Application of a Circulating Fluidized Bed Process for the Chemical Looping Combustion of Solid Fuels

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Introduction

In recent years more concerns have arisen about CO_2 emission due to global warming. Among available or proposed technologies, chemical looping combustion[1] (CLC) is the most promising technology to combine fuel combustion and CO_2 purification. It uses a solid oxygen carrier to transfer the oxygen from the air to fuel in a reducer and oxidizer. Thus, air is never mixed with the fuel, and the CO_2 does not become diluted by the nitrogen of the flue gas. NO_x formation can be largely eliminated. A number of metals have been discussed in the literature,[2] such as oxides of Fe, Ni, Co, Cu, Mn.

Solid fuels such as coal and biomass have been ignored in CLC process due to technical problems, including the separation of oxygen carrier from fuel and ash, the possible interaction between the fuel ash and oxygen carriers and the combustion of unburned carbon particles in the oxidizer due to the circulation of solid fuel particles. The adaptation of the CLC to the combustion of solid fuels presents many challenges.

In this paper, an innovative concept – application of a CFB combined with a moving bed on the chemical looping combustion of solid fuels is introduced.

Technical Approach

Is it possible to add solid fuel into a reducer directly? There exist several technical difficulties. The reaction rate between solid fuel and the oxygen carrier is slow for a solid fuel due to low solid-solid contact efficiency and reactivity. The solid fuel gasification rate is always 1000 times slower compared to combustion at the same evaluated temperature.

In order to overcome the technical difficulties mentioned, it is proposed that a CFB coupled with a moving bed be used for the chemical looping combustion of solid fuels. In this approach, the facility will consist of three major components – a high-velocity riser acting as an oxidizer, a down-flow moving bed acting as a gasifier and a low-velocity bubbling 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 two loop seals for oxygen carrier circulation.

Kinetic Analysis. The CLC process is governed by the prevailing chemical thermodynamics and kinetics. The gasification rate could be fast enough to match the rate of oxygen carrier reduction in the down-flow moving bed.

All reactions related to the pyrolysis and gasification of fossil fuel are endothermic, as illustrated by Equations (1), (2) and (3). 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 fossil fuel gasification process is the reduction reaction of oxygen carrier with the syngas produced.

$C_nH_mO_p \rightarrow (p\text{-}n)CO_2 + (2n\text{-}p)CO + (2/m)H_2$, 5 Kcal/mol (1)
$C + H_2O \rightarrow CO + H_2$, 28.3 Kcal/mol (2)
$C + CO_2 \rightarrow 2CO$, 38.4 Kcal/mol (3)

Just a few metal oxides that have been developed as oxygen carriers for the CLC process show exothermic properties when reacted with carbon. The possible reactions related to oxygen carrier candidates and carbon in the reducer are shown in Table 1. Thus, the enthalpy of solid fuel combustion in the chemical looping process is equal to the sum of the enthalpies of the two steps. Copper oxide shows an exothermic property 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 [3]

$C + O_2 \rightarrow CO_2$, -392.75 KJ/mol
Endothermic
$2\ NiO + C \rightarrow 2\ Ni + CO_2$, 75.21KJ/mol
$2\ MnO + C \rightarrow 2\ Mn + CO_2$, 378.98 KJ/mol,
$2\ Mn_3O_4 + C \rightarrow 6\ MnO + CO_2$, 56.7 KJ/mol
$2/3\ Fe_2O_3 + C \rightarrow 4/3\ Fe + CO_2$, 146.37 KJ/mol
$2\ PbO + C \rightarrow Pb + CO_2$, 32.82 KJ/mol
Exothermic
$2\ CuO + C \rightarrow Cu + CO_2$, -96.51 KJ/mol
$2\ Cu_2O + C \rightarrow 4\ Cu + CO_2$, -61.04
$2\ Mn_2O_3 + C \rightarrow 4\ MnO + CO_2$, -33KJ/mol

Lead is a hazardous element and not used. Manganese oxides could produce non-reactive compounds. Also, there is a thermodynamic limitation in the reduction reaction of manganese. Most of oxygen in copper oxide is active for reaction with methane, and the highest efficiency could be achieved. Thus, it is selected as the preliminary candidates for oxygen carriers for the CLC for solid fuel combustion.

Thermodynamics Analysis. Chemical reaction thermodynamics phase diagram for the reduction reactions by CO produced in solid fuel gasification process are shown in Figures 1.

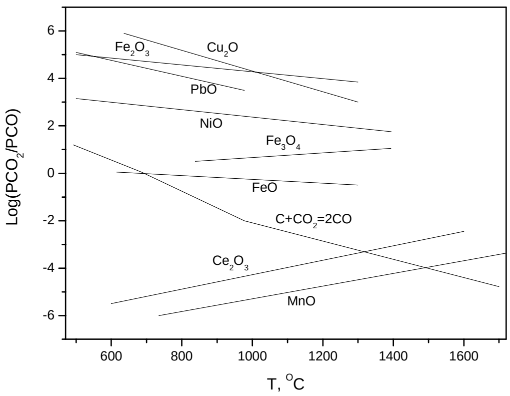

Figure 1. Variation of the thermodynamics equilibrium factor for MeO-CO as a function of temperature[3]

Figure 1 shows that the ratio varies from approximately 10^5 for the reduction of Cu_2O to values on the order of 10^{-5} or less for the reduction of MnO to Mn. 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. The reduction of manganese 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 1, above the simultaneous equilibrium temperature where two curves for the reduction of metal oxides and the Boudouard reaction intersect, MnO needs to be above 1600^{o}C, which is impossible in the CLC due to high temperature. 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. Thus, using NiO, Cu_2O, CuO and PbO as oxygen carriers could result in higher ratios of $P_{CO2}/P_{CO.}$

Similarly, analysis of the reduction of metal oxides with H_2 shows that it 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 H_2 at high temperature is a better reducing agent than CO for oxygen carriers.

Process Analysis. The volume of the gas flow in the air reactor is much larger than that in a reducing reactor because a large amount of nitrogen in the air is carried in. Moreover, the oxidizing rate of the oxygen carrier is much faster than the rate of the reducing reaction. Thus, a high gas velocity is chosen in the oxidizing reactor to keep a reasonable size reactor and to reduce the capital cost. In the reducer, long residence times, on the order of minutes, is needed for solid fuel gasification and oxygen carrier reduction due to slow reaction rates. Meanwhile, only a small amount of gas is needed for fossil fuel gasification, so a down-flow moving bed was selected. In accordance with the huge density and size differences between ash and the oxygen carrier, a low-velocity bubbling bed was chosen to separate the oxygen carrier from fuel ash as well as unburned carbon. The whole system uses two loop seals for oxygen carrier circulation.

Conclusions

Purifying CO_2 in an efficient and energy-saving way is the first and most important step for its sequestration. Chemical looping combustion could achieve this goal when it is applied to solid fuel in a highly practical way. An innovative concept was proposed to apply a CFB combined with a moving bed in the CLC of solid fuels. A coal gasification process which occurs in the moving bed in a loop seal, will be combined with a reduction process of metal oxide to achieve direct utilization of solid fuel. Thermodynamics Analysis showed that using Cu_2O, CuO as oxygen carriers could result in higher ratios of P_{CO2}/P_{CO} in solid fuel CLC process.

References

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