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Study on Nitrous Oxide Emission in Boiler Furnace

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A theoretical investigation on a kinetic mechanism of nitrous oxide formation in flames with different fuels was carried out for purposes of minimizing the total NO_X yield. The effect of fuel type and combustion condition on N_2O emission is discussed. It is found that N_2O constitutes a relatively small fraction of the total NO_X formation, but it is of great importance to both NO formation and NO reduction from fuel nitrogen (N^f) and molecular nitrogen (N_2).

Keywords: nitrogen oxide, nitrous oxide, kinetic mechanism, fuel combustion.

INTRODUCTION

The nitrogen oxides (NO_X) yield usually is determined by nitric oxide (NO). Nitrous oxide concentration in total NO_X yield is low. Experimental measurements of N_2O concentrations in exhaust gas with different fuels showed that N_2O levels in furnaces usually do not exceed 5-16 ppm[1,2]. N_2O concentration with exhaust gas into the atmosphere is lower. For example, the jetting level of N_2O for different fuel fired boilers are: for pulverized coal 0.2-0.8 ppm, for fuel oil 0.1-0.8 ppm, for natural gas ≤0.2 ppm[2,3]. This proves that the jetting levels of N_2O air low. But according to some experimental results[4] N_2O is of great importance to both NO formation and NO reduction from fuel nitrogen (N^f) and molecular nitrogen (N_2). As noted in some reports[4], a significant amount of N_2O is formed as a by-product of the $RAPRENO_X$ process and N_2O is an important nitrogen oxide under fuel lean conditions. Hence, the mechanism for N_2O formation and removal is of interest.

Series of numerical experiments for boiler furnace with heavy oil or natural gas under different conditions are completed in this paper. All computations use mathematical model reported in author's previous work[5]. N_2O formation mechanism and its effective factors are discussed through the analysis of the calculated results.

NITROUS OXIDE FORMATION MECHANISM

Studies indicate that N_2O is a very short lived species in fuel combustion process. Calculated (by this paper) concentration of the N_2O in flame with fuel oil containing N^f is illustrated in Fig.1. From this figure it can be seen that the N_2O formation is taking place in the two zones. N_2O is formed in primary flame zone at first and rapidly reaches a peat level, then nearly all of the formed N_2O is consumed. Its concentration in the gas stream tends to zero. Fig.2 shows principal N_2O formation dynamic process in flame with natural gas. In this figure the concentration profiles of partial intermediate substances and nitrogen oxide (NO) for
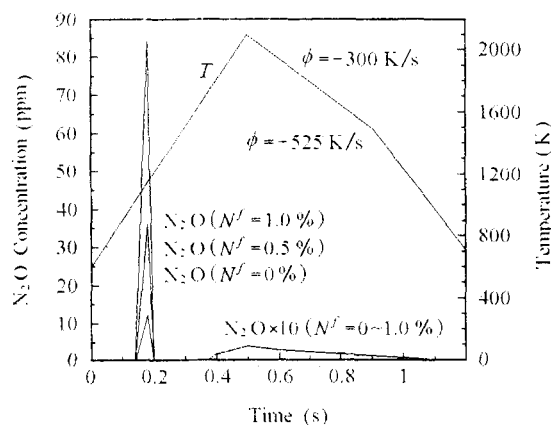

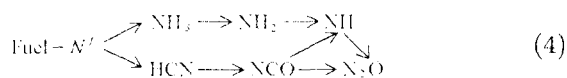Fig.1 Dynamics of nitrous oxide yield in oil-flame

study of N_2O formation mechanism are illustrated. Second zone of N_2O formation is in the high-temperature flame region. Maximal value of formed N_2O in this zone is small, but afterwards all of the N_2O is removed (see Fig.1).

As compared with boiler furnaces, the process of fuel combustion in gas turbines is significantly different both in the air allocation and in the residence time of the exhaust gas in combustion chamber. But dynamics of N_2O emission is essentially the same in both cases. N_2O jetting concentration from gas turbines is the same order of magnitude as boiler furnaces.

From analysis of N_2O and NO formation process it can be seen that N_2O always reaches maximum earlier than NO does in process of combustion not only with natural gas but also in case with fuel oil containing N^f. It may be determined from analysis of the reaction integrals that the principal channels of N_2O formation include the following reactions:

$$N_2 + HO_2 \rightarrow N_2O + OH \tag{1}$$

$$NCO + NO \rightarrow N_2O + CO \tag{2}$$

$$NH + NO \rightarrow N_2O + H \tag{3}$$
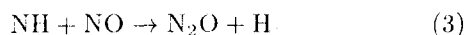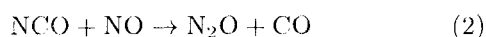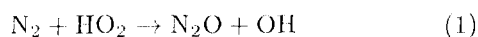
In gas flame, the principal channel of N_2O formation is reaction (1). The rate of this reaction depends on the HO_2 concentration. From Fig.2 it can be seen that a large amount of HO_2 is formed in the low-temperature region in the flame. Reactions (2) and (3) are the important channel of N_2O formation in flames with liquid (oil) and solid (coal) fuels. Since fuel nitrogen (N^f) is released from fuel into the gas phase mainly as HCN and NH_3 during the devolatilization process[6], the following process may be obtained:

$$Fuel-N' \underset{\searrow\ HCN \longrightarrow NCO \longrightarrow N_2O}{\overset{\nearrow\ NH_3 \longrightarrow NH_2 \longrightarrow NH}{\diagdown}} \tag{4}$$

Experimental data[7] also proved the above mentioned conversion process from fuel nitrogen to N_2O. In these experiments additive containing HCN is injected into nonburning zone. Experimental results show that N_2O yield was increased as a consequence of process (4). In this paper calculated results also show that N_2O yield in flame with 425 ppm of added HCN is increased by 20%, but injecting 10 ppm NO into the same flame did not change the N_2O yield (see a comparison between Fig.2a and 2b). It can be seen that calculated results coincide with experiments[7]. Rapid increase of concentration of the radicals O, H, OH after the beginning of fuel combustion (see Fig.2) reduces the rates of forward reactions (1)–(3). In this

case, formed N_2O is rapidly removed, forming molecular nitrogen (N_2). The most important N_2O removal channels are the following reactions:

$$N_2O + H \rightarrow N_2 + OH \tag{5}$$

$$N_2O + OH \rightarrow N_2 + HO_2 \tag{-1}$$
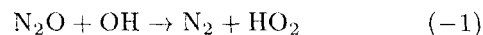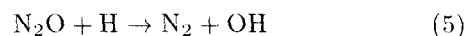
Analysis of the reaction integrals shows that N_2O removal reactions, forming NO, in fact, do not go on because the rates of reaction (6) and (7):

$$N_2O + O \rightarrow N_2 + NO \tag{6}$$

$$N_2O + H \rightarrow NO + NH \tag{7}$$
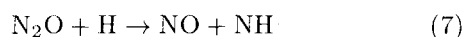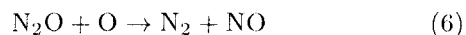
are very small.

Thus, formed N_2O in primary flame zone is almost fully converted to N_2. An important result can be obtained from the above discussion: the more fuel nitrogen is converted to N_2O in primary flame zone, the less final value of NO_X concentration in flue gas. According to report of Ref.[8], thermal pretreatment of pulverized coal can decrease NO formation. Perhaps it can be explained as follows: during the thermal treatment of pulverized coal, a part of the fuel nitrogen is first converted to N_2O by (4) and then N_2O is removed, forming N_2. From this it can be seen that if volatile ignition can be retard and the supply and mixing with secondary air flow can be postponed in pulverized coal combustion process, then fuel nitrogen is removed first by channel (4), forming N_2O, and then the N_2O is fully converted to N_2. Thereby, finally NO_X yield will be decreased.

In RAPRENO$_X$ process we also found a large amount of N_2O. RAPRENO$_X$ is one of several promising NO_X abatement schemes based on aftertreatment of combustor exhaust products. In RAPRENO$_X$ cyanuric acid is injected into an exhaust stream for reducing NO. The mechanism of the RAPRENO$_X$ process is discussed in more detail by Miller and Bowman[9]. Fig.3 shows the experimental data[4] and calculations from this study. Concentrations of principal species in RAPRENO$_X$ process are illustrated in this figure. From Fig.3 it can be seen that selection of process temperature is very important because effectiveness of the process directly depends on temperature. Analysis of reaction integrals, supplied by calculation, shows that mechanism of RAPRENO$_X$ includes following reactions:

$$(HOCN)_3 \rightarrow 3^*HNCO \tag{8}$$

$$HNCO + OH \rightarrow NCO + H_2O \tag{9}$$

$$NCO + NO \rightarrow N_2O + CO \tag{10}$$
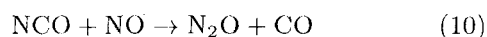
Then N_2O is converted to molecular nitrogen (N_2) by reactions (5) and (-1).
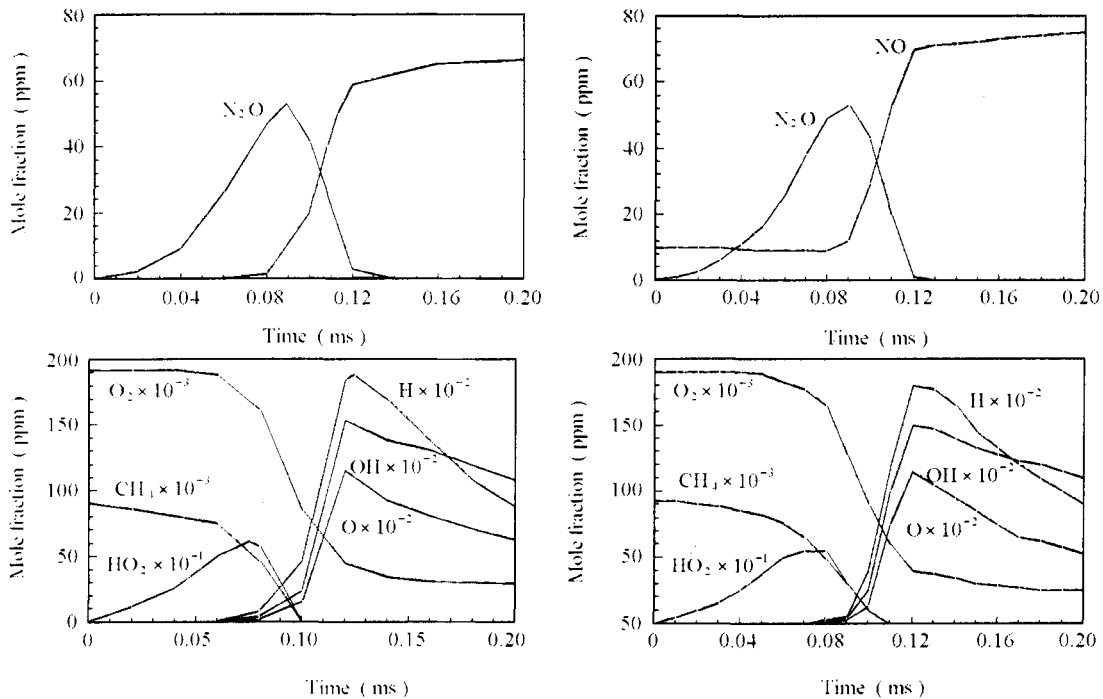
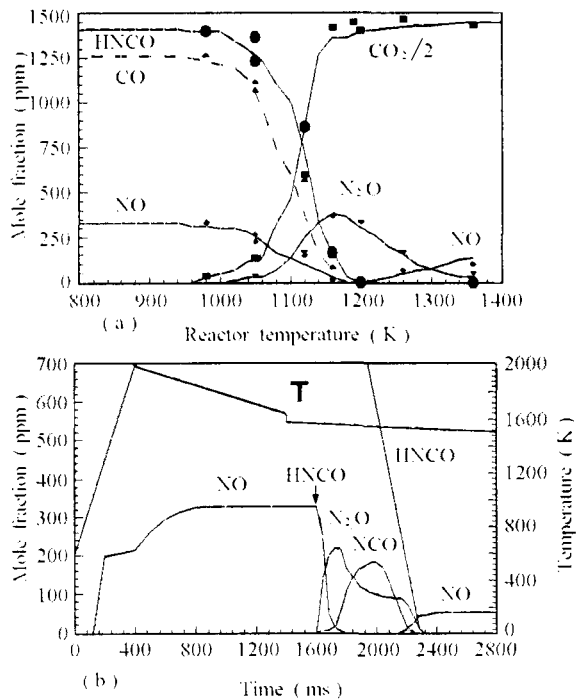**Fig.2** Calculated concentrations of NO, N_2O and partial intermediate radicals in gas-flame

Fig.3 Measured[4] (a) and calculated by this paper (b) species concentions in $REPRENO_x$ process

From above discussions it can be seen that N_2O is always is a very short lifetime intermediate substance both in primary flame zone and in passage of exhaust gas, and nearly all of the N_2O will be converted to molecular nitrogen (N_2). Presence of N_2O formation and removal process reduces part of NO and decreases final NO_X yield.

EFFECTIVE FACTORS ON N_2O EMISSION

Effective factors on N_2O emission include fuel type and combustion conditions, such as fuel structure (as ratio of carbon and hydrogen atom in fuel content C/H), fuel nitrogen content (N^f), excess air (α), flame temperature (T), flame heating and cooling rates (ϕ), etc.

Effect of the ratio C/H on N_2O emission and maximal value N_2O_{max} are shown in Fig.4 (calculated by the results in this paper). Maximal value of N_2O_{max}, not depending on stoichiometric ratio (α), is always observed in CH_4-flame and minimal value — in H_2-flame (see Fig.4). It depends on HO_2 concentration in flame. Fig.4b shows that maximal value of N_2O_{max} is reached in combustion of gaseous fuels with minor molecular weight (C/H=0.2-0.3) for different α. Effect of fuel nitrogen (N^f) on N_2O emission is shown in Fig.1. N_2O emission in flames with fuel containing N^f depends not only on content N^f, but on rates of reactions, corresponding to forming N_2O formation in primary flame zone, but concentration N_2O in exhaust gas nearly does not depend on content N^f.
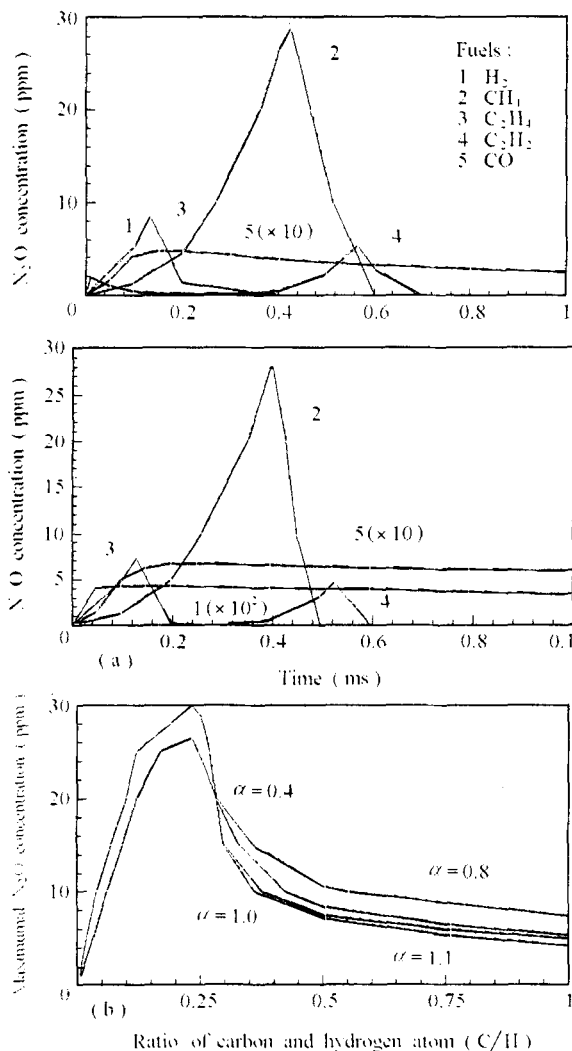
Fig.4 Influence of gaseous fuel content on N_2O emission

Effect of excess air (α) on N_2O emission is illustrated in Fig.5 (calculated by this paper results). Process of N_2O formation moves to root of flame, and the rates of N_2O formation and removal increase with increasing α. Effect of α on N_2O_{max} is different for various kind of fuel (Fig.5a). For example, with increasing α, N_2O_{max} is directly proportionally increasing in CH_4-, H_2- and CO-flames and linearly decreasing in C_2H_4- and C_2H_2-flames, since the HO_2 has different dynamics of formation in flames with different fuels.

Flame temperature is one of the most important factors of effect on combustion process. Fig.5 also shows the effect of temperature on N_2O_{max}. Fuel burn out time is enormously abated and NO is rapidly formed with increasing flame temperature. In this case, formed N_2O yield, of course, is increased. Only when T >1900 K, α has obvious influence on N_2O emission (Fig.5b).

Maximal flame temperature and rates of the flame heating and cooling have a little influence on N_2O

yield both in primary flame zone and in high-temperature burning region. Even if T_{max}=2100 K, final N_2O yield does not exceed 0.15 ppm.

Injecting exhaust gas or water into furnace can effectively reduces thermal NO formation because of decreasing flame temperature and rate of flame heating, but these techniques, in principal, have no effect on N_2O reduction.
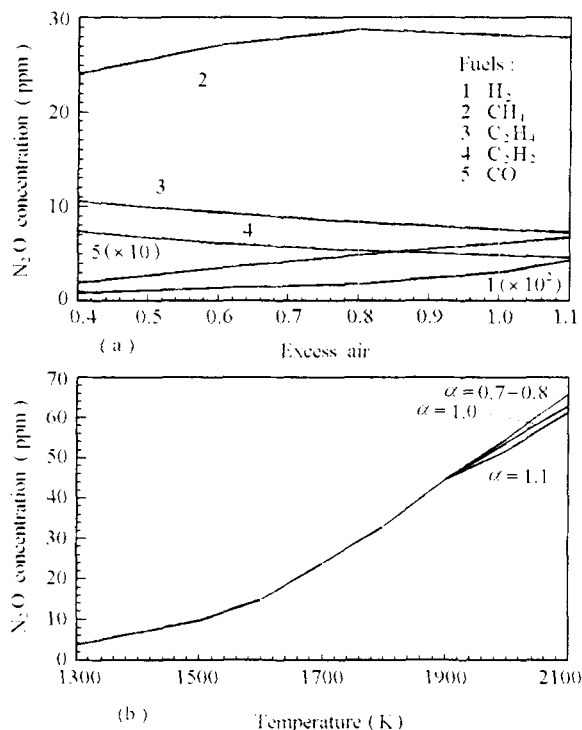

Fig.5 Effect of excess air and flame temperature on N_2O yield

CONCLUSIONS

The conclusions can be summarized:

(a) Nitrous oxide formation is related to NO emission along flame. Relatively large N_2O yield is formed in the primary flame zone during a very short time interval, but formed N_2O is rapidly and nearly fully converted to N_2 after reaching maximal value of N_2O_{max}. The mechanism of N_2O emission is described by reactions (1)–(3) and (5).

(b) Inject additive containing nitrogen (as cyanuric acid) into passage of exhaust gas in suitable temperature region can reduce NO and notably abate NO_x yield.

(c) Concentration of N_2O in flue gas is very low. Its contribution to total NO_x yield may be neglected.

(d) N_2O takes very important effect on abatement of NO_x yield. If conversion of fuel nitrogen to N_2O

in primary burning zone can be achieved, then fuel–NO formation may be decreased, since all of the N_2O will be reduced to molecular nitrogen (N_2) in later combustion process.

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