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NO$_x$ emission from incineration of organic liquid waste in a circulating fluidized bed

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Abstract−An incineration test of a toxic chemical organic waste liquid was conducted on a circulating fluidized bed (CFB) incinerator. The flue gas was measured online with the advanced SAE-19 flue gas analyzer. The effects of several factors, in terms of flow rate of waste liquid, ratio of waste liquid injected into dense bed of the CFB, excess air coefficient, the secondary air fraction and bed temperature on NO$_x$ emissions, were verified. The experimental results show that NO emissions in flue gas increase with increase in the flow rate of the waste liquid injected into the bed or the excess air coefficient or the bed temperature and those decrease with increase in the ratio of waste liquid injected into the dense bed of the CFB or the secondary air fraction. During the test runs, NO$_x$ concentration in flue gas met the national regulation on NO$_x$ emissions due to suppressive effect of low temperature and staged combustion in CFB on NO$_x$ formation.

Key words: Red Waste Liquid, Incineration, Circulating Fluidized Bed (CFB), Emission

INTRODUCTION

Organic waste liquid is one of the major wastes produced by the chemical and petroleum refinery industries. Due to its content of harmful organic compounds, in some cases, this kind of liquid is recognized as a hazardous waste. Organic waste liquids are being increasingly generated. Without disposal, this will seriously affect human health and national development. Among various methods and trends in the development of organic waste liquid disposal in the world, incineration is considered as a good option because of its significant advantages of weight and volume reduction and the possibility of heat recovery as hot water and/or steam [1-6].

Many types of thermal oxidation systems in existence today are suitable for the destruction of organic hazardous wastes. Few, however, offer the versatility of fluidized beds. Past research and commercial fluidized bed installations have demonstrated the ability of fluidized beds to successfully destroy organic constituents in a wide assortment of gas, liquid, sludge, and solid wastes. The significant advantages of circulating fluidized-bed incinerators over conventional incinerators for disposing of different kinds of organic waste liquids include their relatively uniform temperature distribution, high pyrolysis rate of the waste liquid with high thermal capacity of inert material, high combustion efficiency, ability to reduce emission of nitrogen oxide for their staged combustion and low bed temperature [7-11]. In the 1980s some companies in Italy tried to incinerate basic waste liquid and a company in Germany incinerated waste liquid in a furnace with natural gas as auxiliary fuel, the temperature between 900-1,000 °C; organic material in the waste liquid was drastically decomposed, but pollutant emissions were serious. In the 1990s, Nichols K.M. introduced a method reclaiming the alkali salt and incinerated the remaining liquid with diesel oil. But the pollutant emission problem has not been solved [12,13]. A company in Cangzhou, China incinerated toxic chemical organic waste liquid with an oil-fired incinerator; unfortunately, concentrated trinitrotoluene (TNT) powders were deposited in the flue gas pass and an explosion happened. Recently, great importance has been attached to incineration of organic waste liquid in CFB in China. But few theoretical studies have been carried out, and even fewer successful projects have been reported.

This paper presents a detailed discussion of incineration tests of the toxic chemical organic waste liquid and the effects of several factors, in terms of the flow rate of waste liquid, ratio of waste liquid injected into dense bed of the CFB, excess air coefficient and the secondary air fraction on NO$_x$ emissions were verified (Usually, NO is in the majority of total NO$_x$ of CFB, and so the paper mainly focuses on NO emissions.). The results provide a database for CFB incinerator design and pollutant control during the incineration.

EXPERIMENTAL

1. Apparatus

Fig. 1 shows a schematic diagram of the experimental apparatus, which consists of a circulating fluidized bed incinerator, start-up burner, forced and induced draught fans, fuel feeder, two waste liquid injectors, cyclone separator and the loop seal, measurement system and control panel. There are four regions along the height of circulating fluidized bed (CFB): wind box, dense bed, transition zone and dilute phase region. The CFB furnace is 7 m high, and the cross-section area in the dense bed is 230 mm×230 mm; the height of the dilute phase region is 5.64 m with the cross-section area of 460 mm× 395 mm. Two waste liquid injectors were equipped at the dense bed region and the dilute phase region, respectively and the corresponding flow meters controlling the flow rate of waste liquid and atomizing air were also equipped, to gain good atomization effect and uniform distribution of waste liquid in the bed. In the instrumenta-

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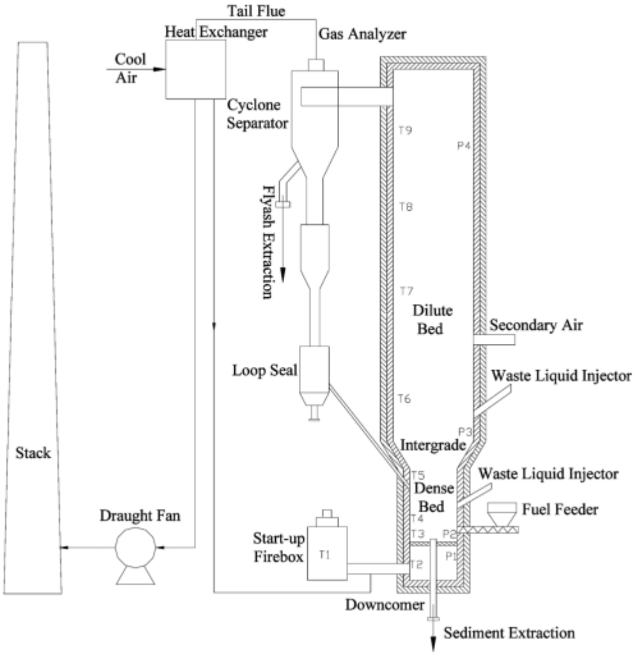

Fig. 1. Schematic diagram of circulating fluidized bed incinerator.

tion system, four pressure measuring points, eight thermal couples, two gas flow meters, solid particles sampling in the dense bed, fly ash sampling and gas sampling in the dilute phase region were arranged, as shown in Fig. 1.

In the experiment, the combustor was started up by using fluidizing gas at around 700 °C generated from a diesel oil burner. When bed temperature reached 500 °C, coal was fed into the bed via a screw feeder. Once the dense bed temperature reached steadily 900 °C, the burner was turned off and circulation of fly ash was started. Finally, when the circulation of fly ash and bed temperature were stable, waste liquid was injected into the fluidized bed and the experiment started.

2. Characteristics of Fuel and Waste Liquid

The auxiliary fuel used for the incineration test was Xuzhou bituminous coal. The ultimate analysis and proximate analysis of the Xuzhou bituminous coal are shown in Tables 1 and 2, respectively. The waste liquid incinerated was from a chemical plant in Cangzhou, Hebei. Its characteristics and components are shown in Table 3. The water content in the organic waste liquid is very high, about 85.6% and content of combustible di-nitro-toluene (DNT) with low quantity of heat is low. During the incineration, NO_x could be released from minerals like Na_2SO_4, $NaNO_3$, Na_2CO_3, organic compound DNT and phenol-sodium in the waste liquid.

Table 1. Ultimate analysis of coal

Ultimate analysis (as received, wt%)						
C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}	A_{ar}	M_{ar}
58.55	3.71	8.87	1.06	0.57	22.35	4.89

3. Measurement and Instrumentation

The flue gas emission test was performed with an on-line gas measurement system (Portable Gas Analyzer SAE-19) during "steady state" periods of the experiments. Concentrations of oxygen, carbon dioxide, carbon monoxide, nitrogen oxides and sulfur dioxide were continuously monitored and recorded.

RESULTS AND DISCUSSIONS

1. Effect of Flow Rate of Waste Liquid on NO Emissions

Fig. 2 presents the effect of flow rate of waste liquid on NO emissions. As can be seen from the experiment, the temperature in the dense bed decreases and the temperature in the dilute bed increases with an increase in the flow rate of the waste liquid incinerated in CFB. To minimize the temperature range, while keeping the excess air and the primary air fraction constant, a suitable amount of coal was added and the heated area of dense bed was regulated. It can be seen that the lowest NO emission recorded was achieved when no waste liquid was incinerated in CFB and it increases as the flow rate of waste liquid increases.

In the experiment, good atomization effect and suitable atomizer location were obtained in the waste liquid injection system that waste liquid rapidly vaporized and the organic compounds decomposed or combusted at high temperature in the incinerator. Materials like DNT, phenol-sodium, $NaNO_3$ with nitrogen-components reacted and behaved in the following ways releasing NO.

$$C_6H_3CH_3(NO_2)_2 + O_2 \rightarrow NO + CO_2 + H_2O \tag{1}$$

$$C_6H_4NO_2NaO \rightarrow NO + CO_2 + H_2O + Na_2O \tag{2}$$

Table 2. Proximate analysis of coal

Proximate analysis (as received, wt%)				Heating value (MJ/kg)
Moisture (M_{tol})	Ash (A_{ar})	Volatile (V_{ar})	Fixed carbon (C_{fix})	LHV
4.89	22.35	27.21	45.55	23.08

Table 3. Characteristics and components of red waste liquid

Components	Molecular formula	Proportion	Characteristics of combustion
DNT	$C_6H_3CH_3(NO_2)_2$	5.4%	Explosive, NO_x emissions
Phenol-sodium	$C_6H_4NO_2NaO$, et al.	2%	NO_x emissions
Mineral	Na_2SO_4, $NaNO_3$, Na_2CO_3	7%	Easy to form low fusion point material, NO_x and CO_2 emissions
Water	H_2O	85.6%	Gasified to vapor, decomposed H and OH

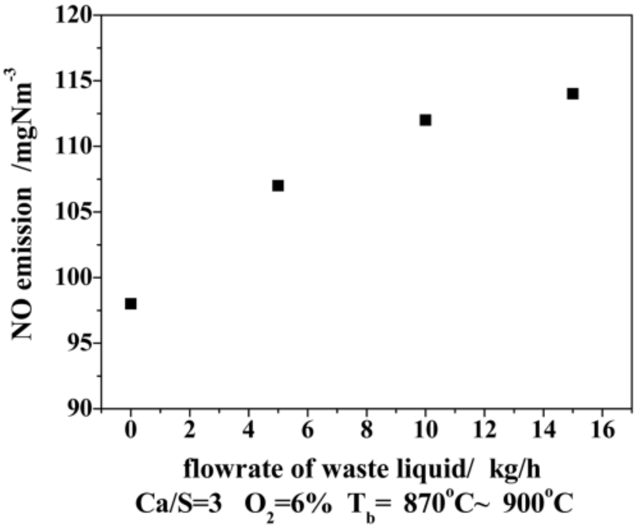

Fig. 2. Effect of flow rate of waste liquid on NO emissions.

$$NaNO_3 \xrightarrow{400\text{-}600\,^{\circ}C} N_2 + O_2 + Na_2O \tag{3}$$

$$NaNO_3 \xrightarrow{700\text{-}865\,^{\circ}C} NO + N_2O + Na_2O \tag{4}$$

As the flow rate of waste liquid increases, the auxiliary fuel amount increases to get a relatively uniform temperature, and yields of NO from the coal combustion increase. Moreover, decomposition of (organic compound) materials with N-components in waste liquid will also increase NO emissions.

Because of the advantages of CFB, suppressive effect of low temperature and staged combustion, NO formation is suppressed or formed NO is reduced by reducing gases and solid radicals and that the maximum NO emission during the tests is still quite low, below 120 mg/Nm^3.

2. Effect of the Secondary Air Fraction on NO Emissions

Fig. 3 presents the effect of the secondary air fraction on NO emissions at three different ratios of coal to waste liquid (R). It can be seen that for the fixed excess air, NO emissions decrease as the secondary air fraction increases and when the ratio of coal to waste liquid increases, NO emissions decrease as the flow rate of waste liquid decreases. By calculation, the nitrogen content in waste liquid is almost the same as that in coal. During all experiments, operational temperature was controlled between 830 °C and 900 °C, thermal NO formation via Zeldovich-mechanisms would be negligible. From the characteristics of DNT, phenol-sodium and NaNO$_3$ in Table 3, at a temperature of about 700 °C, all of them decomposed and NO was released. Hence, both the fuel-NO and NO from waste liquid play an important role in total NO emissions.

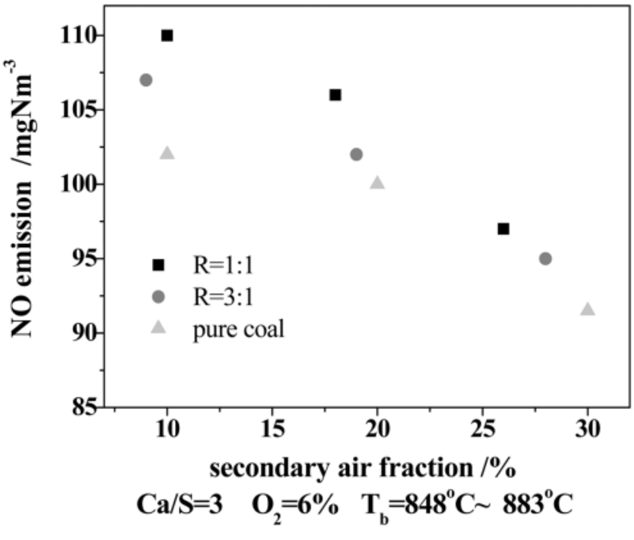

Fig. 3. Effect of the secondary air fraction on NO emissions.

The effect of the secondary air on NO emissions mainly resulted from the change with equilibrium of the following homogeneous and heterogeneous reactions [1,8]:

$$NO + CO(H_2) \rightarrow 0.5N_2 + CO_2(H_2O) \tag{5}$$

$$C + 2NO \rightarrow CO_2 + N_2 \tag{6}$$

$$C + NO \rightarrow CO + N_2 \tag{7}$$

$$2NH_3 + 2.5O_2 \rightarrow 2NO + 3H_2O \tag{8}$$

$$2/3NH_3 + NO \rightarrow 5/6N_2 + H_2O \tag{9}$$

Studies [14] show that a zone near the air distributor is relatively rich in oxygen where NO emissions reach a maximum and gradually decrease upstream to a steady level at the surface of the dense bed region. However, due to the relative mass fuel feeding and bad state of mixing with air and fuel, combustion in CFB is not so drastic that high oxygen content in the flow at the bottom of dense bed leads to significant amount of NO formation. Along the height of the incinerator, the effect of staged combustion and intensive fluidization in dense bed brings on a lack of oxygen in the dense bed and few NO are formed. On the other hand, great heat transfer resistance between the particle surface and gas phase will induce the generation of reducing gases such as NH$_3$, CO and H$_2$ during the combustion and some formed NO is reduced to N$_2$.

From the analysis above, the mixing time of particles below the elevation of the secondary air nozzle increases as the secondary air fraction increases. And as the primary air decreases, the oxygen content in dense bed decreases when particle combustion is not so plentiful for lack of oxygen. Under this reducing atmosphere, a main intermediate like HCN and NH$_n$ (n=1, 2, 3) will be reduced to N$_2$ by the homogeneous reactions of (10)-(13). Furthermore, according to the reduction mechanisms of char brought forward by Geol and De Soete, under the circumstances a zone in the dense bed relatively rich in char and carbon monoxide also would intensify the reduction of NO. Although the O$_2$ content in the dilute bed is higher and part of NO is formed from the volatiles and char nitrogen, N$_2$ in the dense bed cannot be oxidized to thermal NO because of the lower temperature in dilute bed, and the char plays an important role in the NO reduction and reduces the NO formation. Therefore, NO emissions decrease as the secondary air fraction increases.

The reduction reactions of NH and NO are as follows [15]:

$$NH + NH \rightarrow N_2 + H_2 \tag{10}$$

$$NH + N \rightarrow N_2 + H \tag{11}$$

$$NH + NO \rightarrow N_2 + OH \tag{12}$$

$$N + NO \rightarrow N_2 + O \tag{13}$$

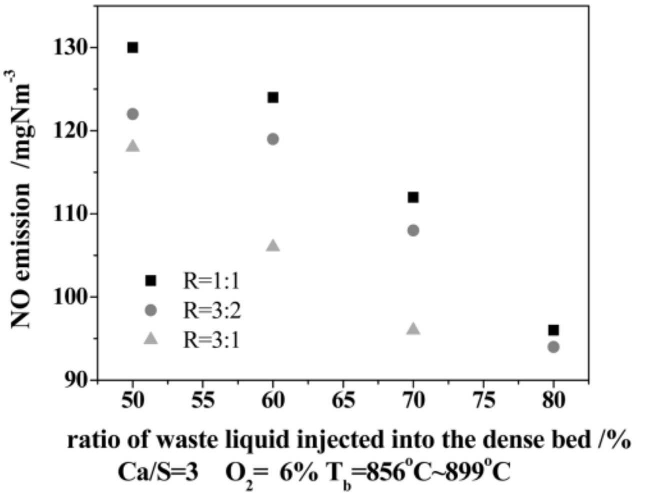

Fig. 4. Effect of the ratio of waste liquid injected into dense bed on NO emissions.

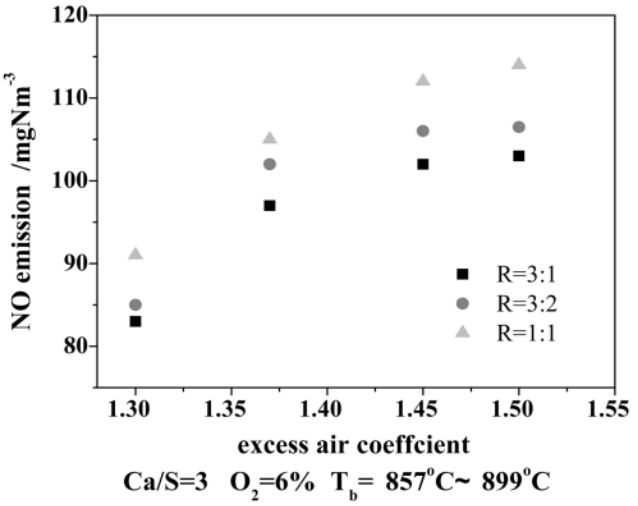

Fig. 5. Effect of the excess air coefficient on NO emissions.

3. Effect of the Ratio of Waste Liquid Injected into Dense Bed on NO Emissions

Fig. 4 presents the effect of ratio of waste liquid injected into the dense bed on NO emissions. It can be seen that NO emissions decrease as the ratio of waste liquid injected into the dense bed increases and the degree of decrease in NO emissions becomes small as R, the ratio of coal to waste liquid, increases. The reason for that can be found in the water content of waste liquid and combustion temperature, and homogeneous reactions and heterogeneous reactions are involved. Waste liquid used in the experiment has high water content and low combustible content. During the incineration, water was first heated and vaporized, which absorbed a great amount of heat and the temperature of the dense bed decreased.

As the fuel nitrogen usually exists in the form of ion together with different hydrocarbons forming annular and catenarian aromatic compounds like C_5H_5N, $C_6H_5NH_2$ with great heat inertia [15], less fuel nitrogen is released and less NO is formed with decrease in temperature, and the reactions $HCN \rightarrow NCO+ON \rightarrow N_2O$ are intensified [15-17]. Though the hydrocarbons react with O_2 to partially oxidize hydrocarbons, they are reactive by NO or NO_2 to form N_2 [18]. The content of radicals like O, OH and H decreased and the reaction rates of NO formation and decomposition slowed, which led to an increase in char and carbon monoxide and the increase in the reduction of NO [19-21]. Furthermore, the vapor resulting from the waste liquid incineration diluted the concentration of oxygen on the particle char surface, which also prevented the nitrogen from forming NO. Moreover, the operational temperature was controlled between 830 °C and 900 °C where rate of reactions (5)-(7) is so rapid that it's in favor of reducing NO emissions. Hence, it is recommended that the ratio of waste liquid injected into dense bed should be suitably controlled to gain high pyrolysis rate of wastes and low NO emissions.

4. Effect of Excess Air Coefficient on NO Emissions

Fig. 5 presents the effect of excess air coefficient on NO emissions. It can be seen that NO emissions increase with increase in excess air coefficient and decrease slightly as the ratio of coal to waste liquid (R) increases. The content of fuel and state of mixing with air and fuels in the dense bed are directly affected by the excess air. The higher the excess air coefficient, the less the particle concentration is, which is not good for incineration of waste liquid. On the other hand, an increase in flue gas velocity and improvement in the heat and material transfer are obtained when the excess air coefficient increases, which is good for combustion. From the analysis above, it can be found that the effect of excess air coefficient to combustion has two sides. To get minimum NO emissions, it is recommended to reduce the amount of excess oxygen in CFB with high combustion efficiencies desired, that is, it's to reduce the ratio of fuel to air.

5. Effect of Temperature on NO Emissions

The experimental results show that NO emissions increase with increase in temperature in CFB and that the increase in NO is mainly due to the fuel combustion. The reason is that during all experiments, the temperature in the main combustion zone was controlled between 850 °C and 900 °C, when the compounds with nitrogen in waste liquid had almost decomposed and formed NO which is little affected by temperature rising. Therefore, an increase in bed temperature only intensifies the conversion rate of fuel nitrogen to NO and that finally brings an increase in NO emissions.

CONCLUSIONS

An incineration experiment of waste liquid and coal was done and emission performance of NO_x was studied in the paper. Experimental results are valuable for incineration of waste liquid to control NO_x emissions in a circulating fluidized bed incinerator. At the same time, the experiment lays a foundation for the design of CFB that is special in incinerating waste liquid.

Because of the suppressive effect of low temperature and staged combustion of CFB, NO emissions were reduced and NO concentrations during all experiments were quite low, far below the emission standard in China (500 mg/m^3) for such a facility. NO emissions increase with increase in the flow rate of waste liquid incinerated or excess air coefficient or the bed temperature and those decrease with increase in ratio of waste liquid injected into dense bed. At certain excess air coefficient, NO emissions decrease with increase in the secondary air fraction. During the incineration of waste liquid, it is recommended to choose the proper flow rate of waste liquid and appropriate ratio of waste liquid injected into dense bed to gain low NO_x emissions and maintain high combustion efficiencies without risk for bed fusion.

NOMENCLATURE

LHV : low heat value [MJ/kg]
T_b : temperature in dense bed [°C]
R : ratio of coal to waste liquid

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