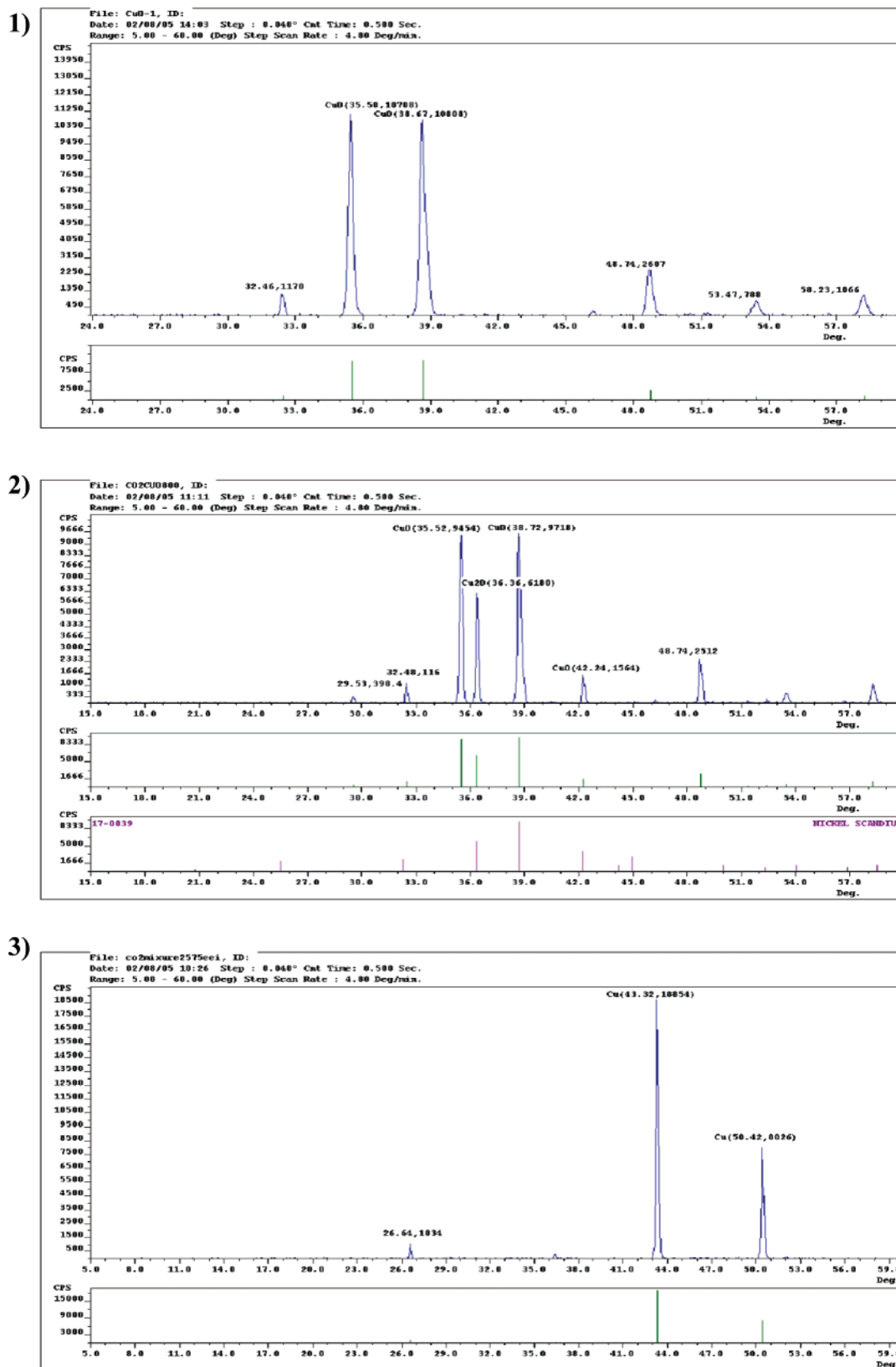


Figure 5. XRD characterization of three solid residue samples: (1) chemically pure CuO sample, (2) reaction product of chemically pure CuO at 800 °C in a CO₂ atmosphere, and (3) reaction product of mixture sample (25% PRB/75% CuO) at 800 °C in a CO₂ atmosphere.

coal and CuO, the mixture sample shows a small peak at the moisture loss stage. However, starting at the partial pyrolysis process (second peak at about 460 °C), the weight loss peaks in the mixture samples become larger. The second peaks from the mixture samples approach the peak of the coal by itself, and the third peaks (at about 800 °C) are even larger than that

of the coal sample. This indicates that CuO reduction can occur 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 alone. The reduction of CuO appears to occur quickly and thoroughly. The tests also indicate the improvement of the char

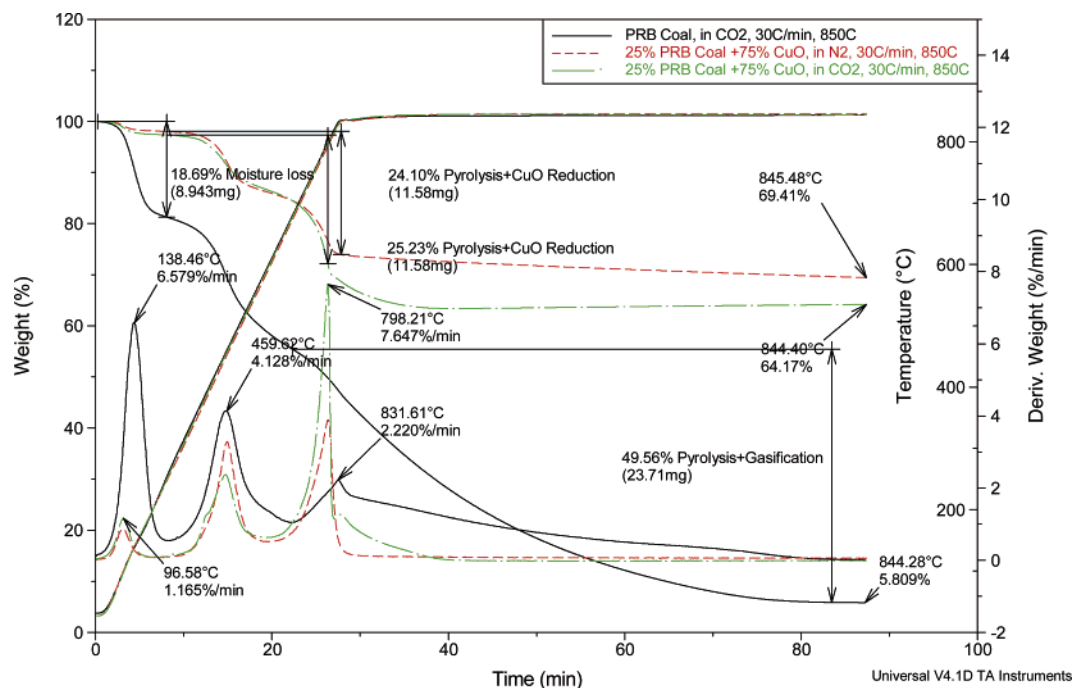


Figure 6. Weight loss curves for PRB coal and mixed samples of PRB coal and CuO in carbon dioxide and nitrogen atmospheres with a temperature ramp of 30 °C/min to 850 °C by SDT.

gasification reactivity by coupling with the CuO reduction, because of the fact that its products are consequently and continuously used for the reduction of CuO.

At the end of the reduction reaction of the mixed samples, about 69% and 64% of the solid residues are left in the N₂ and CO₂ atmospheres, respectively. Stoichiometric calculations show that more than 85% of the CuO has been reduced in the CO₂ atmosphere. A smaller reduction conversion of CuO of 55% is found in the nitrogen atmosphere, probably because of some fixed carbon not being gasified in the N₂ atmosphere to continue supporting the quick CuO reduction reaction by a gaseous reducing agent, assuming that the reactivity of CuO reduction by fixed carbon in coal is lower. This indicates that the gaseous products of the pyrolysis and gasification process should be the major reducing agents for the reduction of CuO in the CLC process and the dominant reduction reaction path should be the gas–solid reaction between gaseous reducing agents and CuO. The improvement of the gasification reactivity may be attributed to the more developed pore structure and specific surface area caused by moisture loss and fast pyrolysis processes, and also the reactivity of PRB coal itself. PRB coal seems to be the optimum solid fuel type for developing the CLC system for solid fuels.

3.2.1. Heat Flow Analysis of the Reduction Process. Corresponding to three thermal decomposition peaks in the TG curves, three heat flow curves (DSC curves) are shown in Figure 7 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 that the reduction of CuO occurs because of its exothermic property and that the heat released by the 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 this study, because CuO can be used as the oxygen carrier to compensate for the heat needed for the endothermic coal gasification reaction.

3.2.2. XRD Characterization of Solid Residues. The 2 θ angles of chemically pure materials of CuO, Cu₂O, and Cu are listed in Table 3 to distinguish different Cu species in the samples.

The XRD characterization of the solid residues from a 15 min reaction of the mixed sample (PRB coal + CuO) in a CO₂ atmosphere at 800 °C in a fixed bed setup was compared to the chemically pure CuO at ambient pressure and 800 °C and is shown in Figure 5. The strong Cu peaks were identified at 2 θ peaks of 43.3° and 50.4° with a relative intensity close to the chemically pure Cu for the mixed sample (PRB coal + CuO) under a CO₂ atmosphere at 800 °C. There are no peaks found either at 36.4° and 42.3° or at 35.5° and 38.7°, which indicates that there is no Cu₂O, which is in agreement with the SDT results. Also, there is no CuO in the residue sample. This implied that CuO can be totally reduced by the PRB coal in a CO₂ atmosphere even at the shorter reaction time at the lower temperature of 800 °C in the fixed bed setup.

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 (lower heating rate). The reactivity and conversion rate of CuO reduction by a PRB coal, which is inexpensive, readily available, and has lower sulfur and chlorine contents, would be very practical in the CLC process for solid fuels.

3.2.3. SEM–EDX Characterization of the Solid Residue from the Mixed Sample at 850 °C. The SEM images of the mixture sample at different magnifications after being treated at 850 °C in a CO₂ atmosphere are shown in Figure 8. The image of the reaction residue at lower magnifications is very similar to that of the CuO sample, which was treated in a CO₂ atmosphere at

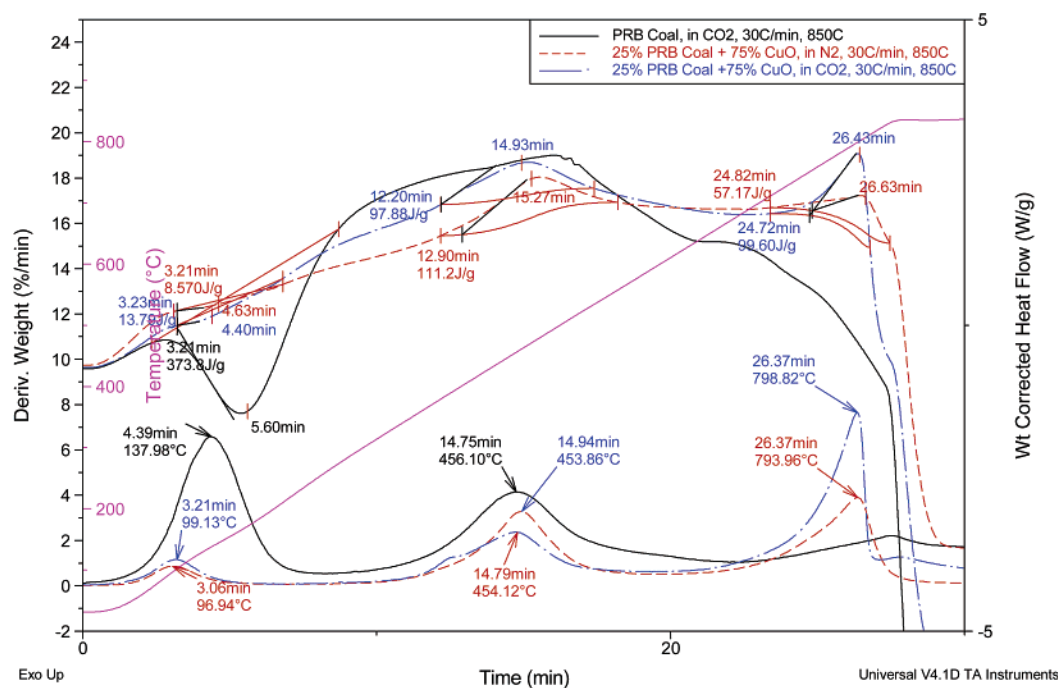


Figure 7. Heat flow curves for the PRB coal and mixture samples of PRB coal and CuO in carbon dioxide and nitrogen with a temperature ramp of 30 °C/min to 850 °C by SDT.

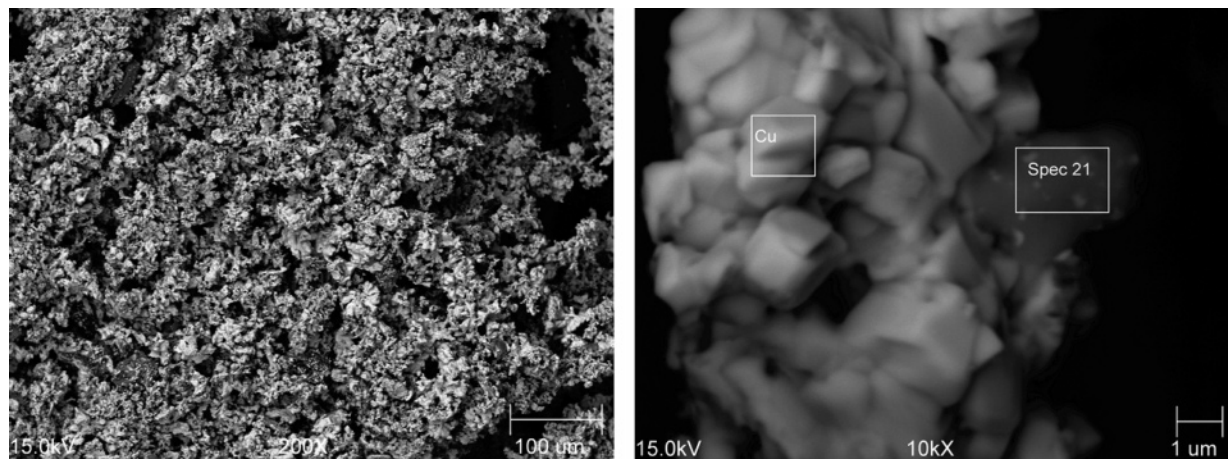


Figure 8. SEM images for the mixed samples of PRB coal and CuO at 850 °C in a CO₂ atmosphere.

Table 3. XRD Spectral Data of Cu Species 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

the same temperature condition, as shown in Figure 4b. Some melted spots were observed in the images at higher magnifications, but not severe. Several sites with different degrees of darkness and brightness were selected for EDX analysis. 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 after searching the whole image.

3.2.4. TGA–MS Characterization—Mechanisms of the CuO Reduction Reaction by Coal Char. In the TGA–MS experiments, evolved gases from the TGA tests were sent through a heated transfer line to a mass spectrometer for the 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 three m/z values—28, 14, and 29. It should be noted that some gaseous species of interest have the same mass-to-charge numbers. The TGA–MS results for the mixture samples in a N₂ atmosphere and heated at 10 °C/min to 850 °C are shown in Figure 9 as 2D spectra of the intensity with respect to time. Validation of the TGA–MS tests was confirmed using a standard material of calcium oxalate, which produces three peaks corresponding to evolved gases of H₂O, CO, and CO₂ under conditions similar to those of the following mixed sample test.

Only one MS peak was found for the mixed sample in a N₂ atmosphere, which corresponded to the major peak from the differential thermogravimetry (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 values of 16 and 12, which correspond to the peak for CO with the same m/z . Normally, $m/z = 28$ would be used to

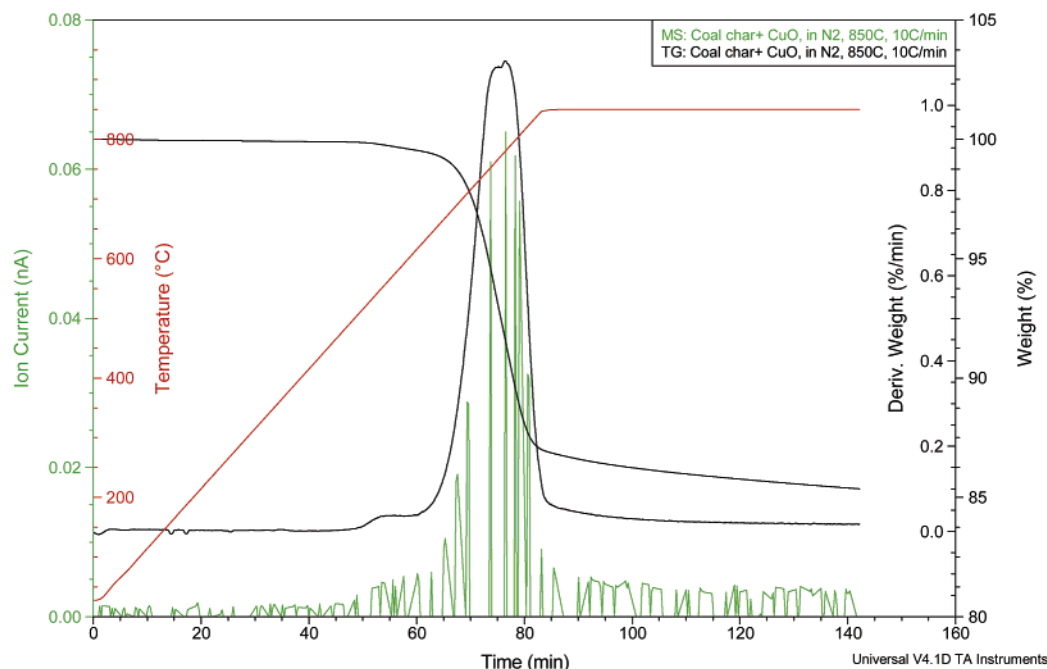


Figure 9. Test results for the mixed sample of coal char and CuO to determine weight loss by TG and evolved gases by mass spectra in a N_2 atmosphere.

monitor CO evolution, but because the carrier gas of N_2 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 CO_2 for the reaction in a CO_2 atmosphere because of the strong background and corresponding ion current (A) from the carrier gas, CO_2 . The TGA–MS tests in N_2 strongly support the possible occurrence of the direct reduction of CuO by coal char with onset temperatures as low as 500 °C.

Combined with the previous SDT tests in N_2 and CO_2 atmospheres for the individual coal samples and also the mixed samples, it was indicated that coal char gasification had an onset at low temperatures (about 500 °C) and the reduction of CuO may occur by interaction with coal char and gaseous pyrolysis products simultaneously, as shown in eq 2. As the temperature increases, the reactivity of char gasification improves and the gaseous gasification product, CO, becomes the main reducing agent for CuO. Thus, reactions 3 and 4 should reasonably dominate the CuO reduction process at higher temperatures. Because of the fast heating rate in industrial facilities (hundreds of degrees per minute), CuO reduction by coals in an industrial facility will occur under higher temperatures at a 99% period of residence time. Thus, reactions 3 and 4 present the dominating process occurring in the reducer.



3.3. CuO Reduction by Other Solid Fuels (PE and Biomass). 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 of solid fuels. In this study, two types of “opportunity fuels”, wood and PE,

were selected as model samples of solid fuels to evaluate their utilization potential in the developing CLC process.

3.3.1. CuO Reduction by Solid Waste—PE. The volatile material content in the low-density PE sample (chemically pure) was 99.8%. Correspondingly, the total weight loss was 99.7% in a N_2 atmosphere, which was very close to its proximate analysis, as shown in Figure 10. The DTG peak temperature and its onset of weight loss temperature were approximately 470 °C and 370 °C, respectively. The maximum rate of weight loss was 24.6%/min in a N_2 atmosphere. Because of the release of CO_2 in the PE pyrolysis process, the onset of weight loss in a CO_2 atmosphere was slightly delayed when compared to the weight loss in N_2 . However, the weight loss in CO_2 reached its peak at 459 °C—faster than that in N_2 because of 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.

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 because of the reasons mentioned previously. The DTG curve did not reach a zero value between peaks, which implies that two different processes occurred in the mixed samples in both N_2 and CO_2 atmospheres and that they overlapped. The first peak in the DTG curve should be attributed to the pyrolysis of PE, and the second peak should be attributed to the pyrolysis of PE with the simultaneous reduction of CuO in the mixed sample. The fact that the mixed sample proceeded faster in CO_2 may be explained by the fact that gaseous reducing agents, which are the result of the gasification process by CO_2 , have more reduction capability. Both peaks for the mixed samples evolve at a lower temperature than those of pure PE samples in the same atmosphere because of the reversible nature of the CuO reduction reaction.

In both atmospheres, the total weight loss from the mixed sample of PE was about 37.8%, which was close to 100% of the theoretical conversion efficiency of the CuO reduction in a mixture ratio of 10:90% of PE to CuO. In this case, test results

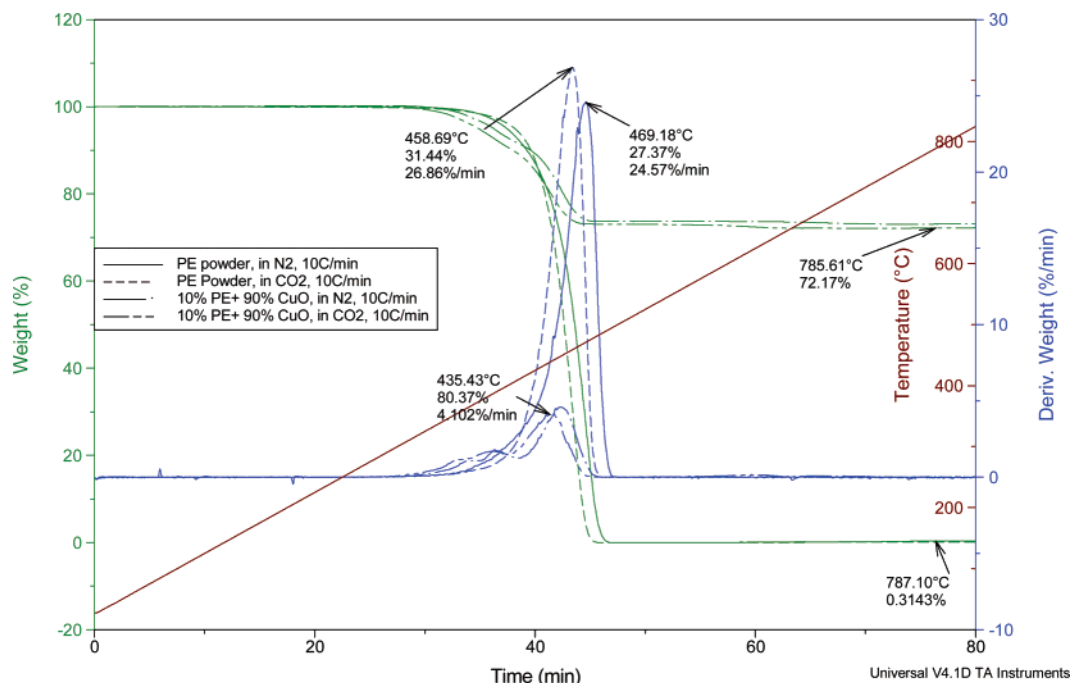


Figure 10. Weight loss curves of the PE sample and the mixed sample of PE and CuO in nitrogen and carbon dioxide atmospheres with a temperature ramp of 10 °C/min to 850 °C by SDT.

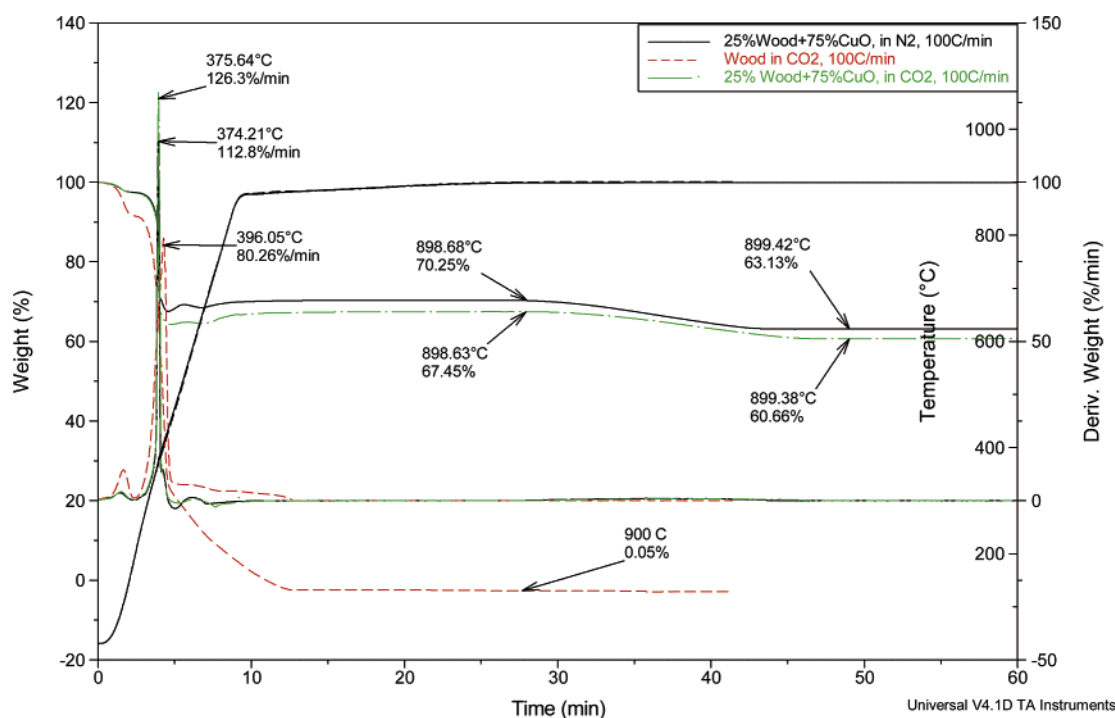


Figure 11. Weight loss curves of the wood sample and the mixed sample of wood and CuO in nitrogen and carbon dioxide atmospheres with a temperature ramp of 100 °C/min to 900 °C by SDT.

showed that there was no Cu_2O species in the reaction products—Cu was the only reduction product. The higher reduction conversion efficiency of CuO resulted from the higher reactivity of pyrolysis and gasification of PE and also the higher gas—solid contact between the gaseous reducing agent and CuO.

3.3.2. CuO reduction by Biomass—Wood. The volatile material content of the wood was 76.1%. However, the total weight loss was 100% in a CO_2 atmosphere because of further gasification of the fixed carbon by available CO_2 . There was no apparent boundary between the pyrolysis of the volatile material and the gasification of the fixed carbon in the wood

sample, as shown in Figure 11. 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 is always in the range of 500–1000 °C/min. Therefore, test results on wood as a solid fuel 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 the full conversion of CuO was just 5 min and could be lower at a higher heating rate. 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

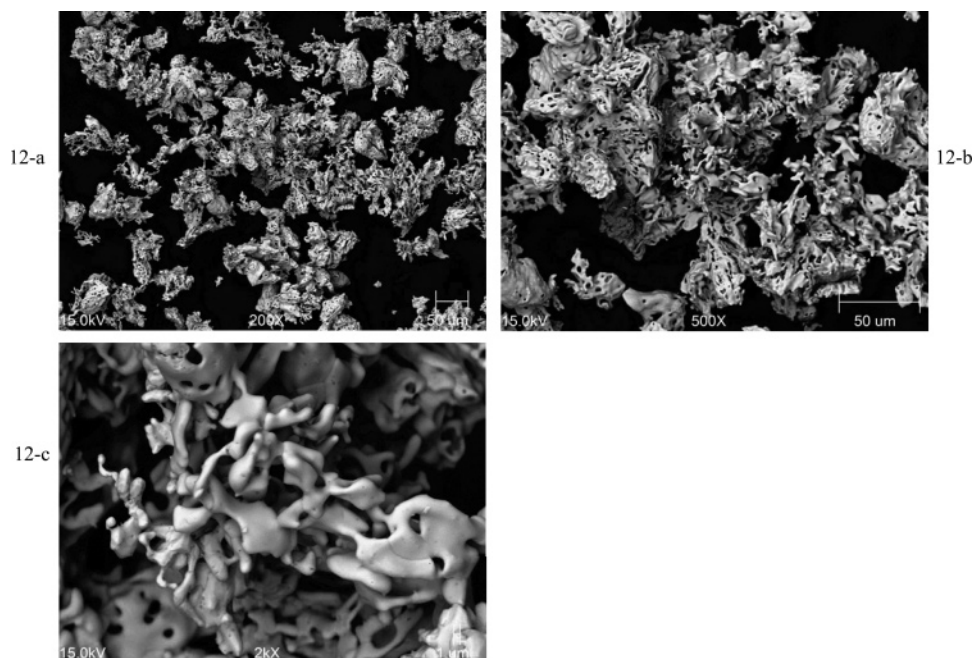


Figure 12. SEM images for the chemically pure CuO and the reaction product of the mixed sample of wood and CuO (25:75%) at 800 °C and under CO₂ conditions.

110%/min, compared with 26.9%/min for the case of PE as a solid fuel. Wood as a model solid fuel shows high reactivity toward the reduction of CuO. All of these results show very attractive and promising opportunities for the utilization of opportunity fuels in the CLC process. In CO₂ atmospheres, the total weight loss from the mixed sample of wood was 40%, which was very close to the 100% theoretical conversion efficiency of the CuO reduction. In this case, there was still no Cu₂O species found in the reaction products—Cu was the only reduction product.

SEM images of the solid reaction products from a mixture of wood and CuO under 800 °C at different magnifications are shown in Figure 12. As shown in Figure 12, at different magnification scales, the dimension of the mixed sample residue was enlarged slightly in some locations, which were so-called hot spots. This implies that the slight melting phenomenon occurred while the test was conducted, although there was a temperature cushion before the melting point of Cu at about 1085 °C. An EDX analysis on the SEM image did not show any evidence of carbon deposits on the Cu produced.

4. Conclusion

Experimental tests on the direct reduction of CuO by the selected solid fuels were conducted using SDT, which simulates a microreactor. The attached MS was used to characterize the evolved gas component. XRD and SEM spectroscopy were used for the characterization of the solid product. The SDT tests and XRD characterization of the solid residue provided evidence that CuO can be fully converted into Cu in a reduction process, either in a direct path by solid fuels, which was verified by a MS analysis under a N₂ atmosphere, or in an indirect path by

pyrolysis and gasification products of solid fuels in the reducer. There is no evidence to show that Cu₂O exists in reducing atmospheres. CuO reduction by gaseous reducing agents can start at lower temperatures, approximately 500 °C. No carbon deposit was found on the surface of the reduced Cu, which was characterized by SEM analysis. Tests indicated that the solid fuels with characteristics of high volatile matter and a high reactivity of the char produced would be desirable for the chemical looping combustion process. Results strongly supported the feasibility of the chemical looping combustion process for selected solid fuels, such as sub-bituminous PRB coal, biomass, and solid wastes.

The actual reduction reactivity of CuO by a PRB coal should be much higher 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 at higher heating rates. It is apparent that the reactivity of the CuO reduction using PRB coal is comparable to that using biomass as a solid fuel. PRB coal is inexpensive, readily available, and has lower sulfur and chlorine contents. Thus, the use of PRB coal, biomass, and other solid wastes shows promise in the development of the chemical looping combustion of solid fuels.

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