

Effect of the Waste Weight on Nitrogen Oxides Formation in a non Temperature-Controlled Laboratory Scale Rotary Kiln

Jean Fidele NZIHOU, Salou HAMIDOU, Medard BOUDA

Abstract— Waste incineration, both urban and industrial, is one of the way of reducing their volume and weight. However, environmentally sound waste incineration can only be achieved if done according to well known physico-chemical conditions. This study focused on the formation and reduction mechanisms of nitrogen oxides (NO_x) with a non temperature-controlled laboratory scale rotary kiln. It was found that NO_x releases vary with the weight of the waste in the kiln. For temperatures lower than 900°C , it appears that NO_x emissions are strongly influenced by the temperature and the local concentration of oxygen. Experiments show the effect of combustible weight on emissions of nitrogen monoxide (NO). NO_2 was not found for peak temperature less than 1012°C or waste weight less than 3kg. In ours experimental conditions, NO is essentially formed by the mechanism of “fuel NO ”. It is highly influenced by local oxygen concentration in the reaction place, but moderately influenced by the temperature. Lack of the kiln’s temperature control implies kiln’s operation temperature variations. We found that these variations are related the combustible load. NO_x and residual O_2 concentration in the kiln’s combustion zone where correlated to the combustible weight.

Keywords — Waste, incineration, laboratory scale rotary kiln, nitrogen oxides, temperature, combustible, pollutants.

1 INTRODUCTION

Thermal treatment of waste is one of the options adopted in recent decades for their elimination. Considerable efforts have been made in mastering the combustion process in order to avoid the transfer of pollutants. The main pollutants meet are nitrogen oxides, carbon oxides and sulfur oxides. Much of the waste consists of organic products which lead to formation of non toxic gases (CO_2 , H_2O , N_2) and toxic substances (NO_x , SO_x , CO_x , Cl_2 , HCl , ...) during the combustion process.

These gases cannot be released into the atmosphere without damage. A good knowledge of their mechanism of formation and destruction (especially for toxic gases), is crucial in order to reduce their releases. These pollutants releases are in one hand linked to poor combustion conditions and in the other hand to the presence of precursor in the raw waste or by-products of combustion. Because experiments with industrial kilns are costly and difficult to carry out, we merely conduct fundamental research with a laboratory scale rotary kiln.

Several studies have already been carried out with temperature-controlled furnaces. That kind of furnaces help investigates at various temperatures and allows one to take the operation temperature as parameter. Furnaces with temperature regulation are often electrically heated. However, there are several contexts (for example fuel heated kilns) where kiln’s temperature is not regulated.

Because the laboratory scale rotary kiln we are using here is fuel heated and has no temperature control system, parameters that could considerably impact on the temperature should be studied.

Our choice is motivated by the fact that operating temperature of a furnace is one of its driving parameters and the effects of toxic gases on human health and the environment. Given the content of polluting gases from incineration systems, all parameters that might affect operation conditions should be studied in order to avoid pollution transfer when working with a non temperature-controlled rotary kiln.

However the complexity of the involved reactions and the high number of possible interactions between pollutants, has led us to restrict the number of pollutants to be studied in this paper.

This paper mainly focused on the nitric monoxide is subdivided as follows: firstly, a small survey of

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interactions between NO and other gaseous pollutants is done and then follows NO formation and reduction mechanisms. Secondly we will experimentally study the effect of the fuel weight on the formation of nitrogen monoxide in a thermal rotary kiln. Finally we will discuss our experimental results under the light of existing studies.

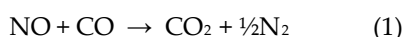
2 LITTERATURE REVIEW

2.1 Interactions between pollutants

Studies on formation and reduction mechanisms of gaseous pollutants shows the existence of significant interactions between these gaseous compounds. These reactions involve a large number of reaction species. Below we will briefly summarize the studies on the interaction of nitrogen oxides with other pollutant gases.

2.2 Nitrogen oxides – Carbon oxides interactions

Emissions of nitric oxide are strongly influenced by the CO concentration. Work by Glarbrog et al. [1] on the oxidation of HNCO have shown that the presence of CO in the reaction medium significantly promoted the oxidation of NO by HNCO. At 930 ° C, it is almost completely oxidized to NO, N₂O and N₂. N₂O concentration increases with temperature up to 1000 ° C and then decreases. The NO concentration is, for its part, an increasing function of temperature. However, when added to the starting mixture of NO, one finds that the CO leads to a reduction of nearly 60% of the initial NO to N₂O and N₂ at temperatures below 1000 ° C. Beyond 1000 ° C, there is an increase in the concentration of NO. The work of Chan et al. [2] showed that the reduction reaction of NO may be heterogeneous or be by direct reaction with CO according to equation:



2.3 Reactions between nitrogen oxides and hydrocarbons

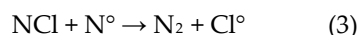
Work made by Dagaut et al. [3] on the reduction of NO by C₂H₆ and Lindstedt et al. [4] on the oxidation of NH₃ show the importance of the interaction of hydrocarbons on the reduction of NO. The effectiveness of the reduction of NO is an increasing function of the concentration of hydrocarbon species and temperature. Indeed, the work of Alzueta et al. [5] shows this result.

2.4 Chlorine – nitrogen oxides interactions

The NO content is substantially reduced by the presence of chlorine in the fumes. N° radicals combine with Cl° atoms to produce intermediate NCl according to the reaction:



NCl in turn reacts with N° radicals to form dinitrogen N₂ according to the reaction:



Consumption of N° radicals thus limits the formation of NO. In addition, studies of Mao and Barat [6] have shown that chlorine atoms react with H° radicals to produce HCl, which by a subsequent reaction with the OH° radical limit CO oxidation.

2.5 Formations mechanisms of nitrogen oxides

Nitrogen oxides formation mechanisms in flames study back to the sixties beginnings. It was driven by concerns of air pollution. On a chemical point of view, nitrogen oxides comprise all compounds of empirical formula N_xO_y with a degree of oxidation of nitrogen ranging from I to V. These compounds are: nitrous oxide (N₂O), nitrogen monoxide (NO), nitrogen dioxide (NO₂, also known as dimer, N₂O₄), nitrogen trioxide (N₂O₃) and nitrogen pentoxide (N₂O₅). Of all these oxides, only NO, NO₂ and N₂O are typically designated as NO_x. From this group, NO and NO₂ play an important role in air pollution [7]. As we will see in the experimental results, NO₂ is only present at high temperature and our measurement apparatus (Testo 350™) had no N₂O measurement cell. We will therefore restrict the study to the mechanisms of formation of NO.

Three mechanisms of formation of nitrogen monoxide during combustion have been identified, namely:

2.6 Mechanism of "thermal NO" (Zel'dovich) [8].

NO is formed from molecular nitrogen of the air during combustion. Production takes place in the flame and requires the provision of a high energy to break the triple bond of dinitrogen molecules. Its formation is possible only at high temperatures above 1250 ° C.

2.7 Mechanism of the "fuel NO" (De Soete) [9], (Miller and Bowman) [10].

NO is formed from the nitrogen contained in the fuel. Its production depends on the richness of the fuel - air mixture and is strongly linked to the local concentration of oxygen in the reaction medium. The nitrogen concentration in the fuel and temperature has little effect on the combustible's NO production.

2.8 Mechanism of the "early NO" or "prompt NO" (Feminore) [11].

It is actually a combination of the two mechanisms mentioned above. Its formation result from molecular nitrogen of the air likes the thermal NO, but in this case it is subjected to reactions with hydrocarbon radicals. Its

mechanism is similar to that of the fuel NO, but takes place in high temperatures conditions ($> 1200^{\circ}\text{C}$) and in the presence of high concentrations of hydrocarbon species.

3 MATERIALS AND METHODS

3.1 The rotary kiln

The kiln used here is a co-current one (fuel, air, secondary air and waste are introduced on the same side). It is composed of four main components: the combustion chamber, the afterburner, the chimney and the driving unit.

The combustion chamber consists of a cylinder slightly inclined (17°), to which is attached the primary burner called burner 1 (RG1). This cylinder has diameter of 88 cm, length of 108 cm, is placed on bearings ball that allow its rotation around its axis of symmetry. In the middle of its axis of symmetry runs a pipe supporting four thermocouples for temperature measure noted T_1 , T_2 , T_3 and T_4 from RG1 primary burner to the afterburner chamber (fig. 1).

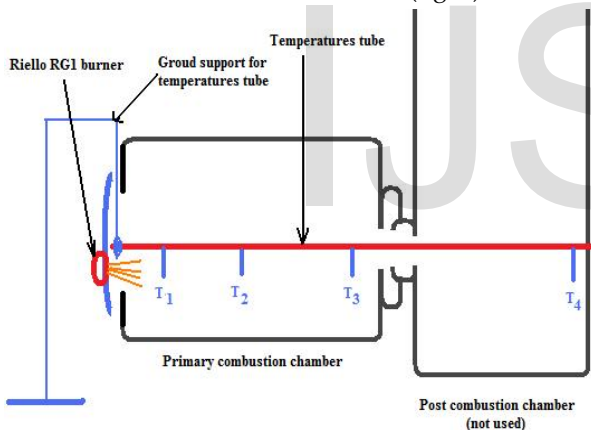


Fig. 1: primary combustion chamber with thermocouples positions

3.2 Data acquisition unit

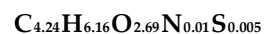
The gases from the combustion are analyzed with a Testo 350 TM, which allows to measure:

- The volume percent of oxygen in the combustion gases (0 to 21%),
- The concentration in parts per million (ppm) of NO_x, CO and SO₂
- The proportion of CO₂ (%), calculated from the concentration of O₂ and CO
- The temperature of the gas in the post-combustion chamber.

Data coming from the Testo 350 TM are sent to the RS232 serial port of the acquisition PC. Four thermocouples are placed inside the primary combustion chamber. These are connected to the centralization box "Clear Signal MX 2000[®]" with a compensation cable. The centralization box is connected to an analog-digital data acquisition card inserted in an ISA slot of the acquisition PC using a S-1800 cable. Data from the combustion gases and the temperatures of the thermocouples are processed with Tespoint TM software.

3.3 The household waste model

Direct studies on industrial facilities are not only too expensive, but also difficult to carry out, mainly because of the heterogeneity of real waste. In addition, because of their heterogeneity and varying composition, experiments with real waste are very complex and difficult to master. For the sake of reproducibility of experiments, we use the model of the combustible fraction of household waste of the city Ouagadougou developed by Nzihou (2005). Composition of the waste used here is 53% wood, 26% cardboard and 21% plastic. The wood used consist of wood is chips furniture manufacturing facilities. The cardboard is made of 2cm x 2cm pieces cut from cardboard packages. Plastics are made from mineral water bottles of which were removed labels, glue and printed papers or plastics. The elemental formula of this waste is:



3.4 Experimental protocol

All experiments were performed according to following procedure:

- measurement of the weight of the waste;
- cleaning the combustion chamber from the previous combustion waste materials;
- preheating furnace to have a temperature of about 150°C . If the experiment follows another, this condition is fulfilled if the oven is kept closed after the previous combustion for less than 10 minutes;
- introduction of waste into the furnace, and closing combustion chamber the door;
- checking and starting up the Testo 350 TM gases measuring apparatus;
- starting the data acquisition software Testpoint TM on the PC;
- starting the rotary kiln and the ignition of the waste;
- the combustion process will be considered as complete

and the acquisition stopped when all the following conditions are met: the residual O₂ concentration stabilizes at more than 19.5%, the CO₂ concentration is less than 1.5% and the temperature at the right side of the afterburning chamber (T₄) is less than 150 °C.

4 RESULTS AND DISCUSSION

We conducted four (04) sets of measures in 2005, 2007, 2008 and 2010. These four sets of measures were intended to ensure the reproducibility of experimental results. Taking in account small experimental variations, we can say that the results are reproducible. Table 1 summarizes the cumulative emissions of nitrogen oxides and the observed temperatures at "hot spot" of the kiln for 2008's set.

Table 1: NO and NO₂ releases and temperatures at various loads

Load	NO ₂ (mg/kg)	NO (mg/kg)	T ₃ max (°C) ¹	T ₃ av (°C) ²
No load	1	0	484	430
0.5kg	0	74	715	486
1kg	1	452	780	515
1.5kg	0	604	942	592
2kg	0	1016	987	646
2.5kg	0	1962	1006	631
3kg	0	1777	1012	674
3.5kg	85	3739	1039	603
4kg	51	5000	1052	668
4.5kg	79	5188	1020	713

Table 1 above shows that:

- cumulative emissions of nitrogen dioxide are virtually nonexistent from 0 to 3 kg load of fuel;
- NO emissions are regularly increases;
- temperatures are regularly increasing from 0 to 4kg of fuel;

Table 2 gives the peak and average emissions of NO.

Table 2: Mean values and maximum peaks of emission of NO as a function of the load of the fuel

Combustible load (kg)	NO Highest peak (mg/kg)	NO Average value (mg/kg)
0.5	6.0	0,6
1.0	18.0	3,65
1.5	22.0	4,87
2.0	36.0	8,19
2.5	79.0	15,91
3.0	53.0	14,39
3.5	144.0	30,28
4.0	137.0	40,51
4.5	155.0	42,11

Examination of table 2 shows that:

- The maximum value of NO (peak emission for each fuel load) increases with the load of the fuel;
- The average NO releases increases with fuel load, except for at 3kg (a decrease).

Fig. 2 shows the evolution of the temperature T₃ at different loads. The general shape of the curves is the same. Temperatures are around 400°C without load (0 kg) with changes in temperature of ± 25 °C. Without load, the kiln is only heated by gasoline fuel. Yet the flow of gasoline fuel and primary air doesn't change at all. This gives us an idea of the variability of temperature and gaseous emissions all over time without noticeable experimental changes. All the curves exhibit a peak temperature. This peak temperature denotes the combustion gases from the pyrolysis of waste constituents [12], [13], [14], [15]. After this peak, temperature decrease exponentially according to Arrhenius law.

Lets us consider in particular the peak temperature (peak temperature) for each fuel combustible load. This temperature (T₃) is given by the thermocouple located in the "combustion zone" (Fig. 3).

¹ Highest maximal (peak) temperature (T₃) among the four (T₁, T₂, T₃ and T₄) recorded in the kiln.

² For N values, the average is calculated with the following formula : $X_{av} = 1/N \sum X_i$

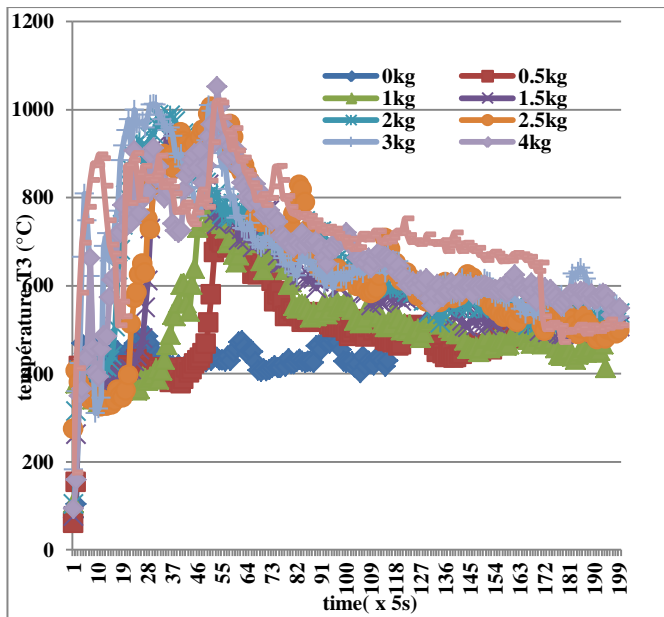


Fig 2: temperatures variations according to the kiln waste fuel

Fig. 2 above show the complexity of temperature variations over time. Curves are difficult to compare even if these have roughly sibling shapes. Temperatures fluctuations appear as random. These temperatures variations are the result of the highly complex nature of the combustion process. We looked for other operating parameters values, less prone to random fluctuations and found that the peak temperature for each waste weight is one of these. Fig. 3 depict peak temperature (Temp max T3) reached for each experiment.

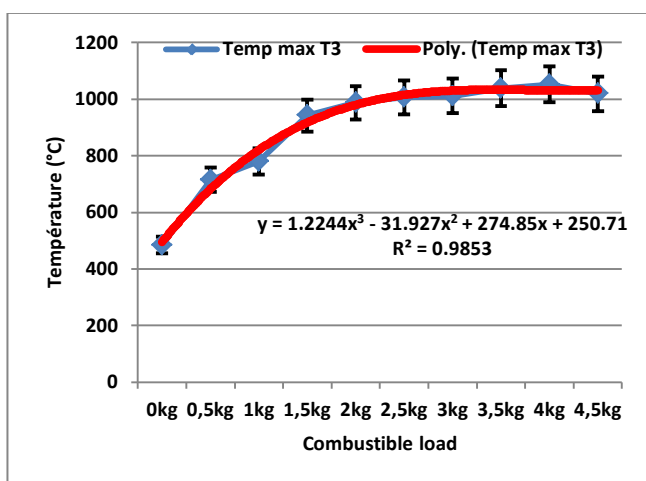


Fig. 3: Evolution of the peak temperature T₃ depending on the load

Fig. 3 suggests a correlation between the temperature (T₃) and fuel mass (m_w)

$$T_3 \text{ max } (^\circ\text{C}) = 1,224m_w^3 - 31,92m_w^2 + 274,8m_w + 250,7$$

From this fig. 3, the following observations and interpretations can be made:

- The determination coefficient of the tendency curve (R = 0.992) is quite close to unity. This suggests a good correlation between the mass and temperature.
- The error bars at seven percent (7%) include all points of the tendency curve;
- The peak temperature appears to decrease beyond 4.5 kg.

The explanation for the latter observation is the following: first the 5 kg mass has not been reached experimentally. The rotary kiln was already to the brim at 4.5 kg and few pieces of fuel were thrown out of the kiln by the air blast of the primary burner. This resulted in a loss of the fuel. This simply confirms that temperature cannot indefinitely grow with the rotary kiln used.

Fig. 4 depicts the evolution of NO emissions during incineration of the combustible fraction of the waste model. To better compare these emissions at each load, we plotted stacked curves. Regarding measures batch, achieving end conditions set out in handling the experimental protocol requires more time when mass increases. But that does not diminish the evolution of NO emissions.

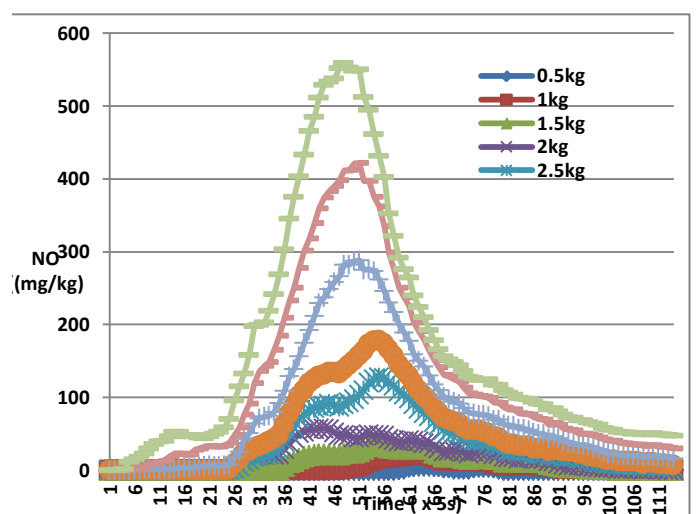


Fig. 4: Emission of NO in the kiln at different loads

From fig. 4 we can make some observations:

- The start time of measurable emissions of NO decreases as the mass increases (it shift from the right to the left). This is explained by the fact that when the mass of the fuel increases, the thermal power (heat available per time unit) increases. One then more quickly reaches higher temperatures when the mass of fuel increase. In fact, this reflects the fact that the level of NO increases with the reaction temperature [10], [16], [17], [18].
- The area covered by each curve, that is to say, the cumulative emissions of NO increases with the load of the fuel.

Fig. 5 shows the evolution of the residual oxygen in the reaction medium depending on the load of the fuel over time. From that fig. 5 the following observations can be made:

- The maximum peak oxygen consumption increase as the fuel load increase;
- The oxygen consumption is low and stable after 8 minutes (~ 105x5s) of ignition whatever the fuel load.

Comparison of fig. 4 and 5 shows that the formation of NO increases in the same direction as the oxygen consumption. We notice a very characteristic peak in fig. 5 giving the oxygen consumption and situated 4 minutes 10 seconds of the start of ignition (5x50 = 250s). This appearance is reflected in the curves of NO formation over time. On the contrary, temperature curves show some stabilization after the 250s of ignition. After 250s, all curves show an exponential decay.

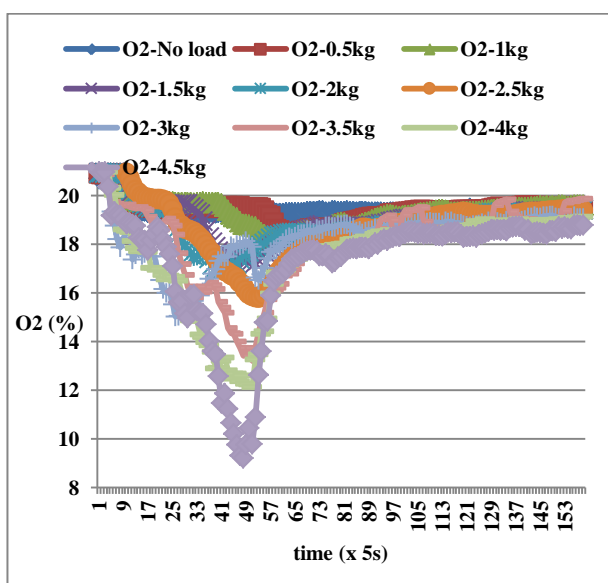


Fig. 5: Evolution of residual oxygen as function of the load over time

This confirms the fact that the formation of NO depends more than O₂ concentration in reaction medium than of temperature as already shown by De Soete [10] and Miller & Bowman [9].

The used waste model elementary formula doesn't contain chlorine. We have not found HCl in our flue gaz. It appears that using a model waste has highly helped us lower the complexity of involved reaction in this batch waste incineration experiments.

5 CONCLUSIONS

This study is non exhaustive and is limited to formations mechanisms of nitrogen oxides. It shows some of the complexity of the reactions involved in the process of burning waste. The use of a waste model helped us avoid introducing chlorine in the experiments. We found that, NO emissions are an increasing function of temperature; those of NO₂ appear at high temperatures beyond 1000°C in our case. The effect of temperature seems parametric and drive the emission levels of NO and NO₂. But the concentration of oxygen consumption is more localized in time, concentrated around 125s from the start of the combustion. Furthermore, temperature appears to be proportional to the mass of the fuel. Therefore we might perhaps consider using the mass of fuel waste as a parameter instead of the temperature in rotary kilns of same type that have no automatic temperature regulator.

Experimental results show that nitric oxide is the largest pollutant in our case. Other oxides of nitrogen are present only in very small quantities.

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