Limestone Decomposition in an O_2/CO_2/Steam Atmosphere Integrated with Coal Combustion

Zehua Li,[†,‡] Yin Wang,[*,‡] Zhiwei Li,[‡] Meng Li,[‡] Kai Xu,[†] Wenqiang Liu,[†] Guangqian Luo,[†] and Hong Yao[*,†]

[†]State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, People's Republic of China

[‡]Key Laboratory of Urban Pollutant Conversion, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian 361021, People's Republic of China

ABSTRACT: Ca looping is one of the most promising technologies for CO_2 capture. Calcined limestone can be used in the Ca-looping system. It is a low-cost approach to decompose limestone integrated with coal combustion in an O_2/CO_2/steam atmosphere. In this approach, coal combustion heat is continuously supplied for limestone decomposition. We aim to obtain high-purity CO_2 exhaust gas and high-reactivity CaO sorbent. High-purity CO_2 exhaust gas is then further compressed or used. High-reactivity sorbent is then used to capture CO_2 from the coal power plant. However, little research was found to investigate limestone decomposition behavior under oxy-steam combustion conditions. In this study, limestone and coal particles were mixed together and decomposed/combusted in a continuously operating fluidized bed reactor in an O_2/CO_2/steam atmosphere. The results show that increasing O_2 and steam supply reduces the emission of CO, H_2, and SO_2, which enhances the purity of CO_2 exhaust gas. Limestone decomposition conversion is also enhanced with the increase of O_2 and steam supply. Besides, most coal sulfur and ash react with small CaO sorbent particles, which flow out of the reactor and remain in the cyclone. The amount of coal sulfur and ash is very low in a large CaO sorbent particle and has little influence on sorbent reactivity. *In situ* coal combustion results in a high particle temperature and high limestone decomposition conversion in the fluidized bed but also results in sorbent sintering and a sorbent reactivity decrease. Fortunately, sorbent reactivity is improved by introducing steam into limestone decomposition and a coal combustion atmosphere.

1. INTRODUCTION

The need to reduce the emission of greenhouse gas CO_2 is becoming increasingly important because of global warming. Ca looping is one of the most promising technologies for CO_2 capture in both post-combustion and pre-combustion.[1,2] Calcined limestone can be used in the Ca-looping system for CO_2 capture. The basic reactions in the Ca-looping system are carbonation and calcination reactions. CaO sorbent absorbs CO_2 to form $CaCO_3$, and then $CaCO_3$ is decomposed to CaO (CO_2 or CO_2/steam atmosphere).[3,4] However, CaO sorbent reactivity decreases under a high calcination temperature.[5,6]

One method to improve CaO sorbent reactivity is steam activation.[7−9] Rong et al.[10] reported that steam hydration of the CaO sorbent after each calcination significantly restrained the rapid decay of CaO sorbent reactivity. Manovic and Anthony[11] found that the CaO sorbent after steam reactivation had even better characteristics for CO_2 capture than that of the natural sorbent. In our previous studies,[3,4,12] we found that above 1293 K is necessary to decompose limestone near completion in a 100% CO_2 atmosphere, while a high decomposition temperature results in the sorbent reactivity decrease.[4] Further, we investigated limestone decomposition behaviors in CO_2, CO_2/N_2, and CO_2/steam atmospheres and found that limestone decomposition conversion and sorbent reactivity could be enhanced in a CO_2/steam atmosphere.[3] Then, we also compared coal combustion behaviors in O_2/CO_2 and O_2/CO_2/steam atmospheres and found that the concentrations of CO, H_2, and CH_4 in the exhaust gas and the contents of sulfur

and $Al_2O_3 + SiO_2$ in the solid product were both lower in an O_2/CO_2/steam atmosphere than an O_2/CO_2 atmosphere.[12] In conclusion, $CaCO_3$ should be decomposed in a CO_2/steam atmosphere to obtain high-reactivity CaO sorbent and nearly pure CO_2 exhaust gas. Steam was introduced into the calcination atmosphere to reduce CO_2 partial pressure, which decreased the decomposition temperature of $CaCO_3$ and increased CaO sorbent reactivity. Besides, sorbent strength is also enhanced by hydration under high steam partial pressure conditions[13] or wet curing core-in-shell pellets with semi-reactive shells.[14]

As shown in Figure 1, the Ca-looping process mainly includes two reactors: a carbonation reactor and a calcination reactor. The concept of this Ca-looping process using dual reactors was first proposed by Shimizu et al.[15] The carbonation reaction is an exothermic reaction, and the heat can be recycled for $CaCO_3$ calcination. In the calcination reactor, the decomposition reaction is an endothermic reaction and a large amount of heat is needed to drive the decomposition reaction. This heat can be supplied from coal combustion because of its low cost and abundance. Moreover, introducing steam into the calcination atmosphere can enhance CaO sorbent reactivity. Therefore, in this study, limestone particles were mixed with coal particles and decomposed/combusted