

The Influence of Bound Nitrogen Content in the Gaseous Fuel on the Formation of NO_x

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This paper describes the experiences with the combustion of gaseous fuel that contains as one of the components the nitrogen of low concentration. Such gaseous fuel with the bound nitrogen is mostly used in the primary steam reformer furnaces.

The main goal of the research was the investigation of the influence of nitrogen content in the gaseous fuel on the formation of NO_x during the combustion process. Two types of low-NO_x burners were tested. The first type of burner was the air-staged burner with the heat output of 0.5 MW and combusted the premixed mixture of fuel and combustion air. The second type of burner was the non-premixed fuel-staged burner with the heat output of 0.9 MW. The main difference between the used burners consists in different way of mixing of fuel with the oxidant (combustion air). As for the premixed burner, the fuel-oxidant mixture enters the combustion chamber premixed with the sub-stoichiometric content of oxygen; the left oxidant comes by the secondary air. As for the non-premixed fuel-staged burner, the all oxidant is mixed with the primary fuel at the outlet of the burner (the air excess is high) and the secondary fuel is combusted downstream in the second stage. The concentration of ammonia NH₃ in the fuel was ranging between 0 - 1 % by volume. The oxygen concentration in the flue gas was maintained in the neighborhood of 3 % on dry basis in all tests. Natural gas was used as the reference "clean" fuel that does not contain the fuel-bound nitrogen.

The results showed that the presence of fuel-bound nitrogen, in this case in the form of ammonia, significantly affects the formation of nitrogen oxides. As for the combustion of pure natural gas, the measured concentration of nitrogen oxides in the flue gas at the outlet of the radiation chamber was 150 mg/m³, respectively 100 mg/m³, when the premixed air-staged burner, respectively non-premixed fuel-staged burner, was used. However, when the fuel containing the ammonia was combusted, the concentration of nitrogen oxides increased several times.

Furthermore it was revealed that during the combustion of gaseous fuel containing the ammonia, ca. 25 % of chemically bound nitrogen in ammonia, respectively ca. 15 %, passed to the form of fuel NO when the premixed air-staged burner, respectively non-remixed fuel-staged burner, was used. Thus it can be concluded that the conversion of chemically fuel-bound nitrogen to the form of nitrogen oxides is also dependent on the combustion regime and type of burner.

1. Introduction

A primary steam reforming furnace is equipped with the group of burners, frequently fired by some kind of gaseous fuel. The combustion control of the thermal NO_x formation has been frequently carried out by the burner design that is configured either as air-staged and/or fuel-staged. Then, the approach of low-NO_x burners results in either "fuel-lean" or "fuel-rich" combustion zones in the furnace (Baukal, 2004).

In air-staging, approximately 70 % of the total amount of the combustion air is directed into the primary combustion zone together with the total amount of required fuel. This makes the primary zone "fuel-rich" in which the formation of NO_x is suppressed due to sub-stoichiometric combustion conditions, i.e. there is lack of oxygen and so the complete combustion of a fuel cannot be achieved. This has two effects: (1) the reduced flame temperature peaks, and, (2) the limited amount of oxygen available for NO_x formation. The balance of the combustion air is directed outside of the primary combustion zone in order to complete the combustion of the fuel (Baukal, 2004).

Most of the low-NO_x burners are designed as fuel-staged (Belohradsky and Kermes, 2012). About 25-35 % of the fuel is directed together with the air into the primary zone. Since there is a high excess of oxygen in the primary flame zone, the formation of NO_x is suppressed due to the reduced peak flame temperatures. Moreover, the prompt NO_x formation (i.e. the breakdown of hydrocarbon radicals in the flame zone such as C, CH, CH₂ may react with the atmospheric nitrogen to form CN, HCN, H₂CN, NH) is also slowed down due to intensely oxidizing conditions (Colannino, 2002). The balance of the fuel is then injected downstream of the main combustion zone.

The rate of the thermal NO_x formation highly depends on the flame temperature, the residence time, and the excess air and/or the air deficit (Baukal, 2004). It is common to specify the air conditions in the combustion zone in terms of the equivalence ratio. The equivalence ratio is defined as the ratio between stoichiometric volumetric ratio of oxygen/fuel and actual volumetric ratio oxygen/fuel. Using this definition, if the equivalence ratio is less than one the combustion runs under the "fuel-lean" conditions, and vice versa (El-Mahallawy and Habik, 2002).

As for the steam reforming furnace the mixture of the off-gas coming from the ammonia synthesis section (that contains chemically bound nitrogen) and the fuel, e.g. natural gas, is usually used. However, this practice is characterized by the increased NO_x formation since the bound nitrogen in the fuel contributes to the formation of fuel NO_x in the combustion zone.

This work was aimed at the comparison of two different types of burners, which are typically used in the primary steam reforming furnaces. The study is focused on the comparison of NO_x formation during the combustion of both pure natural gas and natural gas enriched with ammonia. As a consequence of natural gas enrichment with the ammonia, NO formation is increased. This process is described with the following reaction (Zhenyu et al., 2009):



The nitrogen chemically bound in the fuel (in the form of NH₃) usually oxidizes to NO, however, the rate of conversion can be reduced owing to the competitive reaction of NH₃ with NO depending on the local conditions, especially on the temperature:



The reactions (1) and (2), when NO and N₂ are formed simultaneously, strongly depend on the combustion operating conditions. When the low- NO_x burners combust the non-premixed mixture of fuel and combustion air (referred as fuel-lean) the reaction (2) prevails. On the contrary, when the premixed mixture of fuel and air (referred as fuel-rich) is combusted then the oxidation of bound nitrogen prevails.

The fuel NO makes up the bulk of total NO_x when the fuel containing higher concentration of nitrogen is combusted. The typical conversion accounts for more than 80 %. It is caused by that fuel NO is formed more readily than thermal NO because the N-H and N-C bonds are much weaker than the triple bond in molecular nitrogen which must be broken for thermal NO formation (Hill and Smoot, 2000).

2. Specific objectives

The main aim of research was to study the influence of ammonia concentration in the gaseous fuel on the formation of NO_x. This was compared with the formation of NO_x during the combustion of the fuel that does not contain ammonia.

Two types of low-NO_x burners were investigated. The first of the burners was the premixed air-staged burner that combusts the pre-blended mixture. The heat output of this burner was 0.5 MW. The second type of the burner was used without pre-blending of the mixture with fuel-staged supply (non-premixed fuel stage burner) with the heat output of 1 MW. NH₃ concentration in the fuel was varied in the range of 0–1.8 vol. %. Both burners were operated with the excess of air 3 vol. % of O₂ in dry flue gas.

3. Experimental setup

3.1 Testing facility

The combustion tests were carried out at the burners testing facility (Figure 1). The key apparatus of the facility is the two-shell horizontal water-cooled combustion chamber with the inner diameter of 1 m and the length of 4 m. The cooling shell of chamber is divided into seven individual sections with independent supply of cooling water. Each section is equipped with sensors for measurement of cooling water flow rate,

inlet and outlet temperature. This unique construction enables to partially simulate conditions similar to the ones in fired process heaters and to assess the heat extracted from the hot flue gas to the combustion chamber wall lengthwise the flame. Flue gas is exhausted from the combustion chamber through the flue gas stack where three measurement and sampling spots are located for measuring of pressure in the combustion chamber, flue gas temperature and flue gas compositions (O_2 , CO, NO, NO_2), which is measured using the Testo 350-XL analyzer. The measuring ranges of the gas analyzer were 0–25 % for O_2 , 0–10 000 ppm for CO, 0–3 000 ppm for NO, and 0–500 ppm for NO_2 . The concentrations of species are expressed on a dry volume basis.

3.2 Premixed air-staged burner

The first of the burners used in the experimental study was the two-air-staged ejector burner fired by natural gas. The burner quarl is shaped into the diffuser that enlarges from the diameter of 200 mm to the diameter of 300 mm. The diameter of the nozzle of the ejector is 8.7 mm. The outlet nozzle head consists of 37 nozzles, each nozzle with the diameter of 12.5 mm. The total flow rate of the combustion air is controlled by the primary and the secondary air register. The primary air register controls the flow rate of the primary combustion air that is sucked into the burner due to the ejection effect of the ejector nozzle. The primary combustion air is mixed with fuel in the burner body and the created mixture is then combusted in the combustion chamber behind the nozzle head. The ejector nozzle is usually designed for the air intake of about 70 % of stoichiometric amount of air. The balance of the air is supplied into the burner by means of the secondary air register. This proportion of air is then combusted as the diffusion flame.

The ammonia was injected into the mixture chamber that was located before the burner. The flow rate of ammonia was measured by the flowmeter.

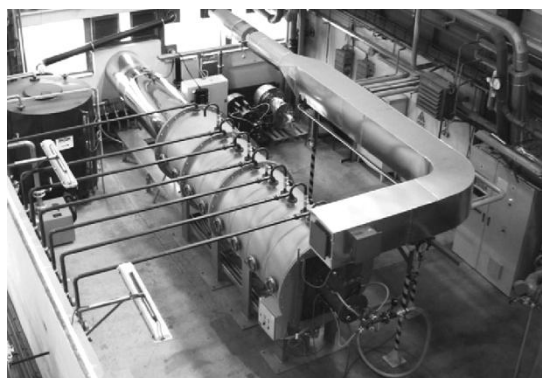


Figure 1: The water-cooled combustion chamber in the burners testing facility

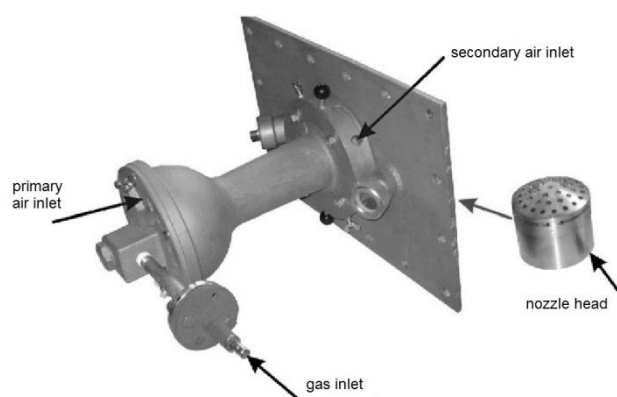


Figure 2: The premixed two-air-staged burner

3.3 Non-premixed fuel-staged burner

The second of the burners used in the experimental study was the two-fuel-staged burner fired by natural gas. The scheme of burner is shown in Figure 3. The inner diameter of the burner quarl is 300 mm. The

gas inlet consists of twelve primary nozzles and eight secondary nozzles. The primary nozzles are drilled in the primary nozzle head and are aligned in two circular sets. There are four nozzles with the diameter of 3.0 mm in the first set and eight nozzles with the diameter of 2.6 mm in the second set. The maximum thermal input of the primary stage can be regulated by the exchangeable primary gas throttle of different diameters placed before the inlet to the primary stage of the burner. During the tests using staged combustion the ratio primary/total fuel was set to 0.3.

The secondary gas inlet is provided by four nozzle heads with the pitch angle of head of 30°. Each head has two nozzles with the diameter of 3.3 mm. The burner is constructed so that it is possible to change the position of secondary nozzle heads towards the burner tile, namely in tangential and radial direction. In the reference tangential position the nozzle heads are oriented directly towards the burner axis. The orientation can be changed both clockwise (in the direction of flame's swirl motion – positive angle) and counter clockwise (negative angle). In the reference radial distance the distance of nozzle heads from the burner axis is 180 mm and can be increased by 50 mm. During the tests using staged combustion the secondary nozzle heads were turned by +20° and their radial distance was set to the maximum (230 mm). The burner is equipped with the so-called flame holder that has the form of swirl generator. The swirl generator consists of eight pitched blades and is mounted to the central burner pipe. Flame ignition was performed with a gaseous premixed natural-draught ignition burner with the thermal input of 18 kW. The ammonia was injected directly into the fuel supply pipe before entering the burner.

4. Plan of combustion tests

The combustion tests were focused on the study of the influence of ammonia content in the fuel on the formation of nitrogen oxides. The concentration of ammonia was varied in the range of 0–1.8 vol. %. The experimental study was carried out using two types of burners. As for the premixed two-air-staged burner the tests were carried out at the nominal thermal input of 0.5 MW. The tests using the non-premixed two-gas-staged burner were performed at two heat outputs: (1) at 0.5 MW so that the results were compared with the results obtained during the tests with the premixed burner, and, (2) at the nominal heat output of 1 MW.

5. Results and discussion

Figure 4 shows the concentration of NO_x [mg/m^3] as a function of the ammonia concentration in the fuel for the premixed air-staged burner. The heat output of the burner is 0.5 MW. From the figure NO_x increases with the increasing ammonia concentration. The graph displays both the theoretical concentration of NO_x at 100 % conversion of ammonia into NO and the measured concentration of NO_x at real ammonia conversion rate.

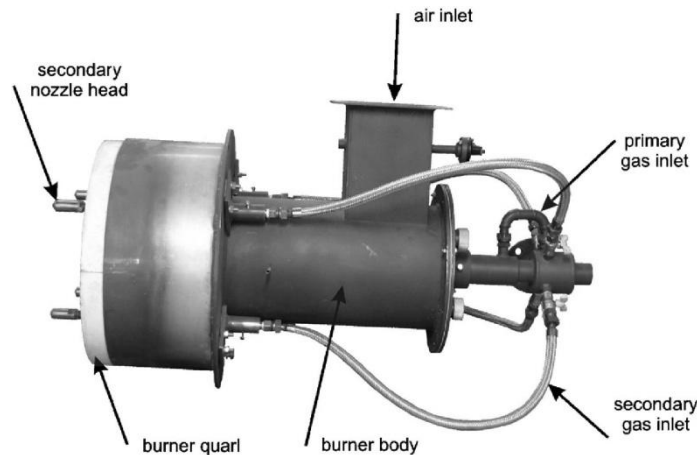


Figure 3: The non-premixed two-gas-staged burner

Figure 5 shows the measured NO_x emissions for the non-premixed gas-staged burner. The combustion tests were carried out according to the plan at two heat outputs (0.5 MW, 1 MW). The tests revealed that the NO_x emission (and thus the ammonia conversion rate as well) is equal for both heat outputs. For this reason only the results obtained during the tests at the nominal heat output (1 MW) are discussed. It is evident from the figure that NO_x concentration again increases with the increasing ammonia concentration

in the fuel. The theoretical concentration of NO_x at the theoretical 100 % conversion rate of bound nitrogen in NH_3 is displayed, too.

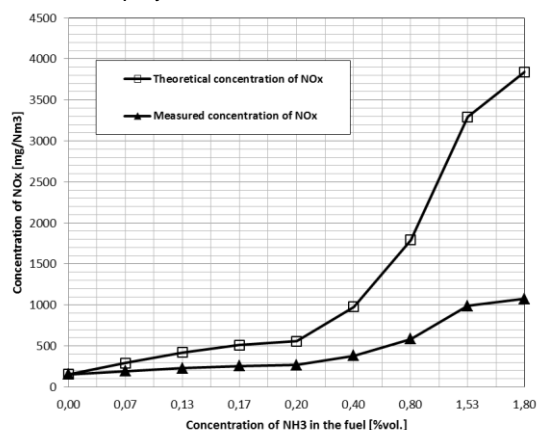


Figure 4: NO_x concentration as a function of ammonia concentration in the fuel for the premixed air-staged burner

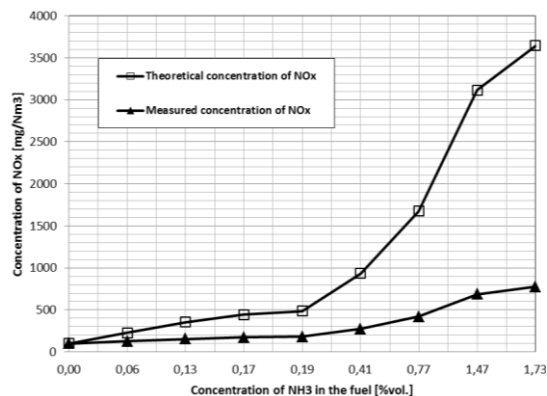


Figure 5: Effect of NH_3 concentration in the fuel on NO_x concentration for the non-premixed gas-staged burner

The comparison of conversion rates of chemically bound nitrogen for both tested burners is shown in Figure 6. From this figure, the conversion rate of ammonia into NO is lower when the non-premixed gas-staged burner was used compared with the premixed air-staged burner. It is evident that the ammonia conversion rate into NO decreases with the increasing ammonia concentration in the fuel for both burners. Moreover, the non-premixed gas-staged burner is characterized by lower level of NO_x emission at both tested regimes, namely with the fuel with and without chemically bound nitrogen, than that at the premixed air-staged burner.

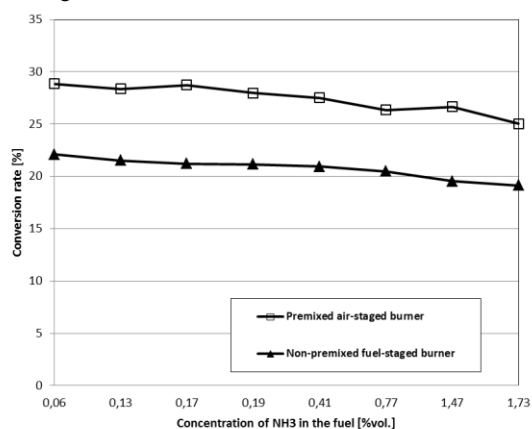


Figure 6: The conversion of chemically bound nitrogen in the fuel into nitrogen oxides

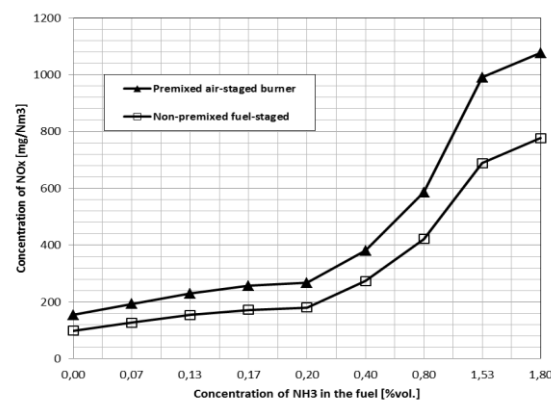


Figure 7: The comparison of NO_x emission in the premixed and non-premixed burner

6. Future work

The future work will be focused on the optimization of burner geometry so that the conversion of bound nitrogen into NO_x is the lowest and the emission regulations are met. Moreover, the research study will investigate the possibility of ammonia atomization in the area close to the flame, possibly directly into the flame. The purpose of this approach is to reduce NO_x emission using the method SNCR (Selective Non-Catalytic Reduction) which is commonly used in real applications and is the most efficient around the temperature of 900 °C.

7. Conclusions

The results showed that the presence of chemically bound nitrogen in the fuel (e.g. in the form of NH_3) significantly influence the formation of nitrogen oxides. When the natural gas was combusted, the concentration of NO_x measured in the flue gas was 150 mg/m^3 for the premixed air-staged burner and 100 mg/m^3 for the non-premixed gas-staged burner. However, the fuel switching to the fuel containing organically bound nitrogen caused the dramatic increase in NO_x .

Based on the balance recalculation it was revealed that the conversion rate of bound nitrogen in ammonia is 27 % and 20 % for the premixed air-staged burner and for the non-premixed gas-staged burner, respectively. In conclusion, the conversion rate of chemically bound nitrogen into fuel NO depends on the combustion mode (staging) and the type of burner (premixed, non-premixed).

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