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NO_X Removal by NH_3 and Flammable Additives in the Selective Non-Catalytic Reduction Process

T. SEREIKA*, K. BUINEVIČIUS, E. PUIDA***, D. PABARČIUS******
**Kaunas University of Technology, Studentų g. 56, LT-51424 Kaunas, Lithuania, E-mail: titas.sereika@ktu.edu*
***Kaunas University of Technology, Studentų g. 56, LT-51424 Kaunas, Lithuania, E-mail: kestutis.buinevicius@ktu.lt*
****Kaunas University of Technology, Studentų g. 56, LT-51424 Kaunas, Lithuania, E-mail: egidijus.puida@ktu.lt*
*****Kaunas University of Technology, Studentų g. 56, LT-51424 Kaunas, Lithuania,*
E-mail: dominykas.pabarcius@ktu.edu

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Nomenclature

NO_X - nitrogen oxides; CO_2 - carbon dioxide; NH_2 – amidogen; OH – hydroxyl; SCR - selective catalytic reduction; SNCR - selective non-catalytic reduction.

1. Introduction

Fuel nitrogen oxides emissions can be reduced by flue gas cleaning or by influencing the combustion process directly [1]. Flue gas cleaning is rarely used measure because of the complex equipment and expensive technologies [2]. Most commonly used measures for NO_X reduction: a small amount of excess air, air distribution or flue gas recirculation to the combustion chamber [3].

While environmental requirements are getting stricter, primary NO_X reduction measures cannot meet them, therefore, secondary NO_X reduction measures, such as selective catalytic reduction (SCN) and selective non-catalytic reduction (SNCR) can be used.

SNCR technology utilizes amine based reagent as reducing agent which does not influence the combustion condition significantly [2]. Compared with SCR, the main advantage of the SNCR technology is lower installation and maintenance costs. SNCR technology is attractive due to its simplicity, catalyst-free system, ease of installation on existing plants, unaffected by fly ash and usability with other NO_X emission control technologies.

The most common NOX reduction method is SCR technology and it is wide overviewed and extensively examined. The main idea of this paper is to figure out SNCR technology efficiency using unconventional additives – flammable additives [4]. Flammable additives are not tested for influence to NO_X reduction.

In this research biomass and furniture production waste pellets were used as fuel. While burning this kind of fuel nitrogen oxides in the flue gas are mainly formed from nitrogen content in the fuel. In thermochemical reactions nitrogen split from the fuel and combines with oxygen contained in the combustion chamber thus allowing to form NO and NO_2 compounds, generally naming them NO_X.

This study presents an experimental investigation of flammable and traditional SNCR additives by combustion of furniture production waste in the temperature range of 1000–1200°C. Flammable additives that were used in the research: CH_4, C_2H_2 and mixture of C_3H_8 and C_4H_{10}. Ammonia NH_3 was selected as the traditional additive, which is mostly used in the SNCR technologies. Basic fuel used in the studies is known for higher nitrogen content. Up to 1400 mg/m^3 NO_X concentrations were measures in the flue gas while burning furniture production waste pellets.

This work assesses the influence of NO_X reduction by SNCR technology with flammable additives. NO_X concentrations with flammable and traditional additives were measures during this research. Comparing the effects of additives in NO_X reduction while burning furniture production waste showed that NH_3 additives reduces primary NO_X by 56%. Flammable additives can reduce up to 76% NO_X emissions in exhaust gasses. Results showed that SNCR technology with flammable additives can change traditional NO_X reduction additives and this technology can be easily installed in the existing boilers.

2. Material and method

2.1. Method

Experiments were carried out in the Combustion research laboratory of Kaunas University of Technology, which has an installed pellets-fired industrial boiler model and all other system elements shown in (Fig. 1).

The main component of the stand is furnace (Fig. 2) which has systems for fuel and air feeding. Furnace and heat exchange surfaces, which are installed above the furnace are the main two components of the water boiler. The design capacity of the boiler is ~ 25-40 kW. To keep stable pressure in the combustion chamber, fan with a frequency converter assists to emit flue gases to the chimney.

Branch pipe for flue gas analysis probe are installed in the flue gas pipe in order to be able to make flue gas analysis and temperature measurements. About 20°C temperature air for combustion is fed from the surrounding environment. Boiler water temperature is maintained to stay in between 65°C and 70°C. Cooling system consisting of a heater block with a cooling fan is always fed with water by pump in order to ensure constant heat transfer.

There are two parameters that control combustion of all used fuel types, first is fuel feeding rate and second – the amount of air that is supplied to the combustion chamber. Generated pollutant concentrations are measured by flue gas analyzer. This analyzer measures temperatures and concentrations of nitrogen oxides, nitrogen monoxide, oxygen and carbon monoxide in the exhaust gases.

Frequency converter, which is mounted on the side of the furnace, is used to determine the constant rate of fuel feeding and according this value converter also regulates the amount of air for combustion. Tank for ash is at the bottom of the grate.

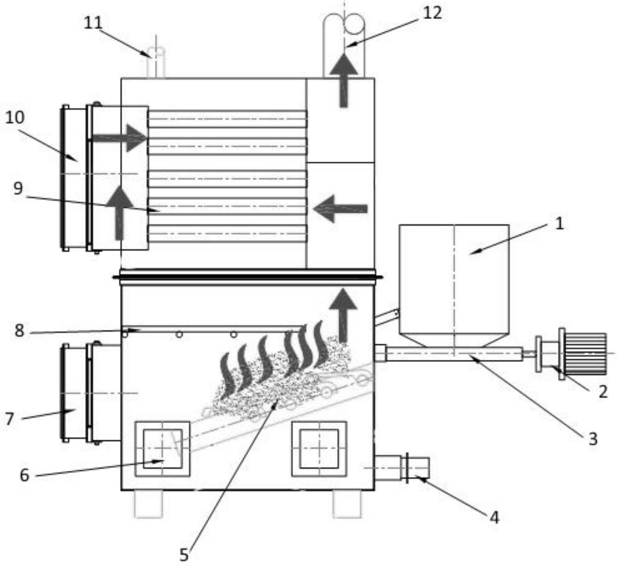

Fig. 1 Laboratory combustion research stand: *1* - fuel container; *2* - electric motor; *3* - mechanical feeder; *4* - primary air inlet; *5* - moving grate; *6* - ash hopper; *7* - inspection window; *8* - secondary air inlet; *9* - fire tube boiler; *10* - inspection door; *11* - heated water outlet; *12* - chimney

2.2. Biomass used in the research

The experiments were accomplished on basic fuel – furniture production waste. Furniture production waste was used as high NO_X concentration generated fuel (with high nitrogen content in mass).

Table 1 illustrates results of the used fuel composition and calorific value.

Table 1

Properties of the substances used in the combustion research

Furniture production waste	Content,
Fuel moisture content *W*, %	8,13
Carbon content, %	48,74
Nitrogen content, %	3,47
Hydrogen content, %	5,70
Sulphur content, %	<0,01
Lower calorific value $Q_{w.f.l}$ kJ/kg	17900

Furniture production waste is formed in the furniture production companies. During the technological process of furniture production some unused parts of wood chipboard, sawdust and defective products remains as a waste. Wood is not the only substance that that this waste consists of, materials such as chemical substances used for treating wood, furniture laminate, cardboard and residues of other packaging can be also found in this waste. Consequently, wood processing companies want to use this waste to meet their own energy needs.

In Lithuania, there are a lot of companies that produce large amount of such waste and the problem is that this waste cannot be used in energy production, because during combustion process it produces high concentrations of NO_X. However, successful reduction of nitrogen oxides, which are formed from fuel bound nitrogen, could mean that furniture production waste fuel can be used in energy production. This would also benefit the environment in the way that there would be less disposed waste and it would also decrease the amount of other biofuel required for energy production.

3. Experimental fuel combustion research

3.1. Experimental fuel combustion research

Experimental fuel combustion research was performed with the aim to examine the efficiency of lowering measure of NO_X in flue gases. The fuel was burnt so that the temperature in the combustion zone will not exceed 1200°C; burning at such temperature mode would allow examining solely the generation of “fuel NO_X”, because this temperature is insufficient for the formation of “thermal NO_X”. At this temperature range its share in the NO_X content is so small, that it has no practical value [1].

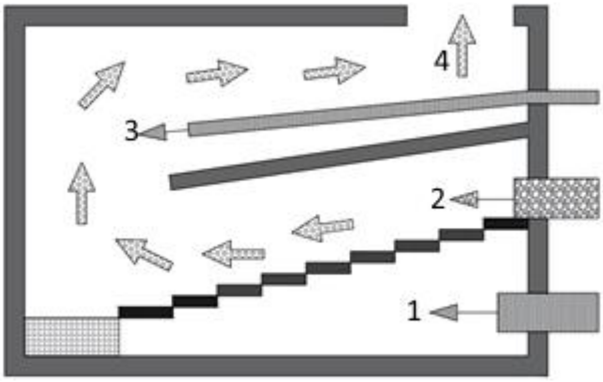

Fig. 2 Furnace: *1* - primary air; *2* - fuel inlet; *3* - secondary air and additives supply; *4* - exhaust gasses

40 percent of the air necessary for combustion is supplied under the fire-grate into the lower layer of the fuel. The remaining 60 percent is supplied above the fuel layer, where combustion products are still at high temperature around 1100°C [4].

Before the nitrogen oxides reduction studies using SCNR technology with various additives are performed, quantity of nitrogen oxides at a 40/60 ratio of air is determined, at the constant power of 20 kW and at sufficient combustion, which describes the amount of CO in the flue gases. (Fig. 3) presents the main CO and NO_X concentrations in flue gases dependence to excess air factor.

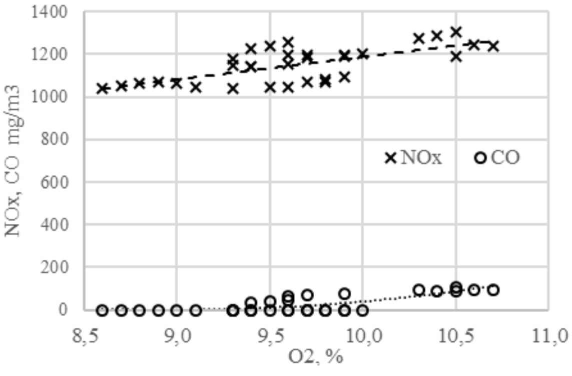

Fig. 3 NO_X and CO values in furniture production waste combustion depending on excess air

Nitrogen oxide concentration increases with air excess in the flue gases. Lowest NO_X concentrations 1108 mg/m^3 recorded at 8,6% excess air. The highest recorded NO_X concentration totaled 1303 mg/m^3 when burning furniture production waste, with nitrogen content in the substance accounting for 3.47%. This shows that big amount of N content in the substances turns to nitrogen oxides.

3.2. Traditional additives for SNRC

The chemistry of SNCR reaction is dominated by radical species such as NH_2 and OH, for ammonia reagents must react with OH to convert into NH_2 firstly, then NH_2 reacts to reduce NO in the flue gas stream.

SNCR reaction is effective in a temperature range of 900–1100°C called temperature window [2]. The temperature window is so narrow that ammoniac reagents could not mix with flue gas thoroughly and have no enough residence time to decompose and react with NO_X adequately, which leads to lower NO_X reduction efficiency (30–50%).

In order to experimentally determine NO_X reduction influence, while using traditional additives (N-NH_3 and N-NH_2) for SNRC process, experimental tests were carried out using the same fuel and maintaining the same combustion conditions as described in 3.1. section. Additives have been supplied with a secondary air. They mix with air and reach into the secondary combustion zone where the temperature is about 1100°C.

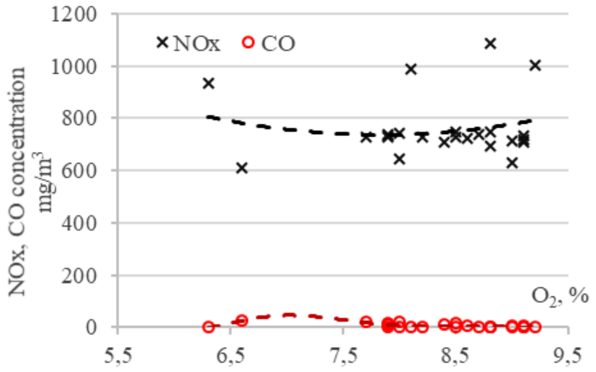

Fig. 4 Exhaust gasses concentration (NO_X and CO) depending on excess air using additive (N-NH_3)

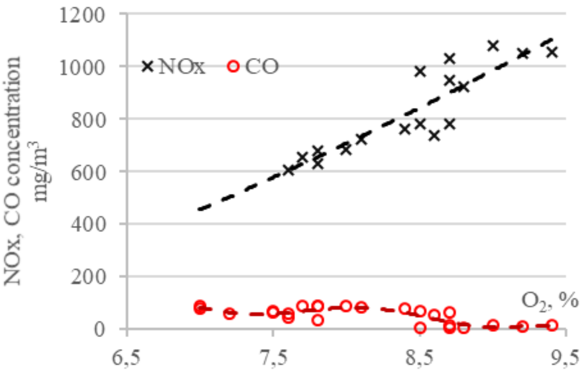

Fig. 5 Exhaust gasses concentration (NO_X and CO) depending on excess air using additive (N-NH_2)

In Figs. 4 and 5 we can see that carbon monoxide concentration, using both additives, are very low and did not reach 200 mg/m^3 across the range of air. So it can be concluded that CO does not have a decisive influence in NO_X reducing when in combustion process SNCR additives are used [5].

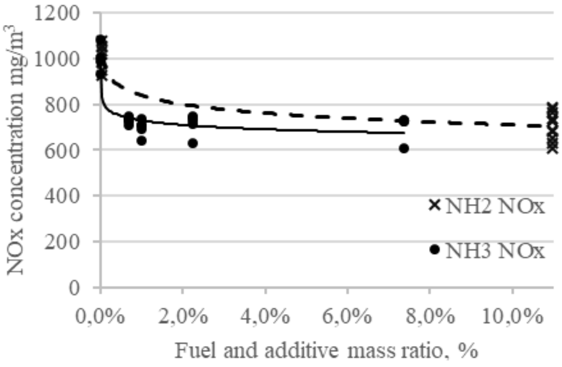

Fig. 6 NO_X reducing with traditional additives

Experimental results show that the higher amount of N-NH_2 or N-NH_3 compounds is supplied to the combustion chamber the greater the reduction of nitrogen oxides is obtained. Although in the combustion chamber have been injected various N-NH_2 or N-NH_3 concentrations in the water (N-NH_2 – 9% ir N-NH_3 – 10%) but the same effect is noticeable - the NO_X emissions are reduced to 45%. The use of these additives with higher concentrations decreases their effectiveness. So on the basis of studies, rational use of these additives in order to reduce NO_X by 40% is by using only half the amount of solution which should reduce NO_X concentration down to 45%.

3.2. Flammable additives for SNRC

Flammable accessories are chosen to extend the reaction time between CO and NO and temperature range [3].

Flammable hydrocarbon gases were chosen in order to the most common flammable components, which can be easily supplied to the combustion chamber. Gases were selected due to good mixing with the air compared to the mixing of liquid additives with air supplied.

Flammable Accessories used in experiments: methane (CH_4 supplied from the low pressure gas supply line), propane-butane mixture (C_3H_8/C_4H_{10} – commonly used as fuel gas in the cars) and acetylene (C_2H_2 used for the synthesis of other chemical elements).

Table 2

Properties of flammable additives

Flammable additive	Flame temperature, °C	Density, kg/m^3	Calorific value, kJ/kg
Methane (CH_4)	1950	0,679	47141
Mixture of propane-butane (C_3H_8/C_4H_{10})	~1970	2,087	46150
Acetylene (C_2H_2)	2550	1,065	48421

When experimental studies were performed, graphs are made showing the NO_X and CO concentration dependence to oxygen in the flue gases. Dependence of NO_X and CO concentration to combustible additives supplied to the combustion chamber (as a percentage of the amount of energy of fuel used for the main inputs and related energy content ratio) is also shown.

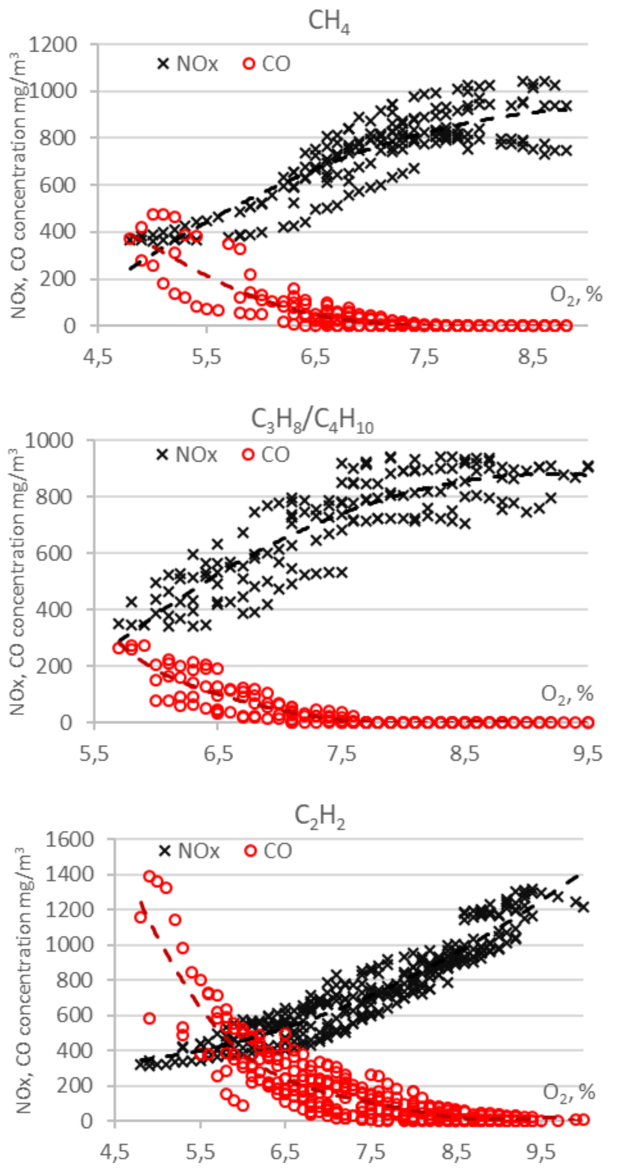

Fig. 7 NO$_X$ and CO concentration values depending on excess air using flammable additives

Lowest NO$_X$ concentrations are recorded using acetylene (316 mg/m^3). When mixture of methane and propane/butane is supplied to the combustion chamber, nitrogen oxide concentration decreased to 363 mg/m^3 and 340 mg/m^3 respectively.

Lowest NO$_X$ was measured at the highest concentrations of carbon monoxide and the minimum excess air. Higher combustion zone temperature contributes to the NO$_X$ reduction conditions. When the maximum amount of the gas, about 17% according to the total amount of energy, is supplied, combustion zone temperature rises from 1100°C to almost 1300°C.

While using flammable additives we observed not only significant decrease in excess air (Fig. 7), but also increase of CO (Fig. 8). Unlike using conventional NO$_X$ reduction additives where CO remain the same in all the additives supplied range. Increasing the injection amount of flammable additives in combustion zone consistently increasing CO concentration of exhaust gasses.

Based on the results in (Fig. 7) it can be concluded that the excess air is reduced due to the supply of combustible gas. This means that the more combustible gases are supplied to the combustion, lower amount of free oxygen remains. The decrease in the oxygen content of less than 6%, there is no longer enough oxygen to complete combustion of all flammable objects, carbon monoxide concentration begins to grow.

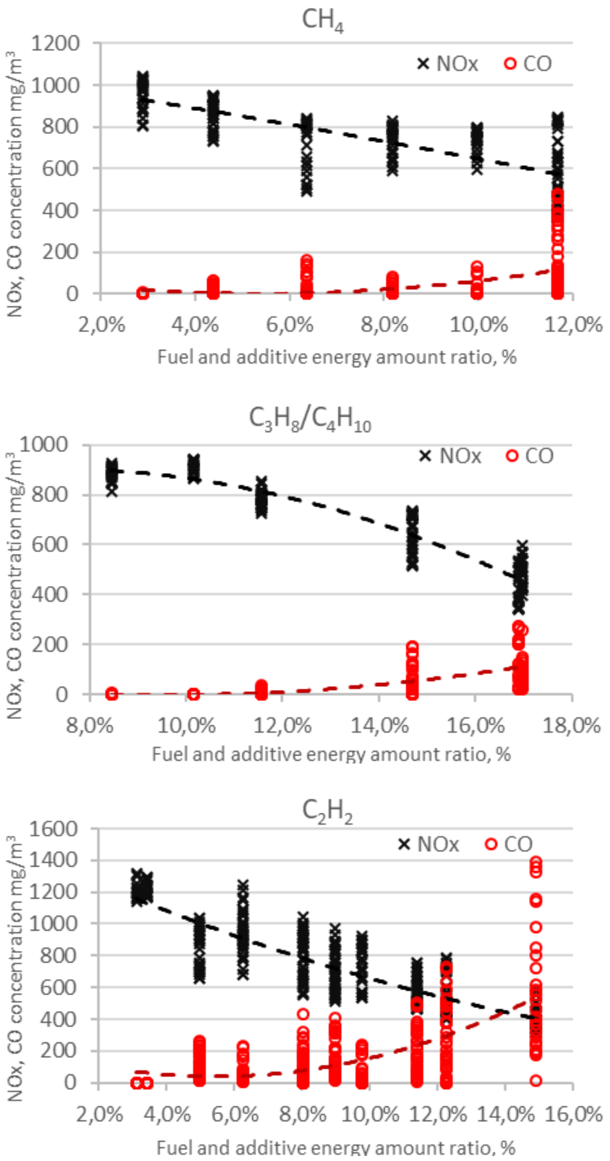

Fig. 8 NO$_X$ and CO concentration values depending on flammable additive inlet

In the absence of free oxygen content, nitrogen secluded from the solid fuel can hardly form a compound with oxygen to NO and NO$_2$. Therefore, while the amount of excess air is decreasing, decreased free oxygen content is one of the reasons why NO$_X$ concentration in the flue gases is reduced [6–9].

Another reason affecting the lower NO$_X$ concentrations - higher CO content in the combustion zone, which adversely affects the formation of NO$_X$. CO effect on nitrogen oxides increases with increment of the combustion zone temperature and time spent at this temperature [10, 11].

In research using flammable additives for SNRC nitrogen oxides concentration was lower from 68,4% up to 72,5 % depends to type and amount of gases used.

NO$_X$ reduction effect already observed while 3% of gases, compared to the total amount of energy, is supplied into the combustion chamber (Fig. 8). In this case, the NO$_X$

concentration in the flue gases degrease by approximately 15,74 %. However, when 6% of gas, compared to the total amount of energy, is supplied, we obtained the same effect as supplying traditional additives, up to 2.5% by mass in relation, to the combustion chamber.

Traditional additives efficiency grows slightly while increasing the amount of it. Therefore, traditional additives cannot significantly reduce NO_X in flue gases. Moreover, often seeking to achieve greater reduction effect, emission have ammonia leaks, because not all the ammonia is reacted with the NO_X.

Flammable additives are superior to ammonia due to higher NO_X reduction efficiency and the best result achieved reducing NO_X up to 73%. Here are no ammonia emissions, only CO may occur. While using flammable additives additional amount of energy is obtained that can be advantageously used.

4. Result verification

4.1. Flue gases dilution evaluation

In order to accurately assess the combustible additives, influence for the formation of nitrogen oxides, the table below shows calculated minimum and maximum concentration reduction of NO_X in the flue gases, because of the combustible gas additives that affect the resulting flue gases volume and composition.

Table 3

Flue gas dilution by flammable additives

Fuel and additive energy amount ratio, % Flammable additives	Flue gas dilution by 1% of flammable additives, %	Flue gas dilution by 16% of flammable additives, %
CH_4	0,90%	14,47%
C_3H_8/C_4H_{10}	0,91%	14,61%
C_2H_2	0,89%	14,19%

Real NO_X reduction effect remains relatively high, after assessing of the flue gas dilution by combustion of flammable additives. After excluding dilution effect, reduction of NO_X concentrations in the flue gases remain: for methane – 58,53%, for propane-butane – 60,15% and for acetylene – 62,23%.

Flue gas assessment was made only to be prove that the main source of nitrogen oxides reduction efficiency was not the dilution of flue gases by supposedly "cleaner" exhaust gases, but including another processes.

4.2. Comparison of NO_X reduction efficiency

In the order to compare traditional and flammable additives efficiency the calculation was made, where additives are measured by mass ratio compared to the main fuel.

As seen in (Fig. 9) ammonia additives has a high efficiency in small quantities (up to 2,5%). The supply of larger amount of additives, NO_X concentration decreases gradually about 10 mg/m^3 with each additional percent of the additive. This means that the system in the conditions and flue gas interactions has maximum limit of the traditional additives at 2.5%. While supplying more additives most of it does not react and is ammonia is emitted with in the flue gases.

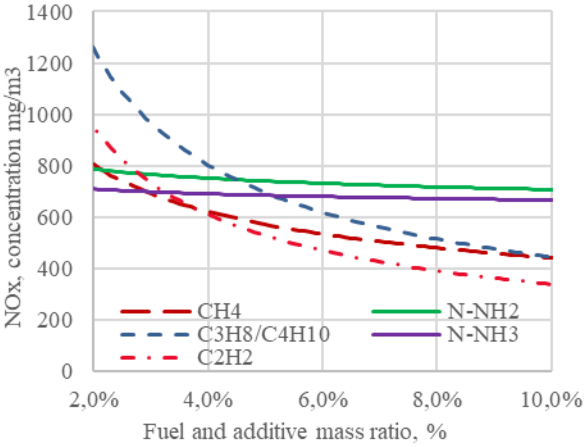

Fig. 9 NO_X concentration reduction effectiveness dependence to flammable and ammonia additives mass ratio to fuel

Flammable additives at small quantities are less efficient, but when supplied more than 3%, NO_X reduction effectiveness outperforms ammonia additives. Flammable additive supply increment from 3% to 10% results in NO_X concentrations reduction from 800 - 1200 mg/m^3 to 360 - 420 mg/m^3. Therefore, flammable additives act effectively in wider supply range.

5. Conclusions

The results show that the excess air can be reduced by flammable gases. The more gases are supplied to the combustion zone, the less of free oxygen remains in exhaust gases.

The oxygen level decreases lower than 6% by injecting a flammable gas more than 10% in to a combustion zone. Low levels of O_2 in combustion zone generates incomplete combustion products which have a positive influence to NO_X reduction process.

Flammable additives have a high NO_X reduction efficiency up to 73%. Additional amount of energy is obtained and can be useful by using flammable additives.

Flue gas dilution with flammable gases shows that additives efficiency to NO_X reduction effect remains relatively high: for methane – 58,53%, for propane-butane – 60,15% and for acetylene – 62,23%.

Small quantities of SNCR chemicals injection (up to 2,5%) has a higher efficiency to NO_X reduction compared with the same amount of flammable additives. However, when supplying flammable gases more than 3%, NO_X reduction outperforms ammonia additives effectiveness. Flammable additives can act effectively in wide range (3% - 10%) of supply.

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T. Sereika, K. Buinevičius, E. Puida, D. Pabarčius

NO_X REMOVAL BY NH_3 AND FLAMMABLE ADDITIVES IN THE SELECTIVE NON-CATALYTIC REDUCTION PROCESS

Summary

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Keywords: NO_X reduction, SNCR, flammable additives.

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