Chemical-Looping Combustion of Coal

with Metal Oxide Oxygen Carriers

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INTRODUCTION

Chemical looping combustion (CLC) has been suggested as an energetically efficient method for producing high-purity CO_2 from combustion of fuel gas. This is an entirely new combustion technology, which involves the use of a metal oxide as an oxygen carrier that transports oxygen from the air to the fuel, avoiding direct contact between fuel and air.

The CLC system is composed of two reactors, an air and a fuel reactor. In the fuel reactor, the fuel in the gaseous form reacts with the metal oxide.

$$\text{Fuel} + \text{Metal oxide} \rightarrow CO_2 + H_2O + \text{Metal or reduced form of metal oxide} \quad (1)$$

In the air reactor, the metal or a reduced form of metal oxide is oxidized to form metal oxide.

$$\text{Metal or reduced form of metal oxide} + O_2 \rightarrow \text{Metal oxide} \quad (2)$$
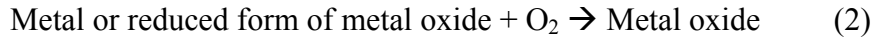
The regenerated metal oxide is ready to initiate a second cycle. The exit gas from the fuel reactor contains CO_2 and H_2O and after condensation of the water produces a pure CO_2, which can be utilized for sequestration. The significant advantage compared to normal combustion is that concentrated CO_2 not diluted with N_2 is obtained in a pure state without expending any major energy required for separation. This could enable combustion devices that produce thermal energy with CO_2 inherently ready for geological sequestration.

It is important to note that the heat of reaction of both reactions (1) and (2) must be equal to the normal combustion heat of reaction between the fuel and oxygen. However, depending on the choice of metal/metal oxide, it is possible that one of the reactions can be endothermic. In a practical application, this means that heat must be

transferred from the exothermic reactor to sustain the endothermic process. This can be accomplished, for example, by using the heat capacity of the circulated metal to carry heat between the reactors, and will be mentioned later.

Only a few studies[1-3] have been conducted on the combustion of solid fuels such as coal. There are many challenges associated with direct CLC of coal using oxygen carriers. The oxygen carrier should have sufficient rate suitable for various reactor systems, sufficient oxygen release capacity facilitating the coal-oxygen carrier interactions, stable reactivity during multiple cycles, high attrition resistance, and low reactivity with ash and other contaminants.

In the present work, various metal oxides—CuO, Fe_2O_3, NiO, Mn_2O_3 and Co_3O_4— were tested as oxygen carriers for direct combustion of coal in the presence of either nitrogen or CO_2. Thermo gravimetric analysis (TGA) was used to determine the rates of reaction and percentage of combustion/oxidation. The calculations of the amount of solid that will be required for designing a large-scale unit will also be discussed.

EXPERIMENTAL

TGA experiments were conducted in a Thermo gravimetric Analyzer (TA Model 2050). Illinois #6 coal was used in this study with particle size of 100 microns. The composition of coal (proximate analysis data) is listed in Table 1.

Table 1: Composition of coal

	Concentration (%)
moisture	7.44
Volatiles	37.97
ash	12.45
H	4.63
C	67.32
N	1.3
S	4.81
O	9.49

The coal was mixed with metal oxides (dry mixing) and the weight ratio was about 0.2 grams of coal to 3-4.5 grams of metal oxide, which corresponds to a volume ratio of metal oxide to coal of about 2.6-3.5 to 1. Thus, excess metal oxide was used in these early studies. Future work will define minimum stoichiometries needed for complete combustion. About 200 mg of the coal/metal oxide mixture was heated in a quartz bowl from ambient to 900-1000 $^{\circ}$C at a heating rate of 15 $^{\circ}$C/min in either pure nitrogen or pure CO_2 at a flow rate of 40 sccm. The sample then was kept isothermal at either 900 or 1000 $^{\circ}$C for about 80 minutes; afterwards, air was introduced at 40 sccm for about 40 minutes.

The fractional conversions (fractional reduction and fractional oxidation) were calculated utilizing the TGA data. The fractional conversion (X) is defined as

$$\text{Fractional Reduction } (X_r) = (M_o - M)/(M_o - M_f)$$

$$\text{Fractional Oxidation } (X_o) = (M - M_f)/(M_{oxd} - M_f)$$

M = *Instantaneous weight of metal oxide-coal mixture at a given time*

M_o = *Initial weight of metal oxide-coal mixture prior to the reaction*

M_f = *Final weight of metal oxide-coal mixture after reaction in either N_2 or CO_2*

        (i.e., reduced metal + ash + unreacted coal)

M_{oxd} = *Weight of completely oxidized sample after introducing air*

The fractional conversion data as a function of time was fitted to obtain the polynomial regression equation. The global rates of reactions (dX/dt) at different fractional conversions (X) were calculated by differentiating the polynomial equation.

Percentage of combustion and percentage of oxygen uptake were obtained utilizing the weight change data from the TGA using the following equations:

Percent combustion = (actual weight loss of coal from TGA/Theoretical weight of coal in the sample) × 100

Percent oxygen consumption = (experimental oxygen consumption / theoretical capacity of oxygen presenting the metal oxide) × 100

Notice that the percent combustion is defined with respect to the sample test time (80 minutes at 900 or 1000 ^{0}C).

RESULTS AND DISCUSSION

The reaction mechanisms of the coal-oxygen carriers are not well defined. It is reported that the gaseous products from coal pyrolysis may initiate the reaction with oxygen carrier[2]. The major goal of the CLC process is to obtain a concentrated CO_2 stream after the combustion process; therefore, the reaction in the fuel reactor has to be conducted in the presence of CO_2 or possibly steam (followed by water condensation). It is hypothesized that the CO produced by coal gasification by CO_2 may initiate the reaction with the oxygen carrier in the fuel reactor. It has also been reported that the gaseous oxygen released from the oxygen carrier could initiate the reaction at high temperatures.[3] Additional thermodynamic studies have reported that direct metal oxide-carbon interaction is also possible with some metal oxides.[2]

a. Thermo Gravimetric Analysis - Base Line Tests with Coal without the Metal Oxide

Baseline tests were conducted with pure coal utilizing N_2 and CO_2. The TGA data when coal was heated in N_2 up to 1000 $^{\circ}$C are shown in Figure 1. A small peak starting at 82 $^{\circ}$C corresponds to dehydration of coal. A larger peak starting at 250 $^{\circ}$C with a maximum at 435 $^{\circ}$C is also observed. This indicates that the coal de-volatilization was initiated at 250 $^{\circ}$C with the maximum rate at 435 $^{\circ}$C. The weight loss due to coal de-volatilization in N_2 was about 45% and no additional weight losses were observed during the heating process in N_2. This weight loss matches the specified volatile matter from the coal proximate analysis as shown in Table 1.

**Figure 1: TGA Profile of Coal in N_2 without Metal oxide**
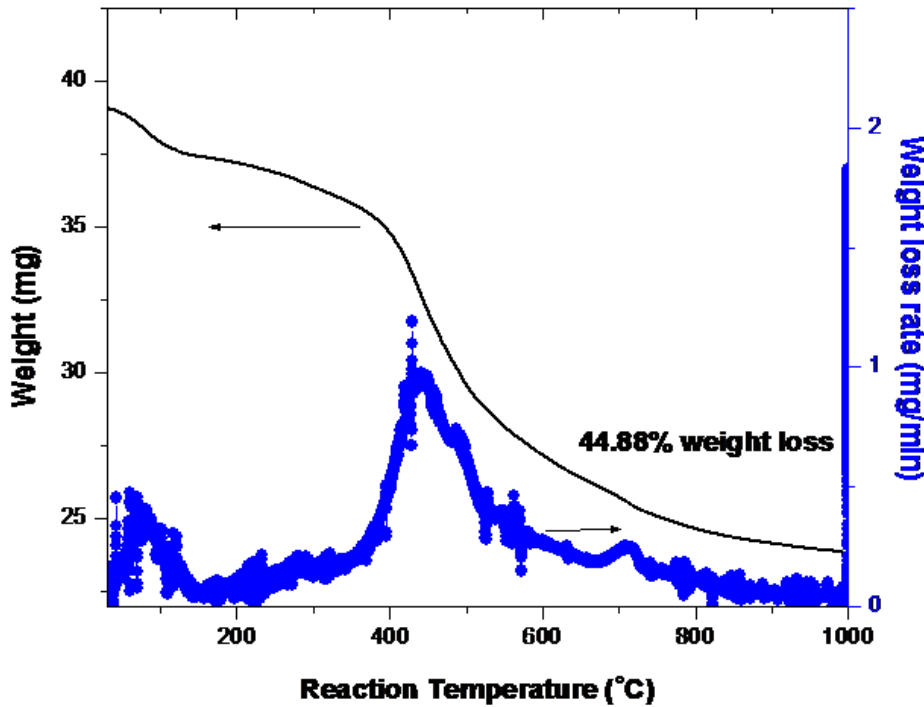
Additional weight loss of 55% due to combustion reaction was observed when air was introduced at 1000 $^{\circ}$C subsequent to the N_2 introduction. When coal was heated in CO_2 the weight loss profile and rate data were similar to that with N_2. This indicated that the presence of CO_2 did not have any significant effect on the process.

b. Thermo Gravimetric Analysis – Tests with Coal and Metal Oxides in N_2 and CO_2

The weight loss profile and corresponding rate data of coal-CuO mixture during the heating in N_2 up to 900 $^{\circ}$C is shown in Figure 2. There is a continuous weight loss with the coal-CuO sample during the heating process which indicated that the CuO contributed to the combustion of coal after the initial pyrolysis reaction. This weight loss corresponds to 100% coal combustion with CuO in the presence of N_2. The rate data shown in Figure

2 indicated the presence of peaks at 425 $^{\circ}$C and 708 $^{\circ}$C. The major peak at 708 $^{\circ}$C is due

to coal combustion by oxygen from CuO and the coal combustion appears to initiate

around 500 $^{\circ}$C. The outlet CO_2 concentration from the TGA during reaction measured

utilizing a mass spectrometer is also shown in Figure 2.

Figure 2: TGA and Mass Spectral Data for Coal Combustion with CuO
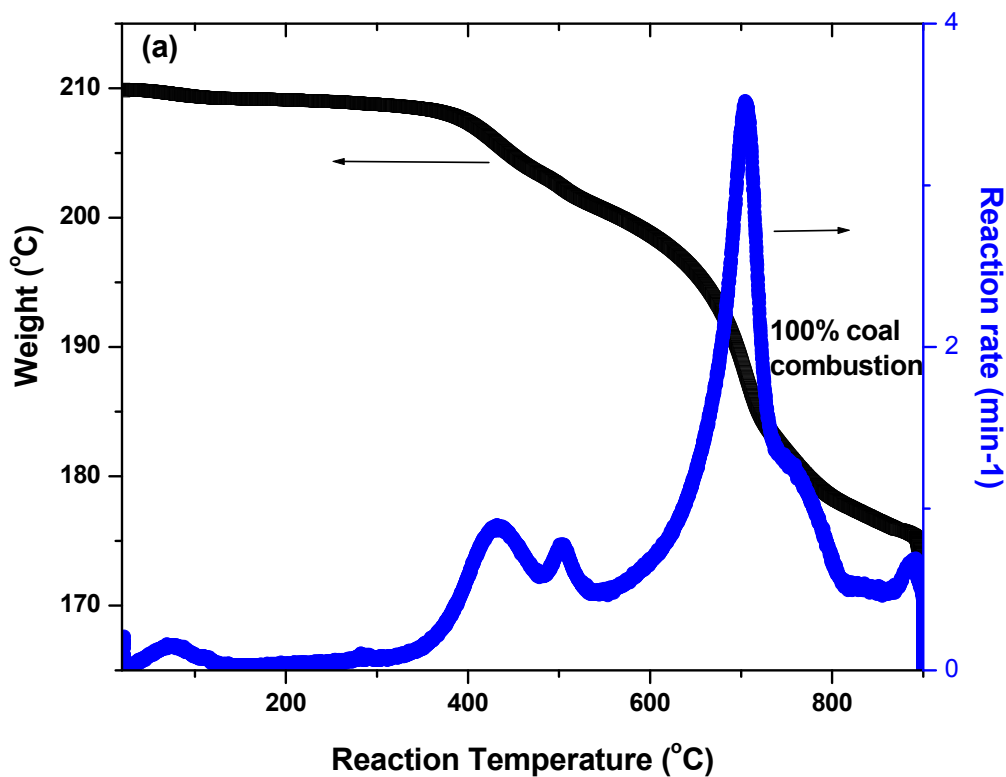
The rate data from the TGA measurements and the outlet CO_2 profile appear to be very

consistent. The TGA data when air was introduced after the reduction reaction with coal-

CuO is shown in Figure 3. A weight gain due to oxidation was observed and reduced

copper was fully oxidized. The rate of oxidation is significantly higher than that for the

reduction reaction.

Figure 3: Oxidation Segment of CuO in Air at 900 °C
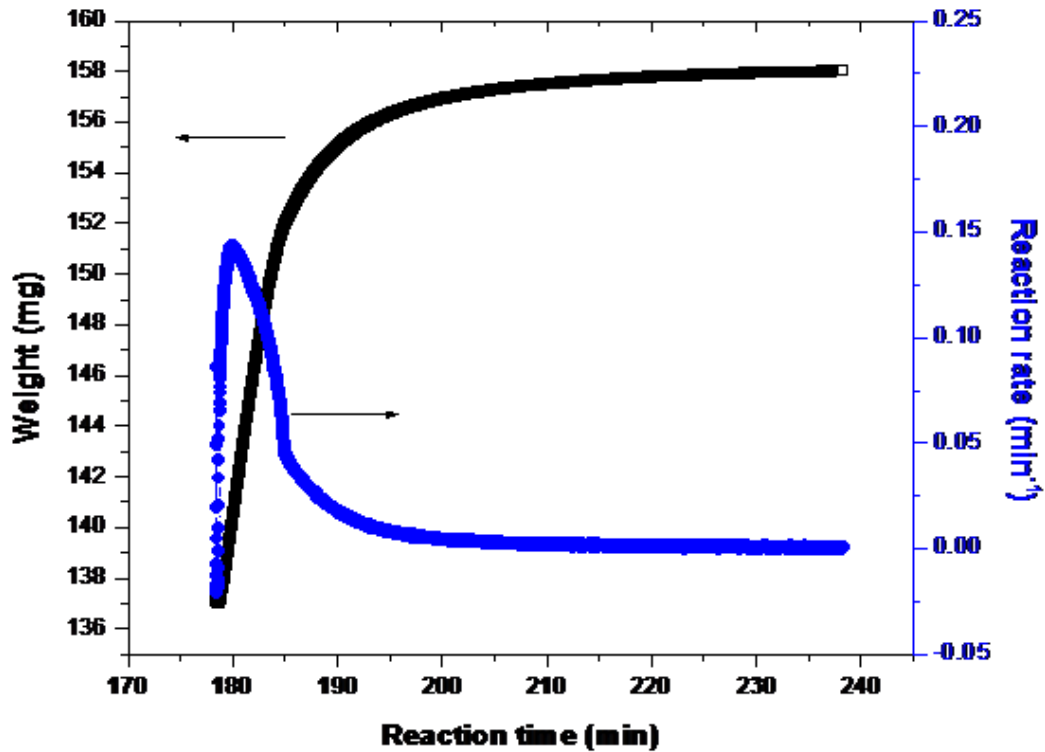
The goal of CLC reaction of coal with metal oxides is to obtain a pure stream of CO_2 after combustion; consequently the combustion reaction of coal with metal oxide should be performed in the presence of CO_2. TGA experiments were also performed with coal and CuO, NiO, Fe_2O_3, Mn_2O_3, and Co_3O_4 in the presence of both N_2 and CO_2; these data are shown in Table 2.

Table 2: Coal-CLC Data of Various Metal Oxides in N_2 and CO_2. Combustion temperature indicates the temperature where the highest combustion rate was observed. Percent combustion is defined with respect to the sample test time (80 minutes at 900 or 1000C)

| sample | gas media | Combustion | | | | Oxidation | | |
		Comb. Temp. (^{o}C)	Comb. Rate (min^{-1})	% combustion	ΔH (kJ/mol)	Oxi. Rate (min^{-1})	oxygen uptake (%)	ΔH (kJ/mol)
CuO	CO_2	703	0.098	100		0.172	98.6	
	N_2	708	0.083	100	-96.5	0.175	99.2	-156
NiO	CO_2	993	0.061	73.05		0.84	77.5	
	N_2	1000	0.017	68.4	75.2	0.82	71.6	-327.7
Fe_2O_3	CO_2	973	0.055	94.9		0.77	93.7 Fe(II)	
	N_2	977	0.05	91.6	79.2	0.78	90.6 Fe(II)	-347.4
Mn_2O_3	CO_2	905	0.011	76.76		0.42	72.2Mn(II)	
	N_2	978	0.01	71	-36.1	0.38	68.3 Mn(II)	-216.4
Co_3O_4	CO_2	781	0.096	83.3		1.74	78.2 Co(II)	
	N_2	781	0.096	83	-8.6	1.74	78.0 Co(II)	-243.9

It is interesting to note that the lowest combustion reaction temperature at 700 $^{\circ}$C and the highest combustion rate were observed for a CuO-coal system. In addition, the combustion reaction with CuO is exothermic (ΔH=-96.5 KJ/mol) which indicates that the heat transfer from the oxidizer to the reducer is not necessary for the reaction to proceed. This is an advantage of the CuO-coal system. The percentage of combustion and oxidation were close to 100% for the CuO which indicated that the complete coal combustion reaction could be obtained with the CuO and reduced copper could be

completely oxidized at 900 $^\circ$C. In the presence of CO_2, the rate of combustion for coal-CuO was slightly higher than that with N_2, but there was no significant effect due to CO_2 for a CuO-coal system.

For Fe_2O_3-coal system, (maximum) combustion rate takes place at a higher temperature (973-977 ^{o}C) than that with CuO. It is possible to achieve about 95% combustion with Fe_2O_3. The percentage of oxidation was about 77 % when the oxidation state change of Fe was assumed to be from Fe(III) to Fe(II) during the CLC reaction. The presence of CO_2 did not have a significant effect on both the reaction rate and the combustion temperature of the Fe_2O_3–coal system.   The heat of the reduction reaction for an Fe_2O_3-coal system is endothermic (ΔH=79.2 KJ/mol) and heat transfer from the oxidizer to the reducer will be necessary for a CLC process with Fe_2O_3, which could be achieved utilizing a heat-carrying inert material, or using the heat capacity of the circulating iron. The combustion rate for Fe_2O_3 appears to be lower than that with the CuO system, but the oxidation rate appears to be higher with Fe_2O_3.

The characteristics of a NiO-coal system were similar to the Fe_2O_3-coal system as shown in Table 1. For NiO-coal the combustion reaction—which is endothermic (ΔH=75.2 KJ/mol)—also takes place at higher temperature of 993 $^\circ$C with a lower reaction rate than that with CuO-coal system. However, for NiO the presence of CO_2 had a significant positive effect on the combustion properties. For Mn_2O_3-coal, the combustion reaction took place at 900 $^\circ$C but showed the lowest combustion rate as compared to that with the other four metal oxides, but the reaction is slightly exothermic (ΔH=-36.1 KJ/mol). The percentage of combustion was similar to that with NiO. For Mn_2O_3, the reduction-

oxidation during the CLC reaction appears to occur between the oxidation states Mn(III) and Mn(II).

The Co_3O_4-coal system appears to be similar to that of CuO with a low combustion temperature of 781 $^{\circ}$C, but the oxidation rate was the highest for the Co_2O_3. The heat of reaction is slightly exothermic (ΔH=-8.6 KJ/mol), yet the percentage of combustion was lower than that with CuO-coal.

From the five metal oxides tested, CuO appeared to have the best combustion characteristics. It had the lowest combustion temperature, highest combustion rate, and highest percentage combustion. The CuO and Cu metals have a lower melting point (~1000 $^{\circ}$C) than other metal oxides. However, the coal combustion reaction with CuO takes place at a lower temperature (700 $^{\circ}$C) than the melting point of copper oxide and may be a potential candidate for the coal CLC process.

An obvious question is determining how solid metal oxide reacts with the solid coal? It may be possible that coal volatiles initiate the reaction between the metal oxide and the solid fuel, with the remaining char gasified by combustion products. However, the coal de-volatilization reaction takes place around 450 $^{\circ}$C and the concentrations of volatile combustion products are very low at the coal combustion temperatures with the metal oxides. As a result, it is not clear whether the volatile combustion products are required to initiate the reaction, and more work is needed to understand the exact mechanism responsible for complete coal combustion.

There are numerous practical issues that must be addressed to develop a complete chemical looping combustion system. Ash separation from the reactor might be accomplished by the density difference between the ash and metal. The quantity, cost,

and durability of the metal oxide are all important considerations. The data presented here are being used to determine which approaches may be successful in a practical device aimed at solid fuel combustion. A key concern is the circulation of hot solids between the reactors. It is helpful to note that existing fluidized catalytic cracking (FCC) reactors have demonstrated significant commercial experience with solid catalyst circulation rates typically 35 tons per minute (or higher), operating with regenerator temperatures of 700C[4].   While the chemical looping process described here is different, the commercial experience of handling large flows of hot solids provides some basis for process development.

CONCLUSIONS

Metal oxides CuO, Fe_2O_3, NiO, Mn_2O_3, and Co_3O_4 showed the ability to provide oxygen for direct combustion of coal. CuO showed the lowest temperature, the highest percentage (100%), and the highest rate for the coal combustion. Reduced Cu metal during the coal combustion can be fully re-oxidized to the copper oxide. The highest oxidation rate was observed with Co_3O_4. Coal combustion reactions with Fe_2O_3, NiO, and Mn_2O_3 took place at higher temperatures (>900 $^{\circ}$C) than that with CuO and Co_3O_4. The presence of CO_2 had a significant positive effect on the coal combustion reaction with NiO. A process of direct coal combustion may be feasible with metal oxides, but it will be necessary to develop an efficient solid circulation process and an ash/metal-oxide separation process. Ash generated during the reaction has a lower density than that of metal oxides and can be separated utilizing density separation.

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