



Technical Note

NO Reduction Scale of Three Typical Chinese Coals during Oxy-Coal Combustion

Xiaowei Hu, Guangqian Luo, Hong Yao*

State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, 430074, China

ABSTRACT

Oxy-coal combustion has become one of the most promising technologies for its ability to capture carbon dioxide and produce low pollutant emissions. In particular, the NO emission from oxy-coal combustion is found to be much lower than that in air combustion, but the NO reduction degree varies. In order to ascertain a rough NO reduction potential for Chinese coals, three types of coals (lignite, bituminous coal and anthracite) were combusted in a drop-tube furnace (DTF) in air and oxy-coal atmosphere during this study. The results showed that oxy-coal combustion could largely reduce NO emission down to 50% for the three coals. The NO reducing potential of oxy-coal technology for the lignite was higher than that for the bituminous coal and the anthracite. High content of volatiles in the lignite was considered as the major reason. NO removal was suppressed in the bituminous coal combustion due to the impacts of CaO and Fe₂O₃.

Keywords: Oxy-coal; NO reduction; Chinese coal.

INTRODUCTION

Severe environmental issues such as green-house effect are mainly caused by the pollutant emission from coal combustion (Chiu *et al.*, 2012; Yu *et al.*, 2012). However, coal-fired power plants that account for more than 70% of the national electricity generation cannot be replaced for several decades in China (International Energy Agency, 2012). Therefore, it is imperative and eco-sustainable to control coal combustion emissions such as CO₂, particulate matter (PM) and NO_x efficiently.

Oxy-coal combustion technology uses recycled flue gas (RFG) instead of N₂ together with pure O₂ as the atmosphere, which could generate high concentration of CO₂ for compression afterwards (Toftegaard *et al.*, 2012). Compared to the traditional air combustion combined with the ammonia adsorption CO₂ recovery method, oxy-coal combustion is more economical (Chen *et al.*, 2012). Oxy-coal combustion has become one of the most applicable technologies in future for its ability to control the pollutants cheaply and effectively (Chan *et al.*, 2012; Pan *et al.*, 2012).

Previous researches explored nitrogen chemistry due to the potential to reduce NO in oxy-coal combustion but the decrements vary. When comparing the NO reduction capacity of oxy-coal combustion for different coals, the ratio of NO emission in oxy-coal to that in air combustion is introduced

rather than the NO emission differences between oxy-coal and air combustion in order to avoid the influence of the nitrogen content in coal. Fig. 1 shows the ratio of NO exhausts from oxy-coal to that from air combustion ranging from 1.25% to 81.8% (Andersson *et al.*, 2008; Shaddix and Molina, 2011; Stadler *et al.*, 2011; Zhang *et al.*, 2011; Liu *et al.*, 2012). The great difference indicates that the coal properties and experimental conditions may largely influence NO reducing potentials. Lignite coal combustion in oxy-coal atmosphere only produced 20% of that in air from the experiment of Andersson *et al.* (2008). Shaddix and Molina (2011) put forward that 20% NO was removed in oxy-coal combustion. And while Zhang *et al.* (2011) pointed that the NO_x emission amount was 40% lower in oxy-coal than in air combustion, Stadler *et al.* (2011) revealed NO emission from oxy-coal combustion shares two-thirds proportion of that from air when German lignite was combusted in a vertical pilot-scale furnace. Still Liu *et al.* (2012) stated that NO emission from oxy-coal combustion with partial CO₂ removal from the RFG was decreased to 1.25% of that in air combustion.

The NO decrement in oxy-coal combustion is mainly caused by the reduction of recycled NO. And it is further determined by the properties of the coal used. However, the relationship between the NO reduction capacity and the coal properties is still controversial. The coal rank or nitrogen content was considered as the important factor influencing the NO reduction from different researches. It is difficult to speculate on the reduction scales of different types of coal, although they may play an instructive and guiding role in NO_x control in oxy-coal combustion. It is essential to have a rough idea of the NO decrement in Chinese coals before the utilization of oxy-coal combustion in China.

* Corresponding author.

Tel./Fax: +86-27-87545526 (O)

E-mail address: hyao@mail.hust.edu.cn

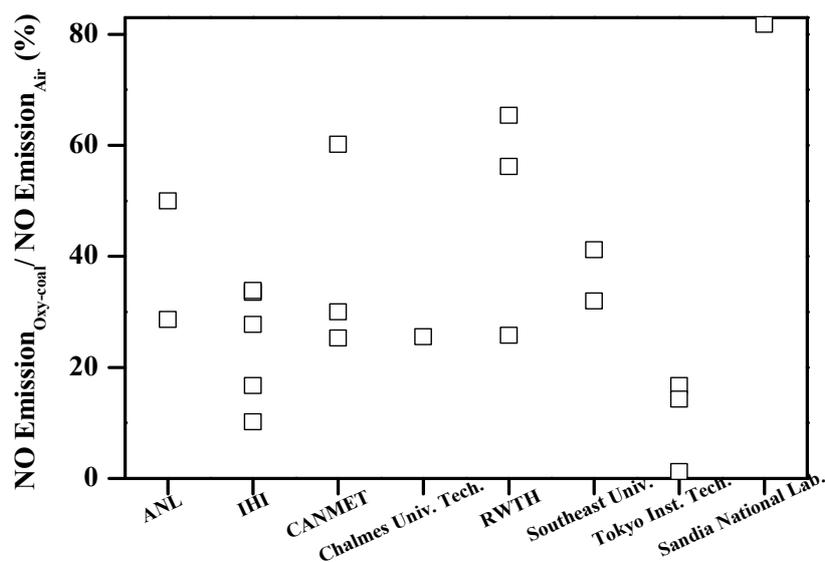


Fig. 1. The ratios of NO exhausted in oxy-coal to that in air combustion from the literatures (Andersson *et al.*, 2008; Shaddix *et al.*, 2011; Stadler *et al.*, 2011; Zhang *et al.*, 2011; Liu *et al.*, 2012).

In this work, three different types of Chinese coals were investigated in a drop-tube furnace (DTF) in air and in oxy-coal conditions separately. The NO concentration in the flue gas was measured to understand the ratios of NO exhausts in oxy-coal to that in air combustion. The relationship between the oxy-coal NO reduction capacity and coal properties was also discussed.

EXPERIMENTAL

A Chinese lignite, a bituminous coal and an anthracite, with grain diameter ranges from 45 to 100 μm , were used as the raw samples. The proximate and ultimate analysis of the coals is presented in Table 1. The volatile contents in both lignite and bituminous coal are over 30% in this study. The alkali and alkali earth metal (AAEM) compositions from X Ray Fluorescence Spectrum Analysis (XRF) data of the three coals are also presented in Table 2. Na and K contents in the three coals are nearly the same. The contents of Ca and Fe in bituminous coal are relatively high and even higher than those in the lignite. All three coals were combusted in a DTF in both air (O_2 and N_2 , O_2/N_2) and oxy-coal (O_2 with recycled flue gas, O_2/RFG) atmosphere at 1373 K to avoid the impact of thermal NO. A brief schematic of the DTF is shown in Fig. 2. The height of the reactor tube was 210 cm, and the inner diameter was 6.2 cm. The feeding rate of each coal was 0.3 g/min. The total inlet gas flow rate was 5000 mL/min. The O_2 fraction was 21%, 27% and 32% (Vol/Vol) in each combustion atmosphere. The recycled ratio in O_2/RFG was 0.8.

The flue gas was passed through a filter and a drying bottle. Then it was monitored by two gas analyzers. CO, CO_2 and O_2 were detected by a custom-made Madur gas analyzer with a detection range of 20%, 100% and 50%. CO and CO_2 sensors use non-disperse infrared (NDIR) method while O_2 sensor uses the electrochemical method for test. NO was measured by a gas analyzer using electrochemical

sensors in the range of 0–5000 10^{-6} Vol/Vol. The CO concentration (not shown here) revealed that the combustions of coal and char were complete in all combustion processes.

RESULTS AND DISCUSSION

Fig. 3 shows the ratios of NO exhausts from oxy-coal to that from air combustion for the lignite, bituminous coal and anthracite at O_2 fraction of 21%, 27% and 32%. It can also be seen that in O_2/RFG atmosphere, lignite combustion emits 30%–40% NO of that in O_2/N_2 . This proportion in bituminous coal and anthracite combustion is 36%–48% and 38%–42%, respectively. It indicates more than half of the NO is reduced in oxy-coal combustion.

Fig. 3 also shows the relationship of the ratios that NO released from oxy-coal to air combustion for the three coals. The ratio of NO emission between oxy-coal and air combustion for the lignite is the lowest under all conditions, which is corresponding to the conclusion that the higher volatile coal may lead to more NO reduction (Álvarez *et al.*, 2012). However, their theory cannot apply to the result of the bituminous coal in the present study. For example, the ratio of NO exhausts from oxy-coal to that from air combustion for the bituminous coal is 48%, which is higher than that of anthracite (40%) at O_2 fraction of 32%.

In order to clarify the effects of these coal properties on NO reduction, the details of the reduction reaction are discussed. From the overall reducing reaction of NO (Eq. (1)), the reducing substance could reduce NO into N_2 in the combustion process. The more reducing matter and longer reaction time, the more NO would be removed. The recycled NO may be reduced by both homogeneous and heterogeneous reactions. NO would be reduced by CH_i (hydrocarbon radicals), H_2 and HCN, which are formed during the devolatilization process through homogeneous reactions, as shown in Eq. (2) and Eq. (3). In the present experiment, the homogeneous reaction time for the three

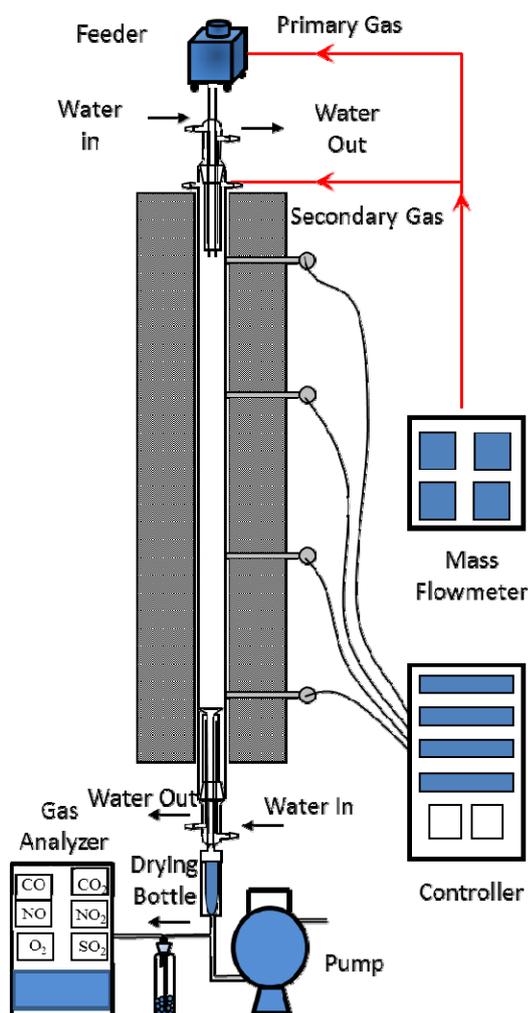
Table 1. Proximate and ultimate analysis of coals.

	Proximate analysis (wt% ad)				Ultimate analysis(wt% ad)				
	M	A	V	FC	C	H	N	S	O*
Lignite	4.30	14.43	37.18	44.09	56.61	5.42	0.82	1.72	16.70
Bituminous	4.44	7.46	31.70	56.40	67.64	3.65	0.80	3.07	12.94
Anthracite	3.86	29.26	7.68	59.20	59.95	1.20	0.92	0.22	4.59

* By difference.

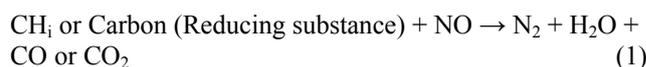
Table 2. AAEM content of coals.

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	Fe ₂ O ₃	CaO
Lignite	0.83	2.65	12.47	46.66	0.52	15.44	0.82	10.52	6.30
Bituminous	0.39	1.13	14.34	29.17	0.68	16.07	0.39	9.50	25.57
Anthracite	1.16	0.98	26.87	43.83	0.75	7.63	1.80	5.01	9.56

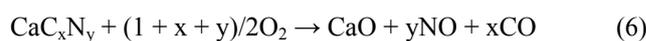
**Fig. 2.** The schematic of the DTF.

coals are approximately the same. Therefore, the attention is mainly paid to the amount of reducing species. The amount of hydrocarbon radicals and volatile-N are quantified by the volatile content in coal during the homogeneous reduction. More volatile matter may be released during devolatilization and more NO could be reduced through homogeneous reactions for the higher-volatile-content coals. Carbon in

char could also reduce NO through heterogeneous reactions as shown in Eq. (4). While the reaction time of heterogeneous removal could be affected by the porous structure. The total NO removal in oxy-coal combustion depends on the combination of NO reduced by both volatile matters and char.



The lignite has the highest volatile content of the three coals, which may cause more NO to be reduced into N₂ through homogeneous reactions during its combustion than that in the bituminous coal and anthracite combustion. In addition, the reaction time of NO heterogeneous removal for the lignite char is longer than for other chars because the higher-volatile-content coal char is spongier (Gao *et al.*, 2010). Both of these result in a large amount of NO removal by the lignite coal. The NO reduction potential of the anthracite is lower than that of the lignite because of the combined impacts of its lower volatile content and denser char structure.



In the bituminous coal combustion the nitrogen chemistry could be affected by the high contents of CaO and Fe₂O₃. For example, the components of the Ca–N intermediates can be formed by the reaction of nitrogen in coal (coal-N) with CaO firstly (Eq. (5)). Then the oxidation of these intermediates may lead to a direct formation of NO through Eq. (6) (Liu *et al.*, 2014). Moreover, carbon as one of the reducing substances is also consumed in the reaction, which weakens NO heterogeneous removal afterwards. The oxidation of HCN (Ren *et al.*, 2011) or NH₃ (Yang *et al.*, 2010) may be accelerated by the catalytic effect of CaO.

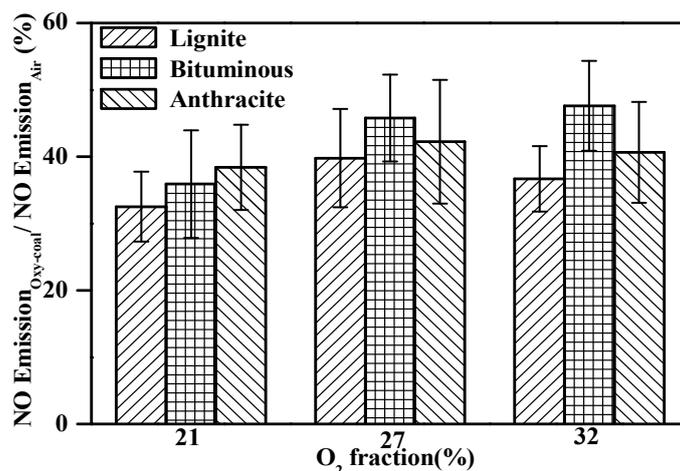


Fig. 3. The ratios of NO exhausted in oxy-coal to that in air combustion for the three coals.

Their opportunities to reduce NO are decreased and consequently NO homogeneous reduction is suppressed. Fe element catalyzes the oxidation rate of nitrogen compounds (Niu *et al.*, 2011). Ca and Fe could also enhance conversion of coal-N to NO (Gu, 2013). During the bituminous coal combustion, NO reduction amount may be decreased due to the changes caused by high proportions of CaO and Fe₂O₃. Therefore the ratio of NO emission between oxy-coal and air combustion for the bituminous coal is higher than that for the anthracite.

CONCLUSIONS

Three Chinese coals were combusted in a DTF under both air and oxy-coal atmosphere. Less than 50% NO was exhausted from oxy-coal combustion comparing with that in air combustion. The NO capacity of the lignite was higher than that of the bituminous coal and anthracite in the present study, which was mainly caused by the highest volatile content. High contents of CaO and Fe₂O₃ suppressed NO reduction during the bituminous coal combustion, which resulted in a lower NO capacity of the bituminous coal than that of the anthracite.

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