

# Influences of Injection Positions of Pyrolytic Wastewater on $\text{NO}_x$ Emission of Semi-coke

Xueting Yang<sup>1,2</sup>, Guoliang Song<sup>1,2,3,\*</sup>, Yuan Xiao<sup>1,2</sup>, Zengcai Ji<sup>1,2</sup> and Chao Wang<sup>1,4</sup>

<sup>1</sup>*Institute of Engineering Thermalphysics, Chinese Academy of Sciences, Beijing 100190, China*

<sup>2</sup>*University of Chinese Academy of Sciences, Beijing 100049, China*

<sup>3</sup>*Dalian National Laboratory for Clean Energy, Dalian 116023, China*

<sup>4</sup>*University of Science & Technology of China, Hefei 230026, China*

*\*Corresponding author*

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**Abstract:** The amount of pyrolytic wastewater produced by coking plant was huge and it was difficult to deal with, there were many defects in conventional pyrolytic wastewater treatment methods. Incineration method could remove most of the organics and harmful substances in pyrolytic wastewater, and generate  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , it truly realized zero discharge of pyrolytic wastewater, but its effects on the combustion and pollutant emissions of semi-coke was not clear, so experiments were carried out in a 0.1 MW circulating fluidized bed test platform to investigate the influences of injection positions of pyrolytic wastewater on the combustion temperature and  $\text{NO}_x$  emission of semi-coke. The results showed that the  $\text{NO}_x$  emission was cut down by 13.81 % and 22.58 % when pyrolytic wastewater was injected into furnace and tail flue, respectively. It indicated that pyrolytic wastewater realized zero discharge when burning with semi-coke, the  $\text{NO}_x$  emission of semi-coke was cut down as well, and it was more appropriate for pyrolytic wastewater to reduce  $\text{NO}_x$  emission in tail flue compared to the furnace.

## 1 INTRODUCTION

A large amount of pyrolytic wastewater is produced every year in the coking plants, the composition of pyrolytic wastewater is complex, containing aromatic and long-chain hydrocarbon organic matters, benzene, volatile phenol, ammonia nitrogen and oil (Ji, 2016, Wang, 2017), so it has characteristics such as high chemical oxygen demand (COD), high chromaticity and poor biodegradability, it is difficult to degrade and recycle (Li, 2017, Wang 2014). The conventional methods are to degrade or flocculate pyrolytic wastewater by microorganism, chemical reagent and physical methods. The processes of conventional methods are complex, which are greatly affected by temperature and the composition of pyrolytic wastewater, so that the treatment capacity of conventional methods is limited. An easy, clean and efficient treatment method desperately needs to be found out. Incineration method is not affected by the temperature and quality of wastewater, and can destroy the molecular structure of harmful

substances through controllable high-temperature chemical reaction. It can remove most of the organics and harmful substances in pyrolytic wastewater and generate  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , truly realizing zero discharge of pyrolytic wastewater (Xiao, 2012).

Literatures about the incineration of coal pyrolytic wastewater are few, Li XF et al. (Li, 2018) found through simulation that the temperature of the furnace reduced when the pyrolytic wastewater enters the circulating fluidized bed furnace for incineration, and the power generation was cut down by about 1.5 % when the coal supply of the system kept stable.

Alar Konist et al. (Konist, 2018) incinerated pyrolytic wastewater from shale oil plants in a 60  $\text{kW}_{\text{th}}$  circulating fluidized bed combustor, the  $\text{NO}_x$  emission was increased by up to 1.8 times when the flow rate of pyrolytic wastewater was 4.6  $\text{kg/h}$ . Alar Konist et al. (Konist, 2019) also carried out experiments in an oil shale fired 250  $\text{MW}_{\text{th}}$  circulating fluidized bed boiler, and found that the incineration of pyrolytic wastewater increased the

NO<sub>x</sub> emission by 27 % and increased oil shale consumption by up to 6 % when the flow rate of pyrolytic wastewater was 13 t/h.

To deal with pyrolytic wastewater in CFB boilers, the appropriate position for incineration and its influences on the operation and pollutant emission of CFB boilers should be investigated. In the experiments of literature (Konist, 2018), the pyrolytic wastewater was incinerated in the lower part of furnace which near the feed position of oil shale, the pyrolytic wastewater was sent to the furnace together with oil shale in literature (Konist, 2019). To figure out the influences of injection positions of coal pyrolytic wastewater on NO<sub>x</sub> emissions of semi-coke, some experiments were carried out in this paper, the injection positions included furnace and tail flue, and it was vital for the

clean and efficient treatment of coal pyrolytic wastewater.

## 2 EXPERIMENTAL SECTION

### 2.1 Fuel Characteristics

The proximate and ultimate analysis of semi-coke used during experiments were shown in Table 1, subscript "ar" represents the as received basis. The particle diameter of semi-coke was 0-1 mm. The pyrolytic wastewater used in experiments came from a coking plant in Shanxi Province, China, and its components were shown in Table 2.

Table 1: Proximate and ultimate analysis of semi-coke.

Proximate Analysis (wt%)				Ultimate Analysis (wt%, ar)					Lower calorific value
M <sub>ar</sub>	A <sub>ar</sub>	V <sub>ar</sub>	FC <sub>ar</sub>	C <sub>ar</sub>	H <sub>ar</sub>	O <sub>ar</sub>	N <sub>ar</sub>	S <sub>ar</sub>	Q <sub>ar,net</sub> (MJ/kg)
4.78	7.06	6.2	81.96	82.54	0.84	3.59	0.82	0.37	28.62

Table 2: Components of pyrolytic wastewater (mg/L).

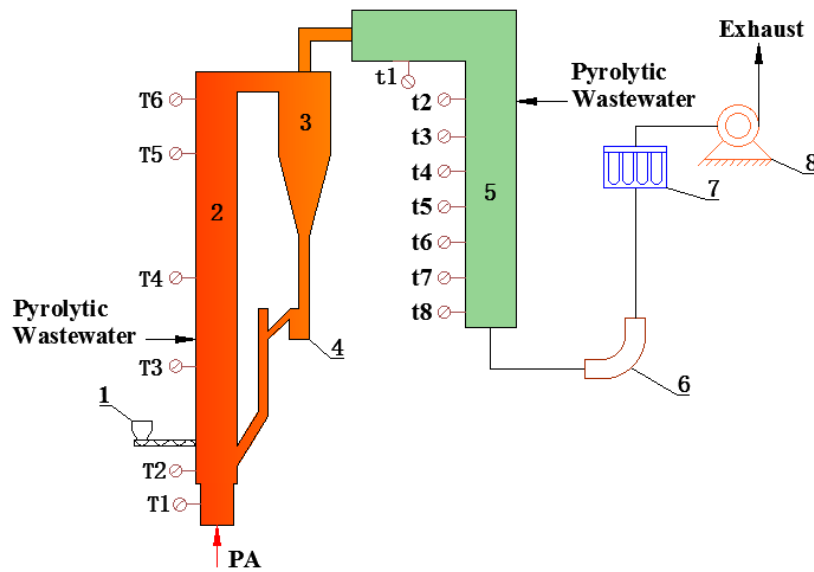
PH	Volatile phenol	Ammonia nitrogen	COD	Oils	Salts	sulfide
9.02	2.84×10 <sup>3</sup>	37.2	3.08×10 <sup>4</sup>	203	6.99×10 <sup>4</sup>	<0.005

### 2.2 Test Platform

Experiments were carried out in a 0.1 MW CFB test platform to investigate the effects of pyrolytic wastewater on the combustion and emission characteristics of semi-coke when pyrolytic wastewater was injected from different positions. As shown in Fig.1, the 0.1 MW CFB test platform was consist of furnace, cyclone, loop seal, tail flue, flue gas cooler, bag filters and induced draft fan. The inner diameter of furnace was 150 mm, there were six thermal couples along the axis of furnace, the inner diameter of tail flue was 150 mm, along which there were eight thermal couples as shown in Fig.1. Pyrolytic wastewater was injected into the furnace

and tail flue from the positions near T3 and t2, respectively, the mass of injected wastewater was about 10 % of semi-coke.

The excess air ratio was controlled around 1.15, the temperature in furnace was around 935°C, pyrolytic wastewater was injected into the furnace in the position near T3, and was injected into tail flue in the position near t2 when the temperature was appropriate. The flue gas was filtered, dried then analyzed by Testo 350 measuring system. In the following discussion, the NO<sub>x</sub> emission had normalized to dry flue gas with an oxygen concentration of 6 %.



1- Screw feeder; 2- CFB furnace; 3- Cyclone; 4- Loop seal; 5- Post-combustion chamber; 6- Flue gas cooler; 7- Bag filters; 8- Induced draft fan

Figure 1: Schematic diagram of 0.1MW CFB test platform.

### 3 RESULTS AND DISCUSSIONS

Compared to the temperature distributions without pyrolytic wastewater, the temperature of tail flue was stable when pyrolytic wastewater was injected into furnace, and the temperature of furnace was stable when pyrolytic wastewater was injected into the tail flue. Fig.2 and Fig.3 showed the temperature distributions of furnace and tail flue in different conditions, respectively.

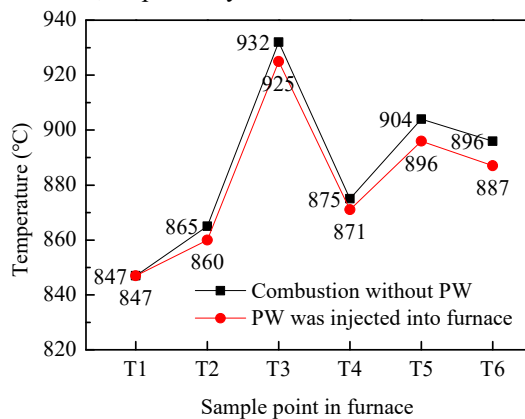


Figure 2: Temperature distribution of furnace.

“PW” represented pyrolytic wastewater. The temperature in furnace decreased slightly when pyrolytic wastewater was injected into T3, the

temperature of T2, T3, T4, T5 and T6 dropped 5 to 9 degrees, while the temperature of T1 did not change due to the heat storage of bed material. It indicated that there was little effect on the temperature of furnace when deal with pyrolytic wastewater in the furnace.

As shown in Fig.3, the temperature of t2 decreased sharply when pyrolytic wastewater was injected into the tail flue, the temperature of t3, t4, t5, t6, t7 and t8 all decreased in varying degrees, and all above 15°C. It could indicate that the temperature change of tail flue was more obvious than that of the furnace when the same percentage of pyrolytic wastewater was injected into furnace and tail flue, respectively.

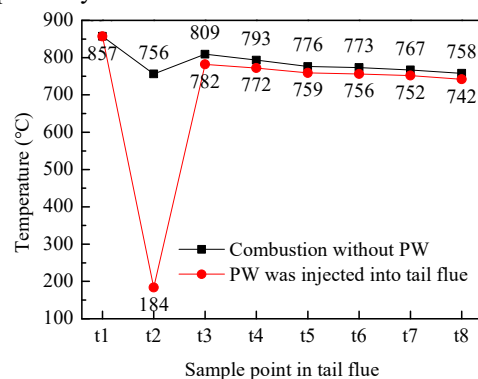


Figure 3: Temperature distribution of tail flue.

There were lots of semi-coke and bed material particles circulating through the furnace, cyclone and loop seal, the heat loss caused by pyrolytic wastewater was soon supplemented, while there were few combustible particles in the tail flue, so that the injection of pyrolytic wastewater led to larger decrease of temperature. Sample point t2 was the nearest point from where pyrolytic wastewater was injected into, much heat was absorbed to evaporate the water when flue gas and fly ash flow by the injection position.

Fig.4 showed the pollutant concentration in flue gas of three cases, respectively, "None" represented no pyrolytic wastewater was injected, and its NO<sub>x</sub> emission concentration was 439.67 mg/m<sup>3</sup>. It was obviously that the NO<sub>x</sub> emission decreased when pyrolytic wastewater was injected into furnace or tail flue, the NO<sub>x</sub> emission were cut down by 13.81 % and 22.58 % when pyrolytic wastewater was injected into furnace and tail flue, respectively. Compared to being injected into the furnace, the NO<sub>x</sub> emission was lower when pyrolytic wastewater was injected into tail flue. It indicated that it was more appropriate for pyrolytic wastewater to reduce NO<sub>x</sub> emission in tail flue.

When pyrolytic wastewater was injected into furnace, the semi-coke particles were in the state of incomplete combustion in the position where pyrolytic wastewater was injected into, part of nitrogen in semi-coke was released, and NH<sub>3</sub> in pyrolytic wastewater reacted with NO<sub>x</sub> through the following reaction (R1), and the organic matters and residual NH<sub>3</sub> (if there was) in pyrolytic wastewater would be oxidized by air.

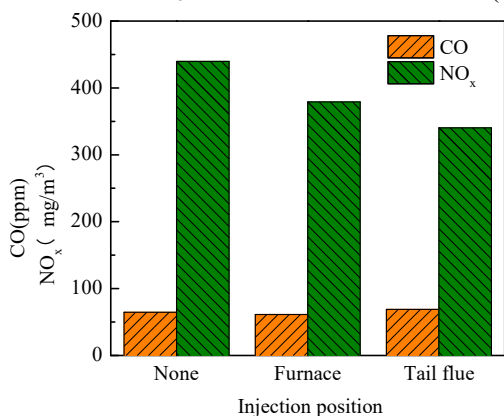
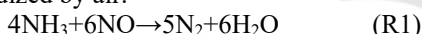


Figure 4: Pollutant concentration in flue gas.

The particles in flue tail were almost burned out, and the NO<sub>x</sub> concentration in the flue gas was high, the organic matters in pyrolytic wastewater such as

hydrocarbons would not be oxidized due to low temperature in the position of t2 when pyrolytic wastewater was injected into tail flue, the CO emission increased as well due to the drop of temperature. Hydrocarbons and NH<sub>3</sub> reacted with NO<sub>x</sub>, so the NO<sub>x</sub> emission was the lowest when pyrolytic wastewater was injected into tail flue.

The incineration of pyrolytic wastewater together with semi-coke could not only realize zero discharge of pyrolytic wastewater, the NO<sub>x</sub> emission of semi-coke was reduced as well. However, the residence time of pyrolytic wastewater was short when it was injected into tail flue, so there was no guarantee of sufficient residence time for the organic matters to decompose.

## 4 CONCLUSIONS

Experiments were carried out to explore the effects of injection positions of pyrolytic wastewater on combustion temperature and pollutant emissions of semi-coke. The main conclusions were as follows:

(1) The temperature change of tail flue was more obvious than furnace when the same percentage of pyrolytic wastewater was injected into furnace and tail flue, respectively.

(2) The NO<sub>x</sub> emission was cut down by 13.81 % and 22.58 % when pyrolytic wastewater was injected into furnace and tail flue, respectively.

(3) It was more appropriate for pyrolytic wastewater to reduce NO<sub>x</sub> emission in tail flue compared to the furnace, but there was no guarantee of sufficient residence time for organic matters to decompose.

## ACKNOWLEDGEMENTS

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